

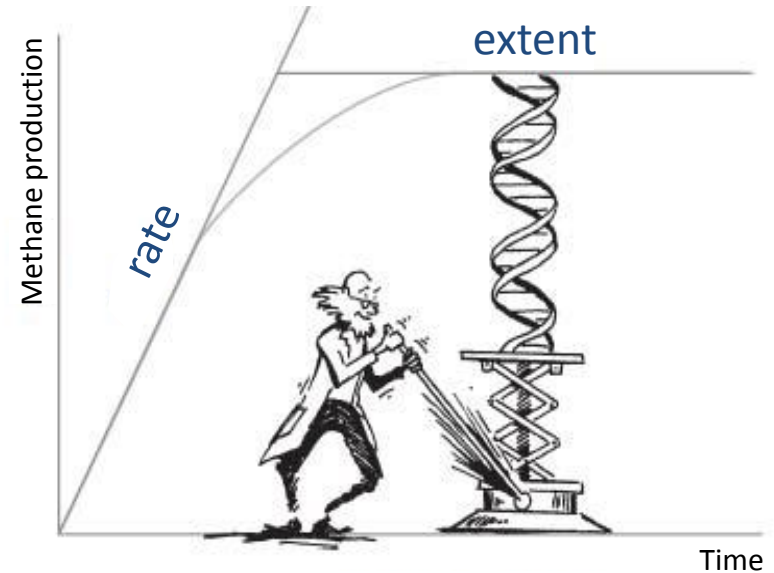
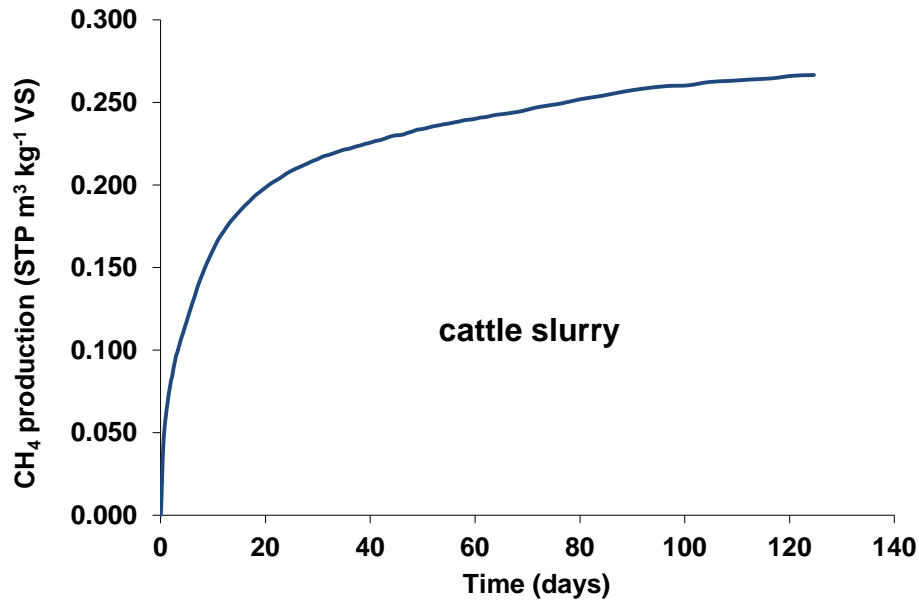
Anaerobic digestion fundamentals II

Thermodynamics

Dr Yue Zhang

AD process consideration

- Kinetics (rate)
- Thermodynamics (extent)

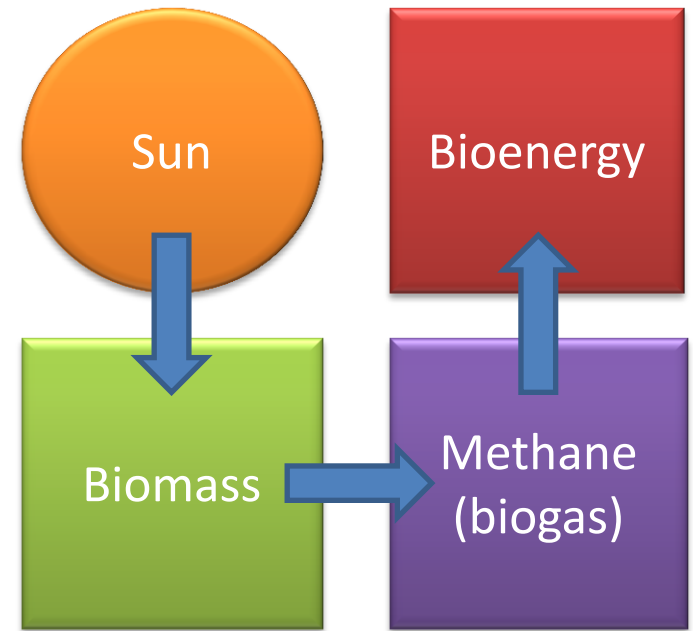


Question:

- Is there an upper limit on specific methane/biogas production?

Contents

- Biomass energy
 - Photosynthesis
 - Calorific value and bomb calorimeter

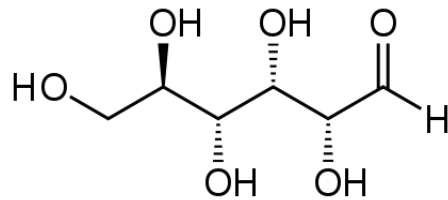


- Estimation of theoretical maximum methane production
 - Elemental analysis and Buswell equation
 - Biochemical composition approach
 - Chemical oxygen demand (COD) approach
- Energy flow and mass flow in AD process

Biomass energy and calorific value

Biomass energy

- Photosynthesis: metabolic synthesis of complex organic material using CO_2 , H_2O , inorganic salts, and energy from the solar radiation



Glucose

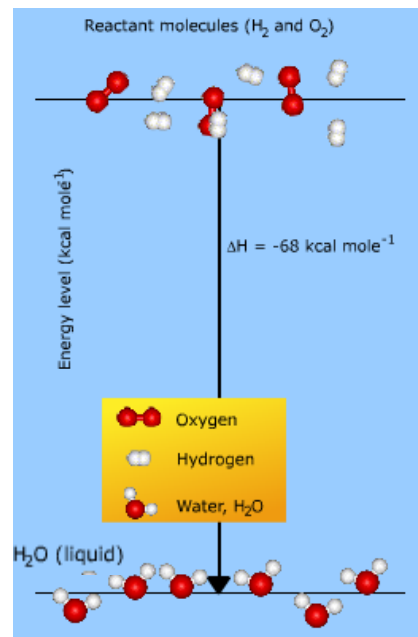
- Chemically-stored energy: chemical bonds
- Energy transferred and utilised through chemical and biological processes

Bond energy

Approximate bond energies at 298 K (kcal mol^{-1})

	C	N	O	F	Si	P	S	Cl	Br	I
H—	98.8	93.4	110.6	134.6	70.4	76.4	81.1	103.2	87.5	71.4
C—	83.1	69.7	84.0	105.4	69.3		62.0	78.5	65.9	57.4
C=	147	147	174				114			
C≡	194	213								
N—	69.7	38.4		64.5				47.7		
N=	147	100								
N≡	213	226								
O—	84.0		33.2	44.2	88.2			48.5		
O=	174		118.3							

Note: these bond energies are not perfect for any one molecule, but are the best average values for a great number of molecules with the same kind of bond.



Source: <http://www.chem.ox.ac.uk/>

Energy units

- Calorie
 - The original scientific unit in which changes in energy were measured
 - One calorie (symbol: cal) is defined as the heat energy required to raise the temperature of 1 g of water by 1 °C
 - The name 'calorie' is used for another unit of energy: large calorie or dietary calorie (symbol: Cal, equiv: kcal)

- Joule

- A derived unit of energy in the International System of Units

$$J = N \cdot m = W \cdot s = C \cdot V$$

- One joule (symbol: J) can be defined as:
 - ❑ The work done in applying a force of 1 N through a distance of 1 m;
 - ❑ The work required to produce 1 W of power for 1 s;
 - ❑ The work required to move an electric charge of 1 C through an electrical potential difference of 1 V.

Energy units

- Conversion between different energy units
 - 1 cal = 4.187 J
 - 1 J = 1 W·s
 - 1 kWh = 3600 kW·s = 3600 kJ = 3.6 MJ
 - 1 kJ = 1×10^3 J; 1 MJ = 1×10^6 J; 1 GJ = 1×10^9 J; 1 TJ = 1×10^{12} J; PJ, EJ, ZJ, YJ
- Energy content of biomass

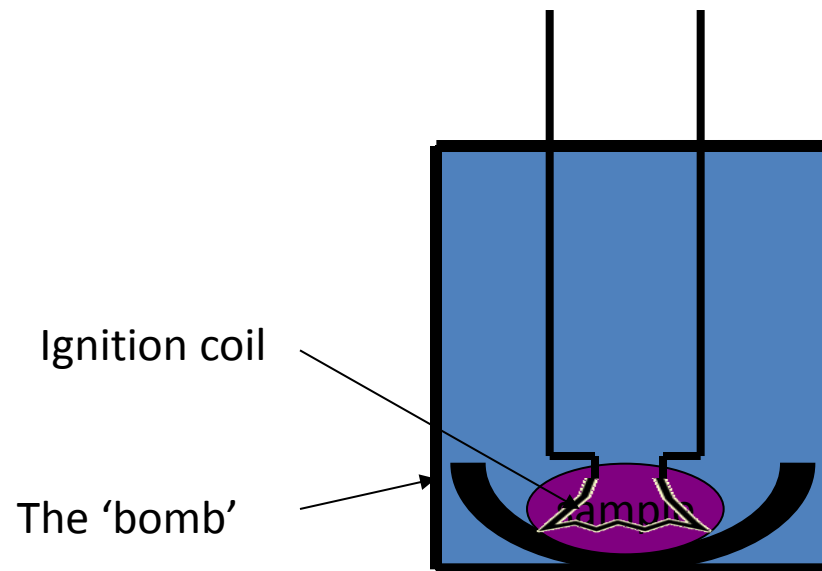
Biomass	Starch	Protein	Lipid
Gross calorific value (MJ kg ⁻¹)	16.6	22.4	37.3

Biomass	Starch	Protein	Lipid
CH ₄ yield (N m ³ kg ⁻¹)	0.415	0.496	1.014

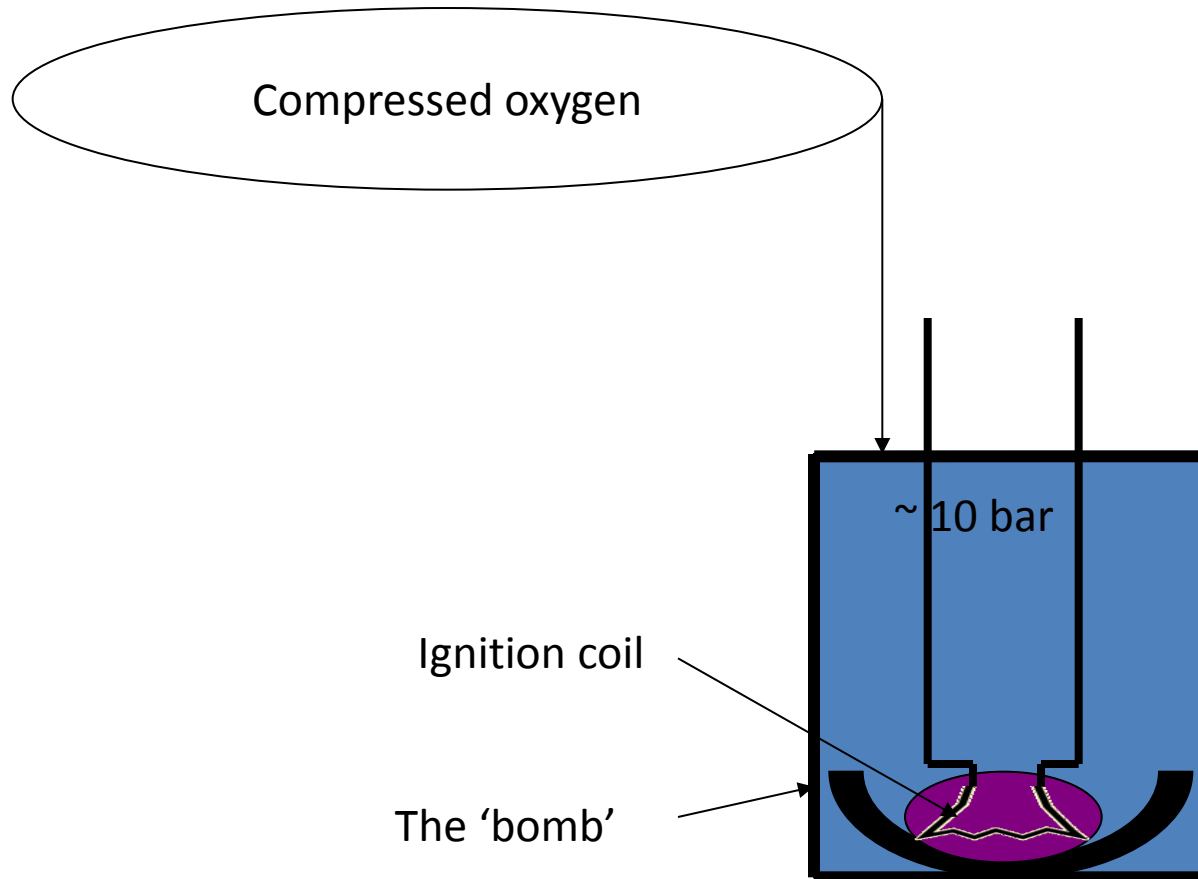
Calorific value (heat of combustion)

- It is the measure of the energy that is chemically available in the substance per unit mass (Units: energy per unit mass, mole or volume e.g. MJ kg⁻¹).
- It is usually determined as heat released upon combustion with oxygen under standard conditions, and measured using a bomb calorimeter.
- The energy recovered by bomb calorimeter is the theoretical maximum bioenergy we can obtain from any biomass.

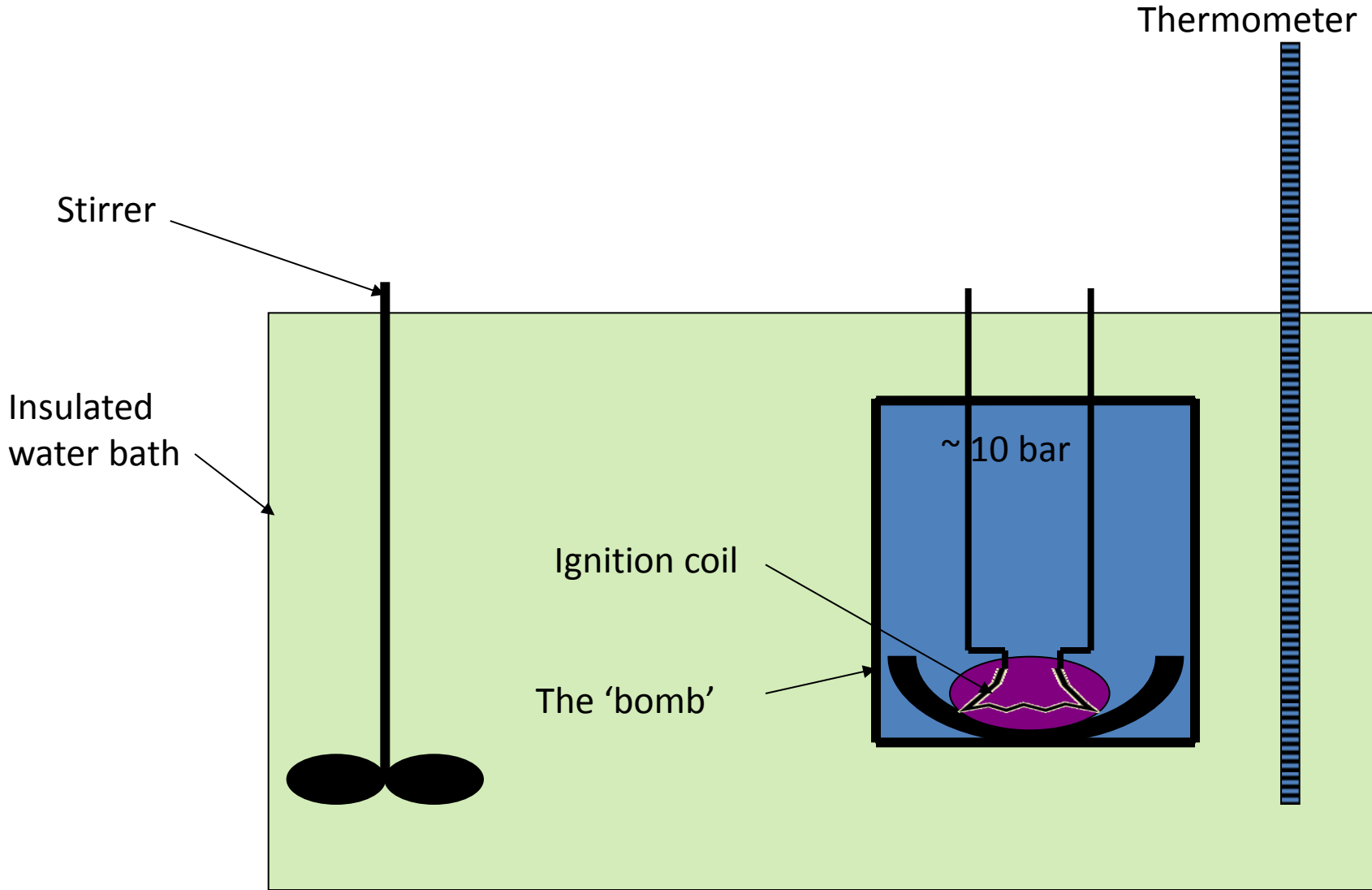
Bomb Calorimetry - Procedure



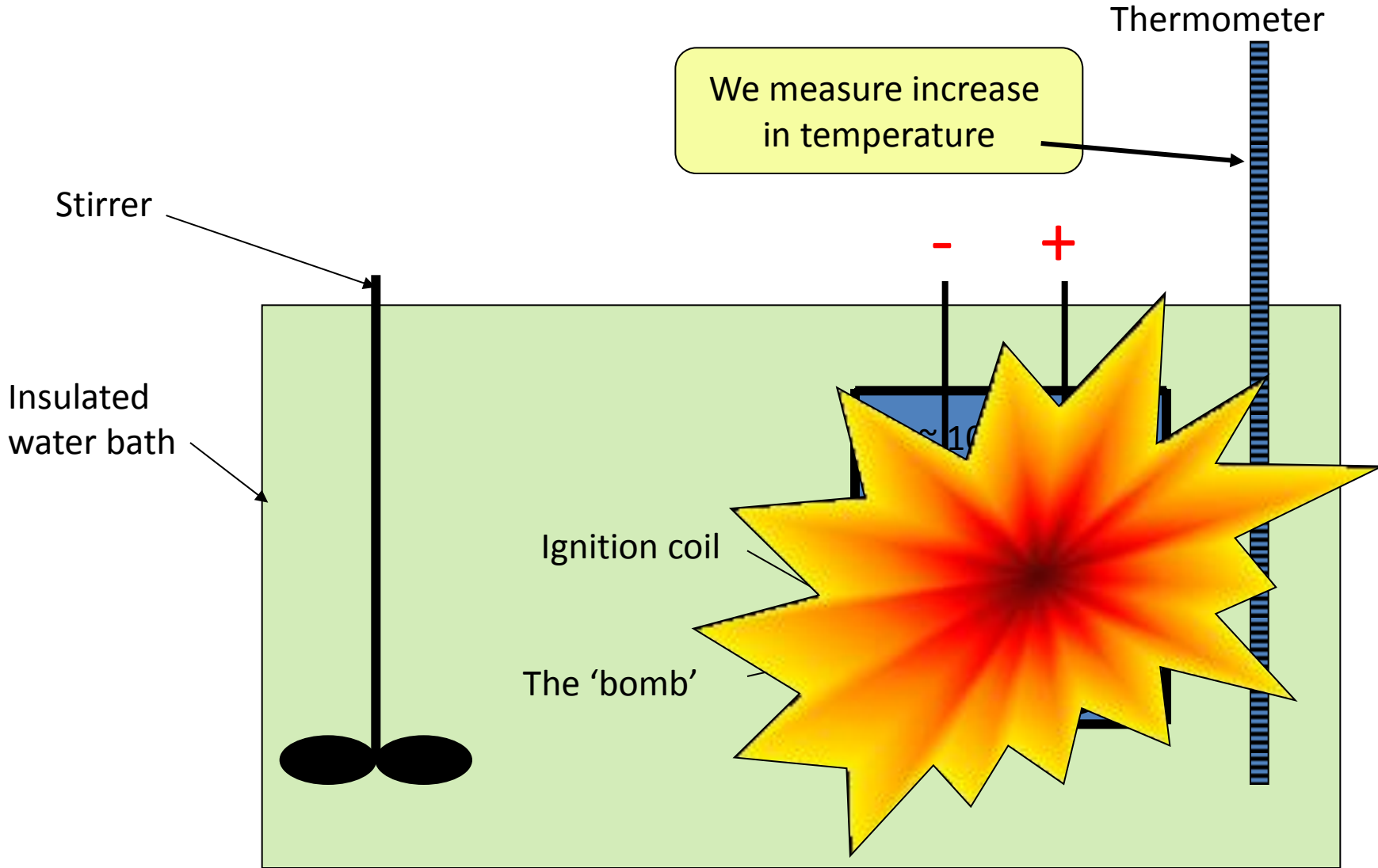
Bomb Calorimetry - Procedure



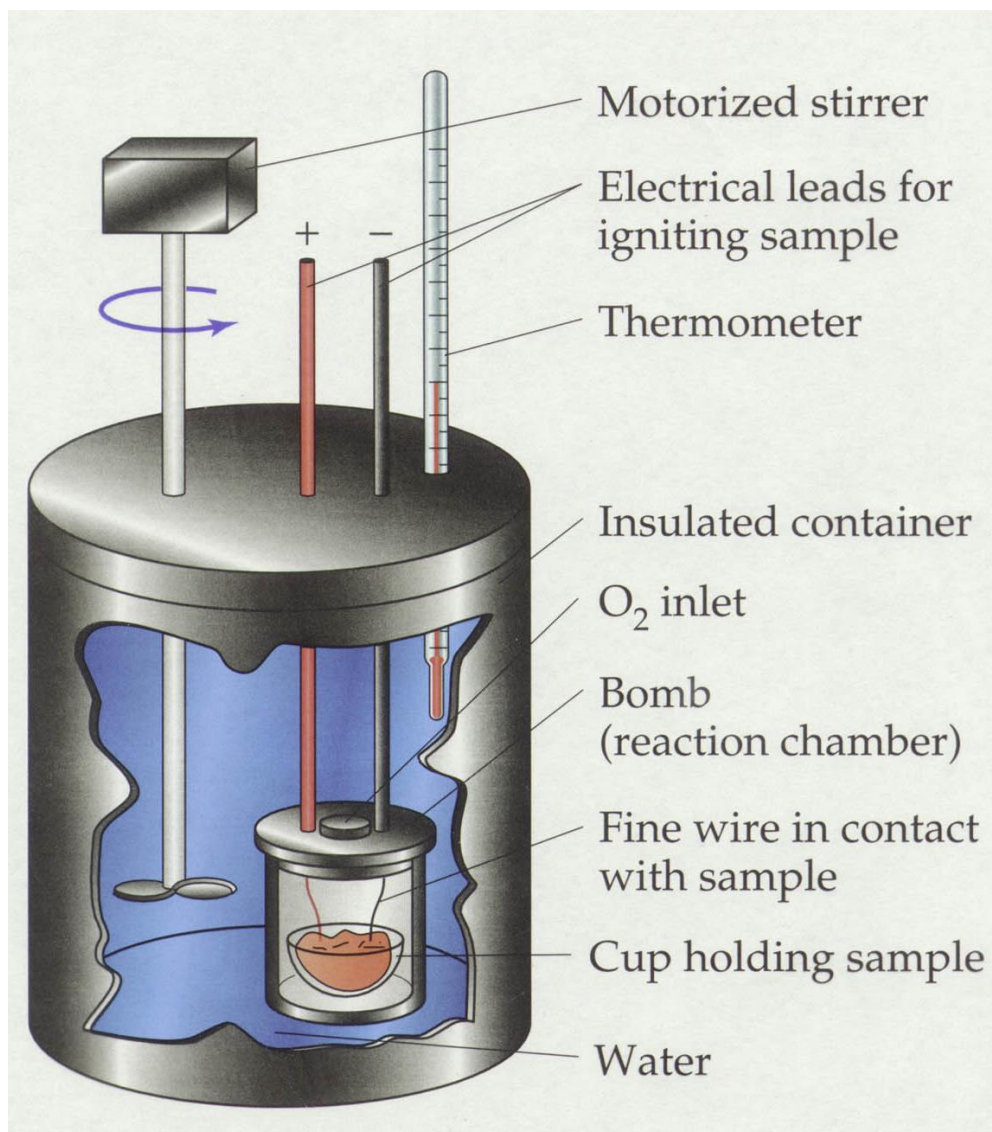
Bomb Calorimetry - Procedure



Bomb Calorimetry - Procedure



The Bomb Calorimeter

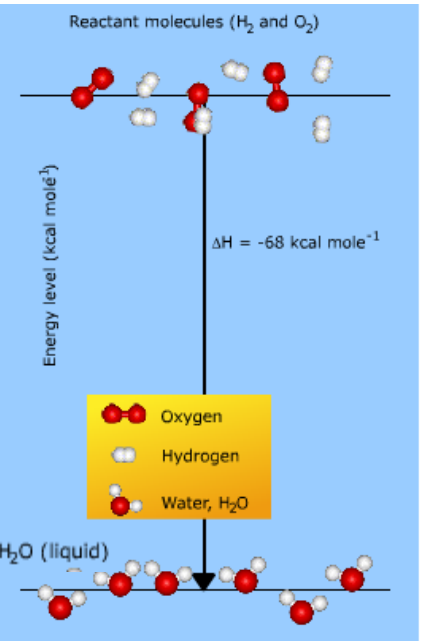


- Temperature increase is used to calculate the energy released
- Other data needed;
 - Heat capacity of the system including the water, bomb, coil etc.
 - Amount of energy input by the ignition coil
 - The sample weight added
- Modern bomb calorimeters do this for us!

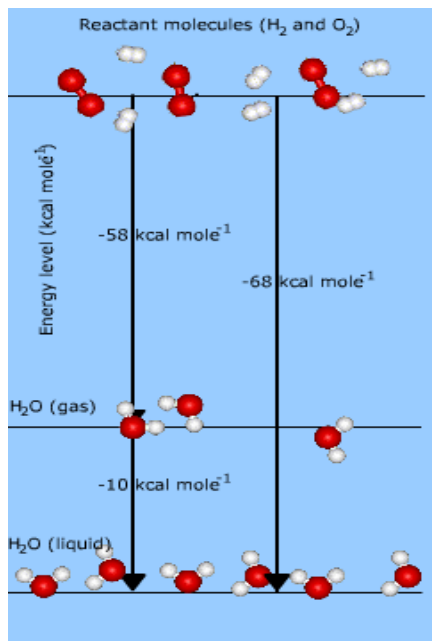
The Bomb Calorimeter



Calorific value: gross vs net



Gross calorific value



Net calorific value

Heat of Condensation

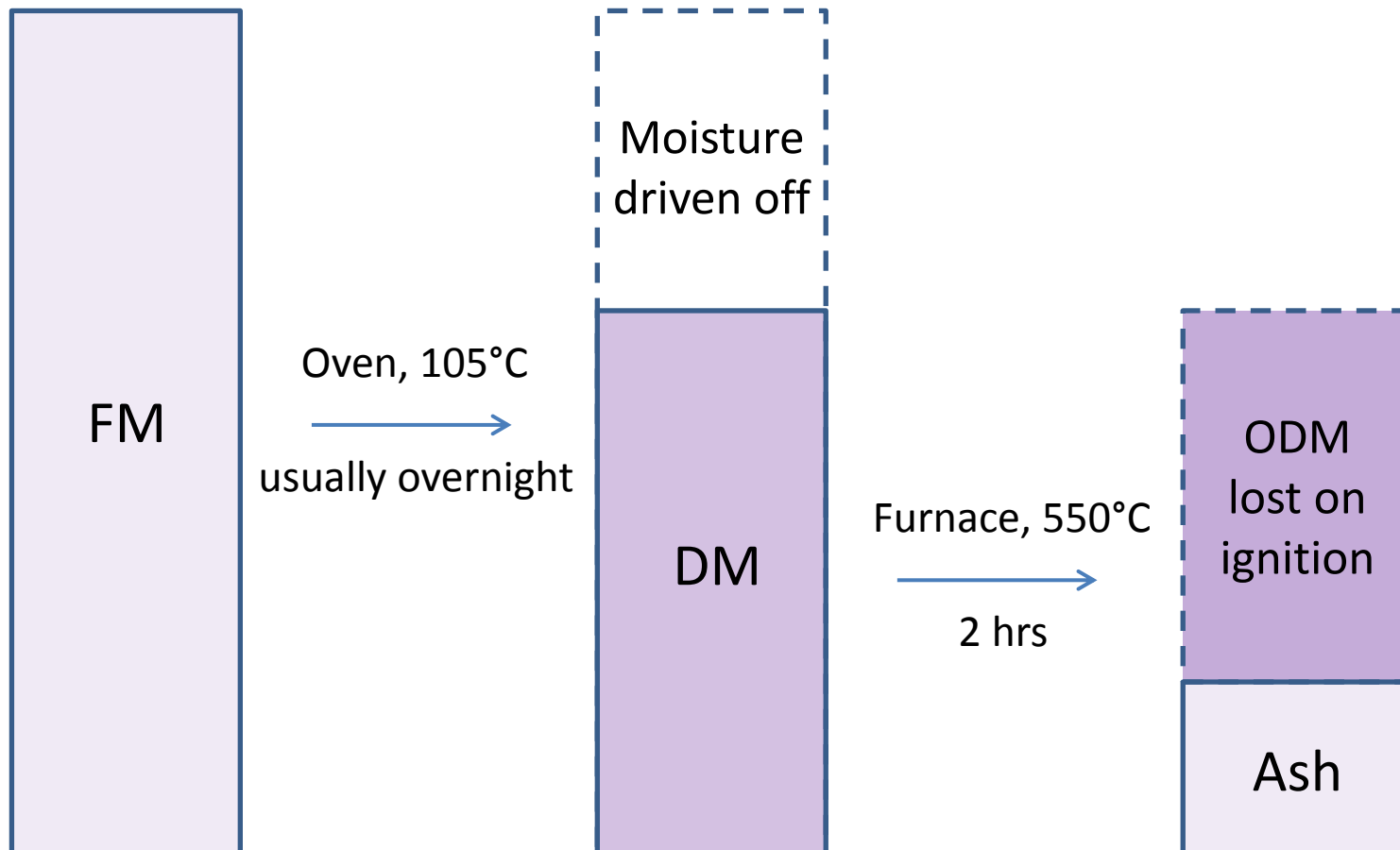
Source: <http://www.chem.ox.ac.uk/>

Calorific value: gross (HHV) vs net (LHV)

- In calorimeter, water vapour formed during the combustion condenses at the end of the measurement, and the latent heat of water condensation contributes to the heat value.
- Calorimeter measures the gross calorific value (GCV) or higher heating value (HHV).
- The latent heat of the water vapour formed using combustion, however, usually cannot be recovered in most thermal processes in bioenergy production. In this case, the net calorific value (NCV) or lower heating value (LHV) should be used to express the amount of energy available.
- $HHV > LHV$ in the context of bioenergy production

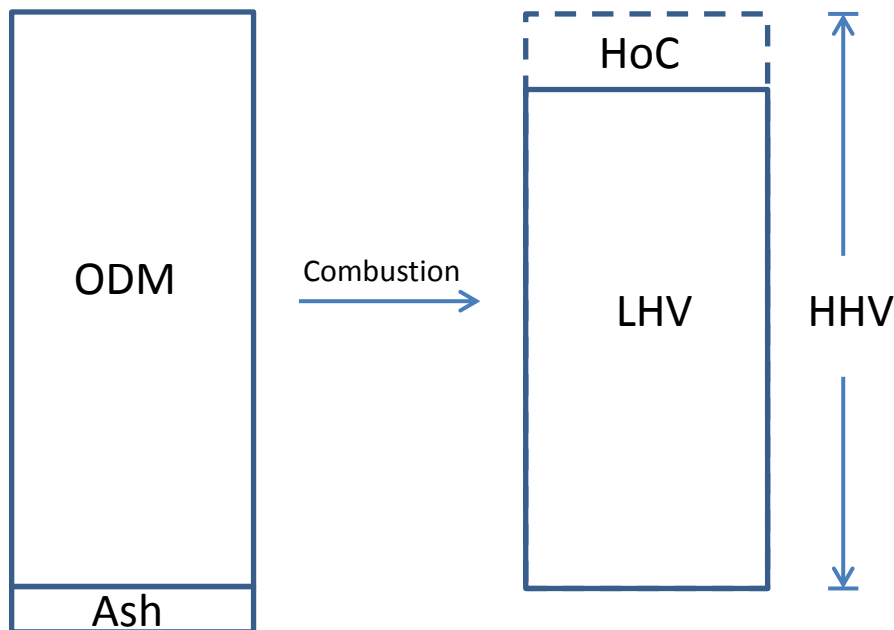
Calorific value: HHV, LHV, water

- Water produced during the combustion
 - $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$
 - $2H_2 + O_2 = 2H_2O$
- Water also present in the biomass as moisture



Calorific value: HHV, LHV, water

When **NO** moisture present in biomass, for 1 kg of dried biomass:



CV:

- Heat energy generated during the combustion of organic matter in biomass

HHV

- Determined using bomb calorimeter using dried material

Water generated

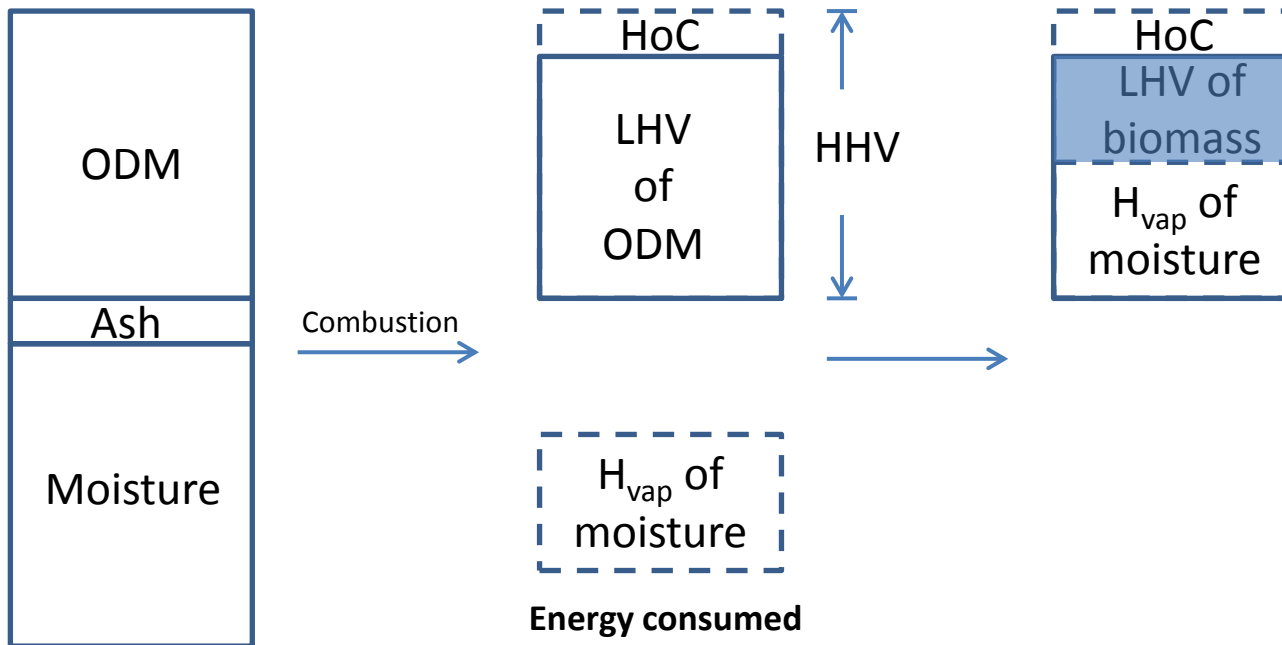
- Leave steam turbine as water vapour

LHV

- Energy available for capture in steam turbine

Calorific value: HHV, LHV, water

When moisture present in biomass, for 1 kg of moist biomass



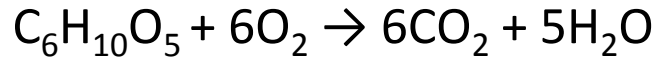
Energy consumed

Heat of evaporation
(=heat of condensation):
energy needed to
evaporate the moisture
in the biomass

Example – HHV & LHV of moist starch

Calculate the LHV for two samples of starch $(C_6H_{10}O_5)_n$ containing 10 and 80% moisture by weight respectively. HHV of starch is 16.6 MJ kg^{-1} and Heat of Condensation of water to 55°C is 2.445 kJ kg^{-1}

1. Write equation for combustion of starch



2. Calculate the LHV of dry starch

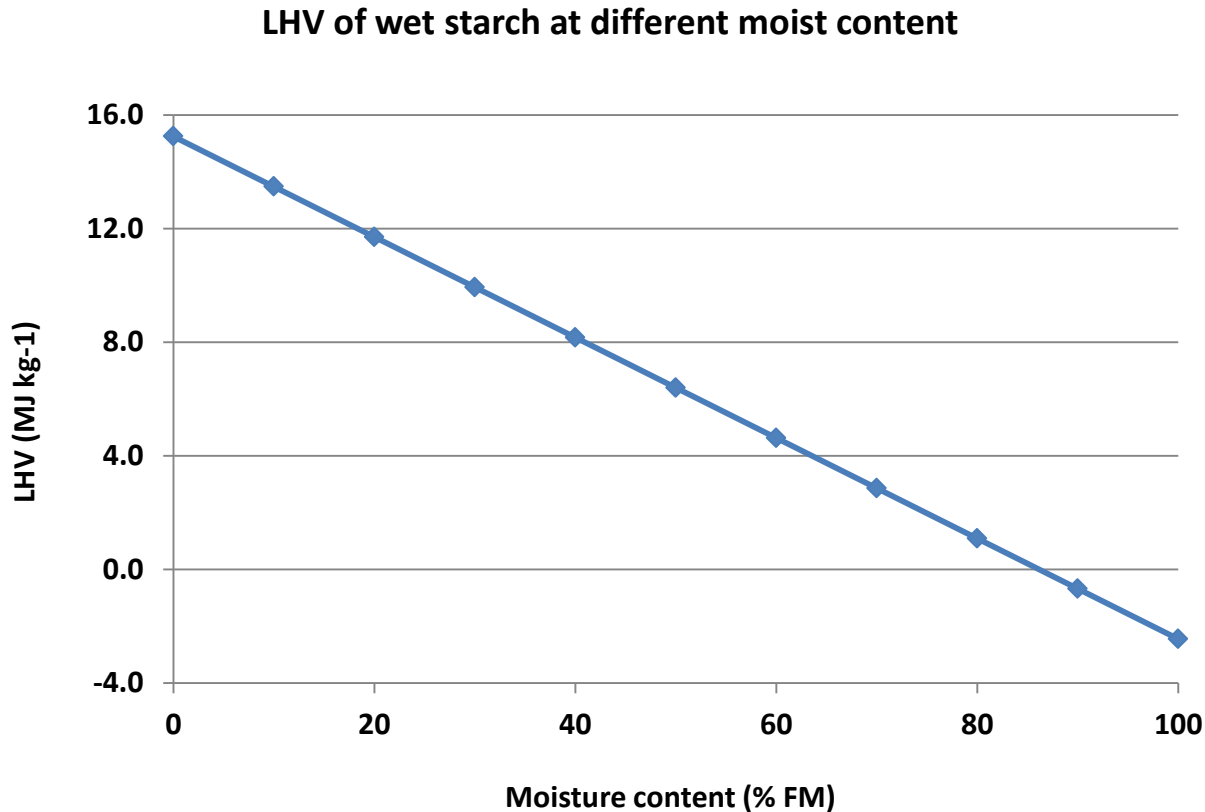
- a. 1 mole starch (monomer) produces 5 moles of water
- b. Molecular weight of starch monomer is 162, water is 18
- c. 162 kg starch produces $5 \times 18 = 90 \text{ kg}$ water
- d. 1 kg starch produces $90/162 = 0.556 \text{ kg}$ water
- e. LHV dry starch =

$$16.6 \text{ MJ kg}^{-1}_{\text{starch}} - (0.556 \text{ kg}_{\text{water}} \text{ kg}^{-1}_{\text{starch}} \times 2.445 \text{ MJ kg}^{-1}_{\text{water}}) = 15.2 \text{ MJ kg}^{-1}$$

3. LHV (10% moisture) = $15.3 \times 0.9 - 2.445 \times 0.1 = 13.5 \text{ MJ kg}^{-1}_{\text{fresh matter}}$

4. LHV (80% moisture) = $15.3 \times 0.2 - 2.445 \times 0.8 = 1.09 \text{ MJ kg}^{-1}_{\text{fresh matter}}$

Example – HHV & LHV of moist starch



Moisture content of the biomass has a significant impact on the conversion process

- Thermochemical conversion processes require a low moisture content biomass, or there will be a negative impact on the overall energy balance
- Biochemical conversion processes can utilise a high moisture content biomass

Empirical equation for HHV of biomass

- HHV of a biomass is related to its elemental composition (DuLong equation)
- Many improvements have been made, including

$$\text{HHV} = (34.1C + 102H - 9.85O + 6.3N + 19.1S) / 100$$

where elements C, H, O, N and S are expressed as mass fraction of biomass on an organic dry matter basis (% ODM)

(Source: International Flame Research Foundation Online Combustion Handbook ISSN 1607-9116: Method from Combustion File 24)

- Elemental composition of biomass

Biomass	Elemental composition (% ODM)					HHV (MJ kg ⁻¹ ODM)	HoC of water (MJ kg ⁻¹ ODM)	LHV (MJ kg ⁻¹ ODM)
	C	H	O	N	S			
starch	44.4	6.2	49.4	-	-	16.6	1.4	15.2
protein	53.1	6.2	28.3	12.4	-	22.4	1.4	21.0
lipid	77.4	11.8	10.9	-	-	37.3	2.6	34.7

References on elemental composition:

Angelidaki I. and Ellegaard L. (2004) Codigestion of manure and organic wastes in centralized biogas plants, Applied Biochemistry and Biotechnology, 109(1-3), 95-105.

- On a ODM basis
 - HHV is positively related to the contents of C and H, and negatively related to that of O
 - The difference between HHV and LHV depends on the content of H

HHV and LHV of biomass

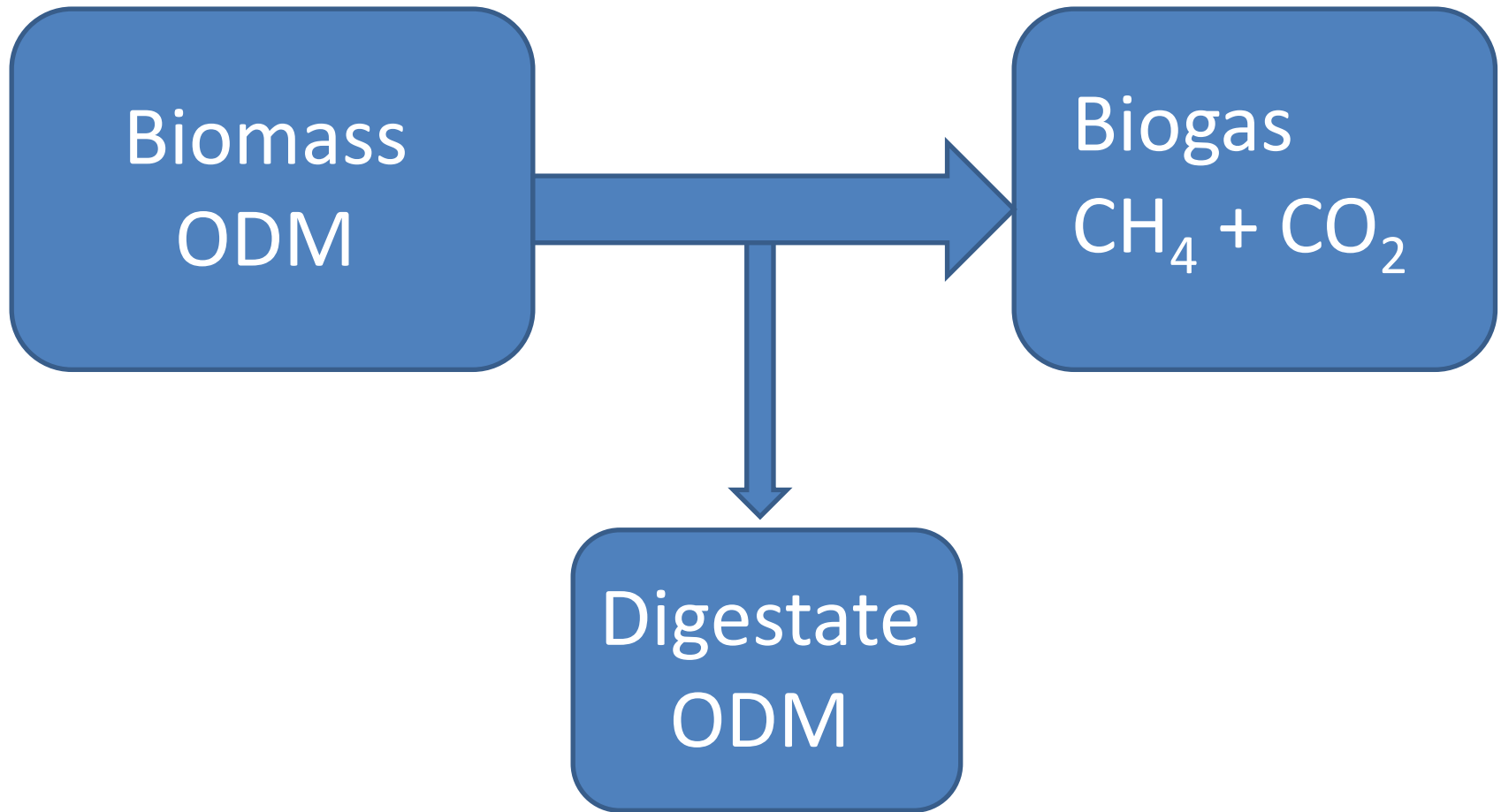
- Most biomass contains water which needs to be accounted for when calculating the HHV and LHV in addition to the water produced by the chemical reaction.
- This allows us to predict the most suitable type of processing
 - LHV gives some indication of the energy that can be extracted from the biomass in a thermal process (e.g. combustion). May not be exact e.g. where heat is recovered by condensation of exhaust.
 - HHV gives the maximum energy that could be extracted from the biomass by any process.
- Where $HHV \gg LHV$ the material is probably better suited for a non-thermal process (e.g. anaerobic digestion, bioethanol), where $HHV \approx LHV$ is often feasible to thermal process.

Use of calorific value in AD 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
- Energy loss during the biochemical reactions in the form of heat
- Part of biomass is difficult to digest
- It provides however a performance benchmark for AD systems

Estimation of theoretical maximum methane production

Anaerobic digestion process



Energy value of biogas



Oxidised carbon –
no energy value



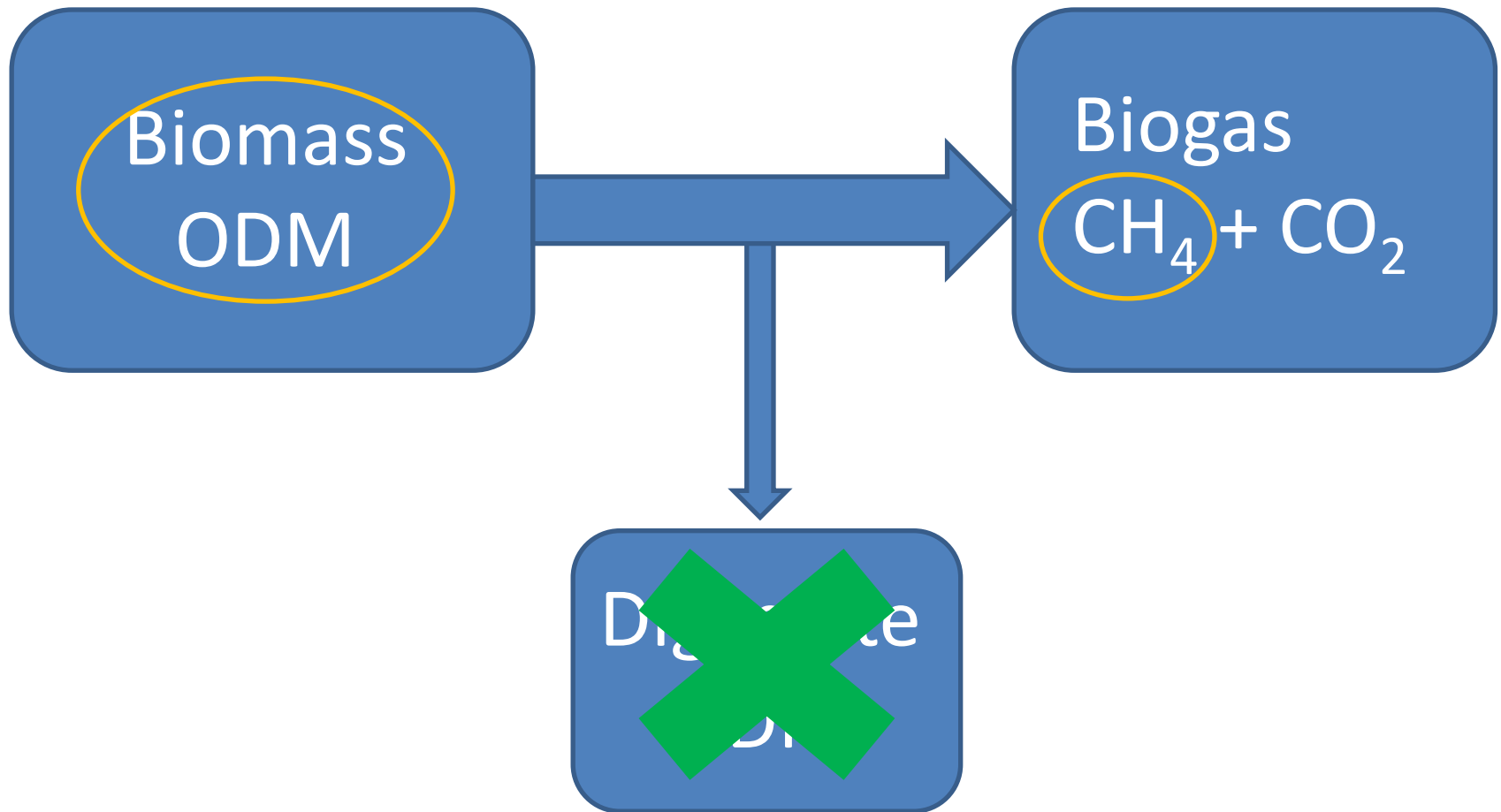
Reduced carbon –
energy value:

HHV: $\sim 55 \text{ MJ kg}^{-1}$ or 40 MJ m^{-3}

LHV: $\sim 50 \text{ MJ kg}^{-1}$ or 36 MJ m^{-3}

Theoretical maximum methane production (1)

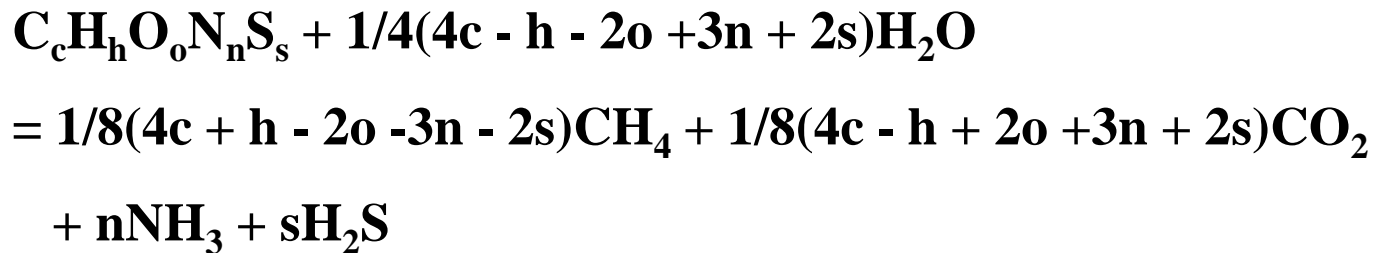
- Calorific value of biomass



Theoretical maximum methane production (2)

- Buswell equation

- Buswell equation provides stoichiometric calculation on the products from the anaerobic breakdown of a generic organic material of chemical composition $C_cH_hO_oN_nS_s$.



where molecular formula subscriptions, c, h, o, n and s, represent the molar proportion of mass fraction of elements C, H, O, N and S in the organic fraction of biomass

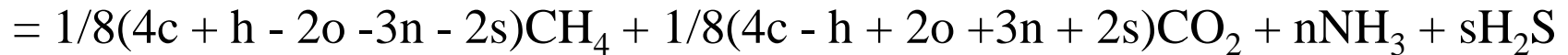
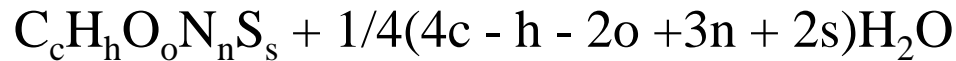
Reference:

Symons, G. E. and A. M. Buswell (1933) The methane fermentation of carbohydrates. *Journal of the American Chemical Society* **55**(5): 2028-2036.
Buswell, A. M. and H. F. Mueller (1952) Mechanism of methane fermentation. *Industrial and Engineering Chemistry* **44**(3): 550-552.

Theoretical maximum methane production (2)

- Buswell equation

- Buswell equation



- Elemental composition of biomass

Biomass	Elemental composition (% ODM)					H ₂ O consumed (kg kg ⁻¹ biomass)	CH ₄ produced (m ³ kg ⁻¹ biomass)	CO ₂ produced (m ³ kg ⁻¹ biomass)
	C	H	O	N	S			
Starch (C ₆ H ₁₀ O ₅) _n	44.4	6.2	49.4	-	-	0.11	0.415	0.415
Protein C ₅ H ₇ NO ₂	53.1	6.2	28.3	12.4	-	0.48	0.496	0.496
Lipid C ₅₇ H ₁₀₄ O ₆	77.4	11.8	10.9	-	-	0.57	1.014	0.431

References on elemental composition:

Angelidaki I. and Ellegaard L. (2004) Codigestion of manure and organic wastes in centralized biogas plants, Applied Biochemistry and Biotechnology, 109(1-3), 95-105.

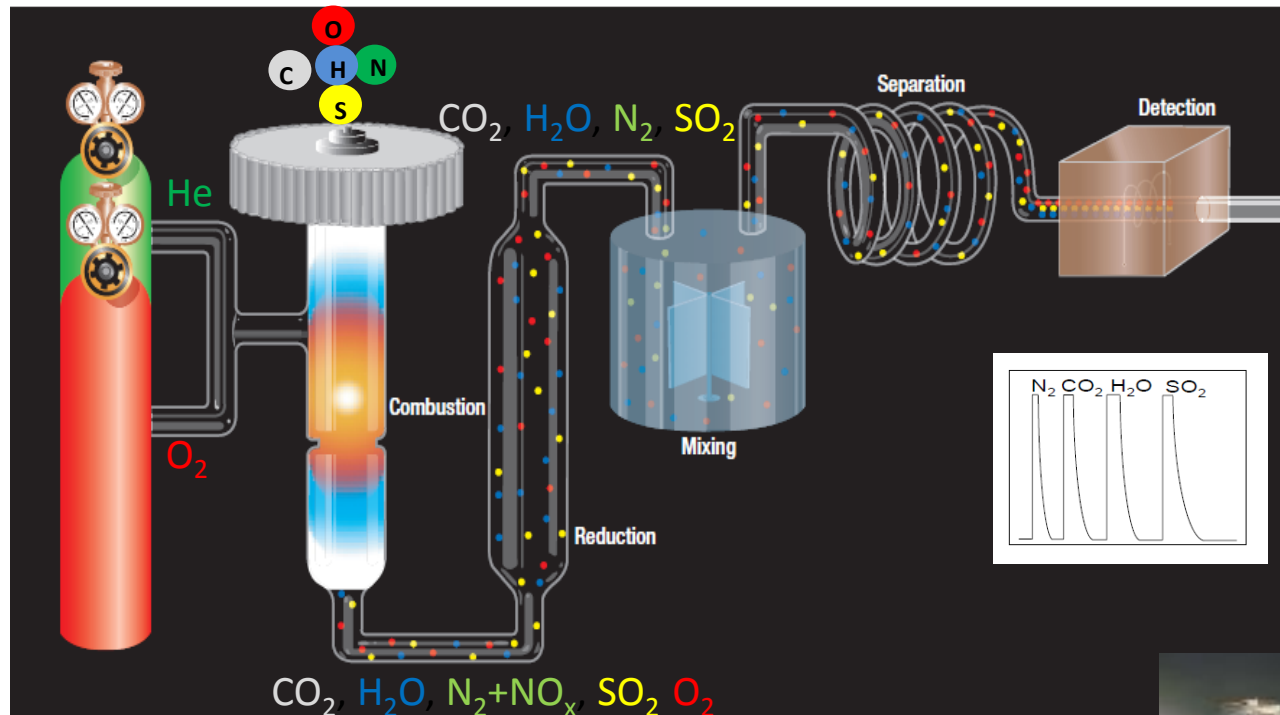
- On a ODM basis

- Methane production is positively related to the contents of C and H, and negatively related to that of O

Theoretical maximum methane production (2)

- Buswell equation

- Elemental analysis (ultimate analysis)



FlashEA 1112

Theoretical maximum methane production (2)

- Buswell equation

- The Buswell equation is used to estimate the theoretical maximum CH_4 production (as it assumes 100% organic biomass breakdown) and related CH_4 and CO_2 proportion, as well as H_2S and NH_3 production.
- CH_4 calculated using Buswell equation is always higher than can be obtained in AD process as small portion of biomass is consumed in the anabolic metabolic pathways and therefore converted to microorganisms
- Part of biomass is difficult to digest
- It provides however another performance benchmark for AD systems

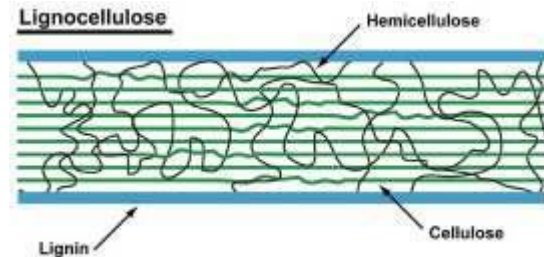
Theoretical maximum methane production (3)

- Biochemical composition

- Biochemical composition is also a set of key parameters used to describe biomass and choose (biochemical) process for biofuel production
- Organic dry matter (in plant biomass) includes
 - Simple sugars
 - Starch
 - Cellulose
 - Hemicellulose
 - Lignin
 - Lipid (fat & oil)
 - Protein
- Effective component(s) & Conversion efficiency?

Carbohydrates

Lignocellulose, or fibre

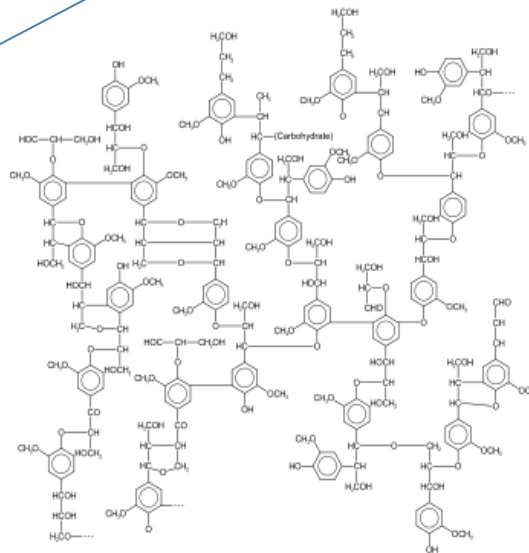


Theoretical maximum methane production (3)

- Biochemical composition

- Simple sugars
- Starch
- Cellulose
- Hemicellulose
- **Lignin**
- Lipid
- Protein

Biogas production via anaerobic digestion



Lignin

Source: Wikipedia

Theoretical maximum methane production (4)

- Chemical oxygen demand

- Chemical oxygen demand (COD) is commonly used in the water and wastewater industry to measure the organic strength of influent and effluent
- COD test is a wet chemistry analysis using strong oxidising reagent under acidic condition and high temperature
- The strength is expressed in 'oxygen equivalents' i.e. the amount of O_2 required to oxidise the organic carbon to CO_2
- The real advantage of the COD test is: when we measure the amount of oxygen consumed by a sample, we are in essence measuring the electrons transferred from the organic compounds to the terminal electron acceptor, *i.e.* O_2

Theoretical maximum methane production (4)

- Chemical oxygen demand

- Generally speaking, anaerobic conversion of complex organic material into biogas can be regarded as a disproportionate reaction of organic carbon: one stoichiometric portion of organic carbon is oxidised to CO_2 , and the rest portion of carbon is reduced to CH_4
- During anaerobic digestion process, electrons flow from oxidised carbon to reduced carbon, rather than captured by external electron acceptors
- Electron balance of anaerobic digestion
 $\text{COD of biomass} = \text{COD of CH}_4$

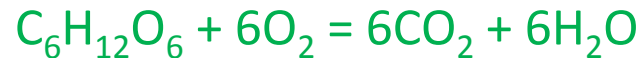
Theoretical maximum methane production (4)

- Chemical oxygen demand

- COD of biomass = COD of CH₄ produced

- Example: 1 mole of glucose C₆H₁₂O₆

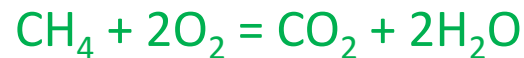
- COD of glucose = 192 g O₂



- Biochemical CH₄ potential of glucose = 3 mole CH₄ mol⁻¹ glucose



- COD of CH₄ = 64 g O₂ mol⁻¹ CH₄



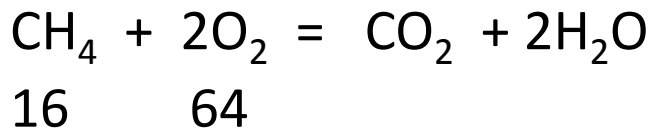
- Total COD of CH₄ produced from 1 mole of glucose = 3 × 64 = 192 g O₂

- COD of glucose = COD of CH₄ produced

Theoretical maximum methane production (4)

- Chemical oxygen demand

- One mole of methane requires 2 moles of oxygen to oxidise it to CO₂ and water, so each gram of methane produced corresponds to the removal of 4 grams of COD

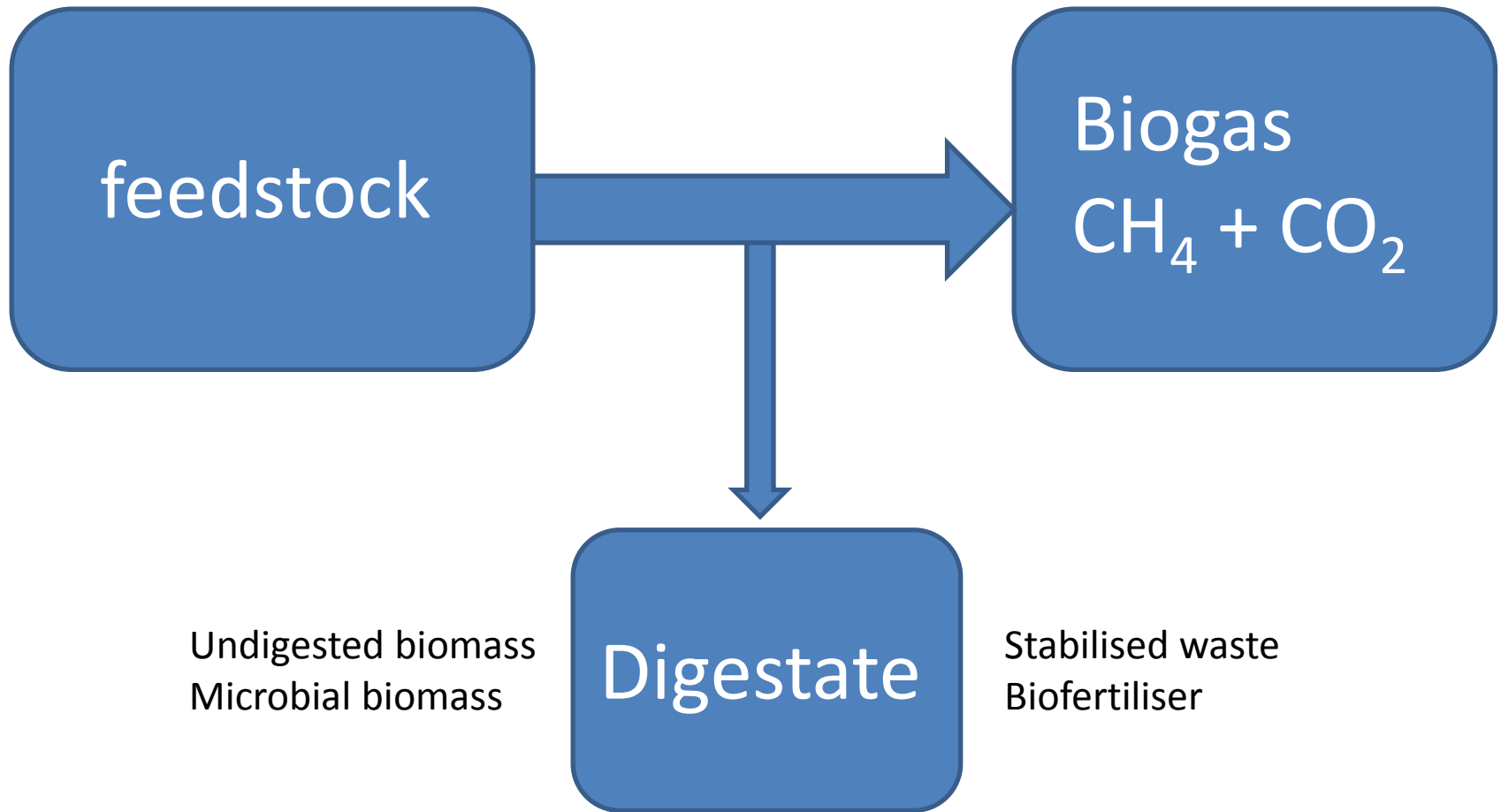


- 1 g of CH₄ produced corresponds to the removal of 4 g of COD
- 1 kg of COD removal is equivalent to 250 g of CH₄
- 250 g of CH₄
 - ⇒ 250/16 = 15.62 moles of CH₄
 - ⇒ 15.62 × 22.4 = 350 STP litres of CH₄ = 0.35 STP m³ of CH₄
- At standard temperature and pressure 1 kg of COD removed will yield 0.35 m³ of CH₄

Anaerobic digestion practice

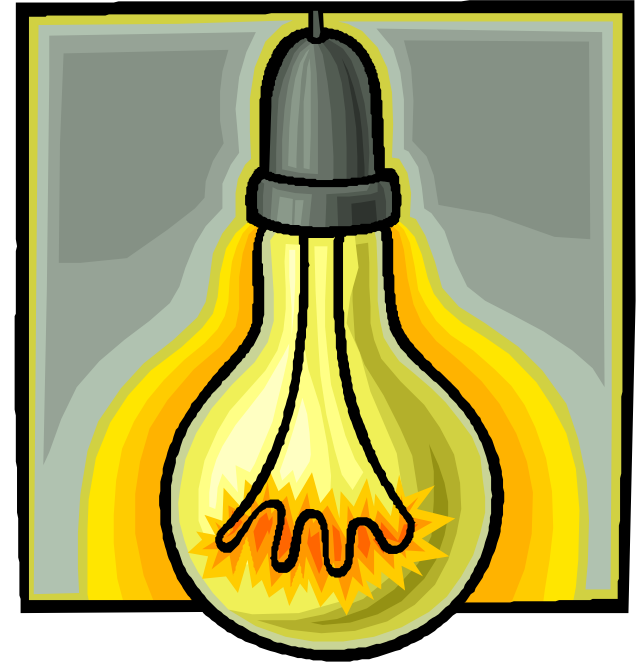
- Part of feed material is difficult to digest
- Another part of feed material is converted to microorganisms
- A third part of feed material is forced out of digester before getting a chance to be digested
- Only a proportion of the feed material is converted to biogas. This proportion is variable according to the characteristics of feed material as well as reactor operating conditions, typically:
 - Food waste 85%
 - Maize silage 80%
 - Biodegradable municipal waste 70%

Energy flow and mass flow in AD

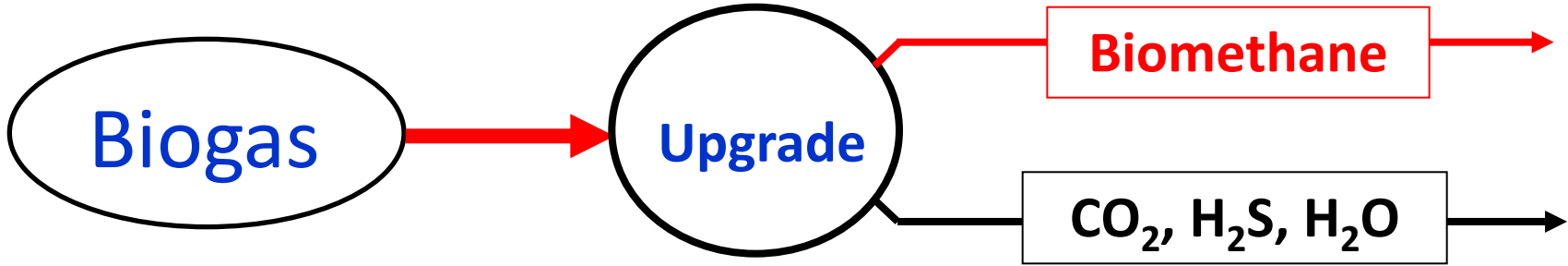
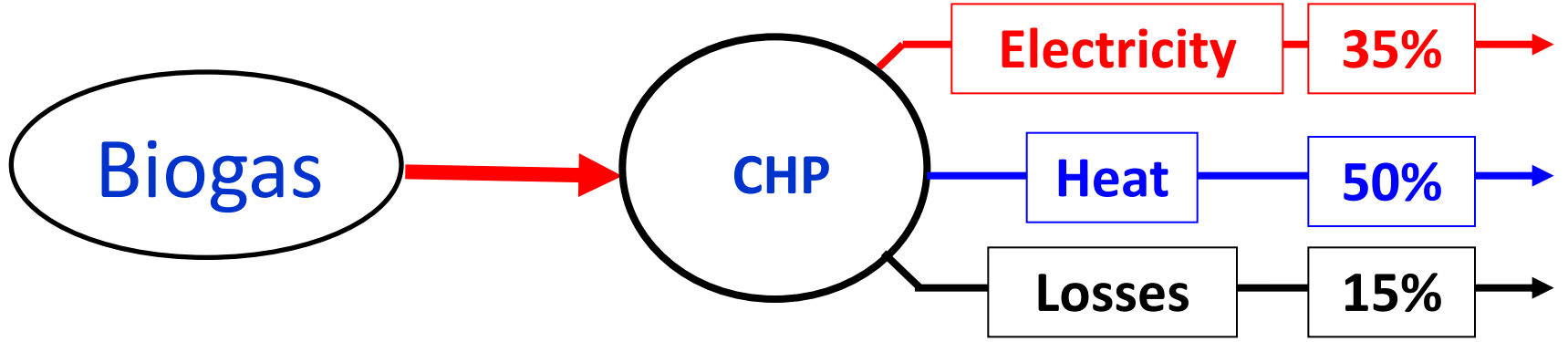
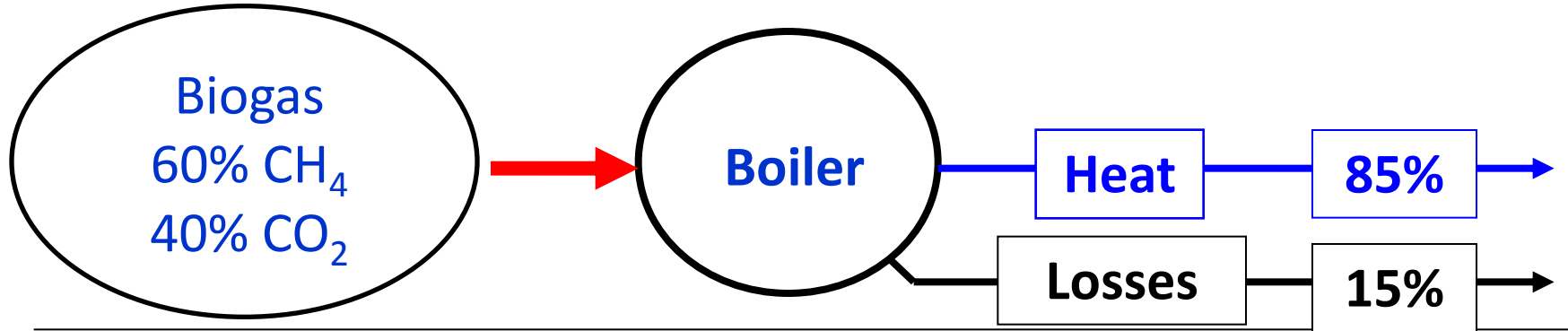


How much energy can we get from AD?

- Up to 75~85% 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



Question: 1m³ of biogas (60% of methane) => ??? kWh of electricity in CHP unit?

Energy flow and mass flow in AD

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)
1.00	0.35	0.40	140.0	0.70	0.55	53.9	71.9	100.6	3622

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)
1.00	5	5.0	20	70	50	0.8	1568	435.4	3622

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 analysis. 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 f
- 6 Methane content of biogas
- 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

Summary

- Biomass energy
- Estimation of theoretical maximum methane production
 - Calorific value
 - Elemental analysis and Buswell equation
 - Biochemical composition approach
 - Chemical oxygen demand approach
- Energy flow and mass flow in AD process
 - Extent of digestion process (conversion efficiency)