Conversion of Wet Waste to Fuel and Value-Added Products using Hydrothermal Carbonization

The Steps of Conducting a Biochemical Methane Potential (BMP) Experiment

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Agenda

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Time (BST)	Session
09:00-09:15	Welcome
09:15-09:45	**Session 1: What is a BMP Test?**
09:45-10:00	Session 1 Q+A
10:00-10:30	**Session 2: Setting up a BMP Test**
10:30-10:45	Session 2 Q+A
10:45-11:00	Break
11:00-11:30	**Session 3: Data Handling and Interpretation**
11:30-11:45	Session 3 Q+A
11:45-12:00	General Discussion and Close

Session 1
What is a BMP Test?

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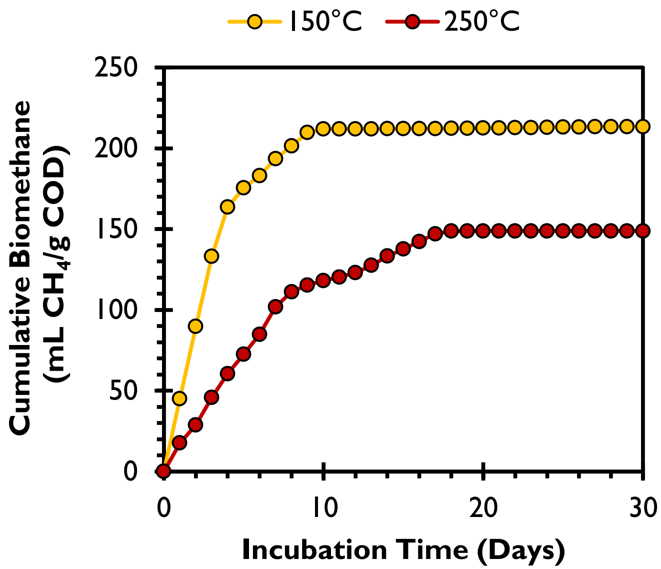
Session 1- What is a BMP Test?

This session will cover:

- Purpose of a BMP test
- Manual and Automatic BMP methodologies
- AMPTS II
- Integration of HTC-AD



Session 1- BMP Test and Equipment

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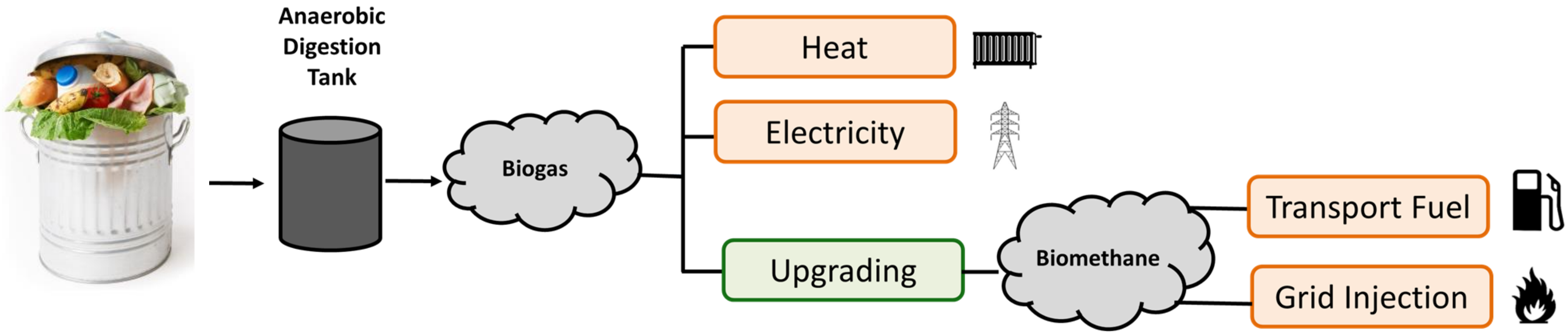
Anaerobic Digestion (AD) involves the biological conversion of organic matter, to produce biogas.

Biogas is a mixture of mainly methane (60%) and carbon dioxide (40%) which can be used directly as a fuel for heat and/or electricity generation.

A biochemical methane potential (BMP) test is a laboratory-scale experiment which provides information of the potential methane yields which can be generated from different feedstocks.



Session 1 - What is a BMP Test?

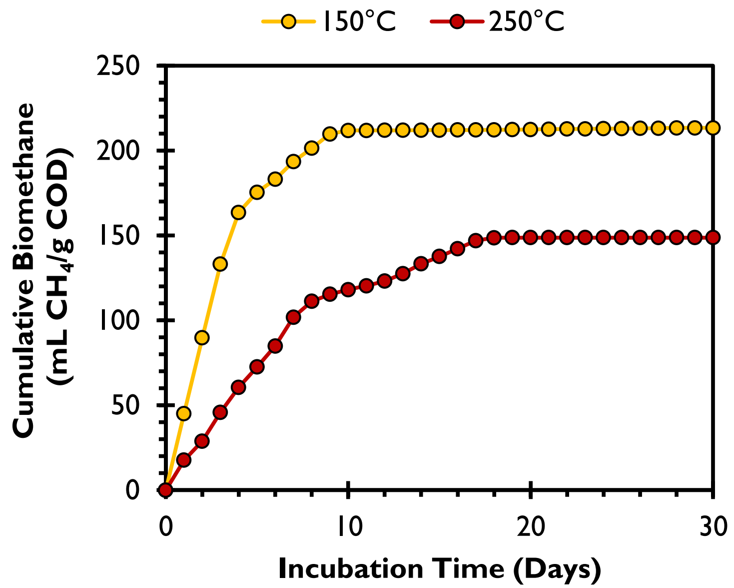
The BMP test measures the maximum amount of biomethane generated from a biomass under ideal conditions.

BMP is measured per mass of organic matter of biomass (VS or COD).

The results from BMP tests allow comparison of the biodegradabilities of different substrates.

These results are used in research and in economic and management decisions for designing and maintaining AD plants

Although methane yields in full-scale digesters are usually lower – hence the BMP tests measure biochemical methane <u>potential</u>



Session 1 – Manual vs Automatic

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Manual
(Manometric Method)

Biogas accumulates in a fixed headspace volume

Biogas volume determined either by measuring headspace pressure or liquid displacement

Composition of biogas measured by GC

Multiple reactors required to measure biogas over a fixed time period

Automatic
(Volumetric Method)

Biogas is generated continuously under constant pressure

Biomethane volume determined by liquid displacement

Composition of biogas is not measured; only biomethane

Session 1 – Manual vs Automatic

	Advantages	Disadvantages
Manual	➢ Potential to measure both biogas and biomethane volumes ➢ Allows monitoring of biochemical parameters during a test	➢ Human error during biogas/biomethane measurements
Automatic (AMPTS II)	➢ Continuous automatic recording of biomethane yield ➢ Automatic normalisation of gas to standard conditions	➢ Cost ➢ Only biomethane measured ➢ No monitoring of biochemical parameters during a test

Session 1 – AMPTS II

Maintains reactors under constant temperature

↑

Water Bath

↑

↓

Gas Scrubber Unit

↓

Removes CO_2 from biogas

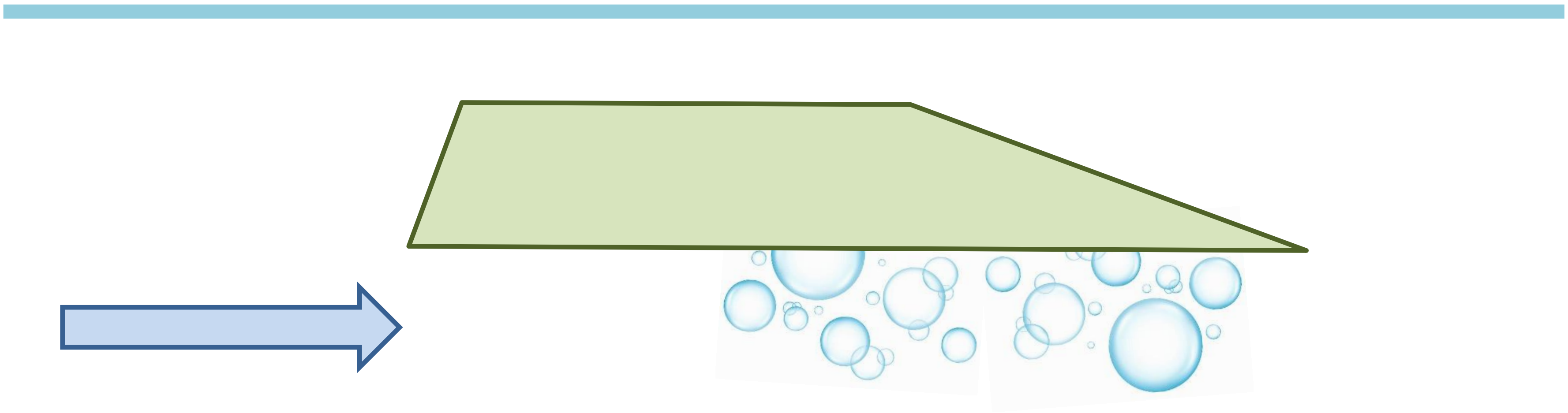
Measures biomethane volume by water displacement under STP (1 atm, 0°C, zero moisture)

↑

Gas Measurement Unit

↑

Session 1 – AMPTS II



Session 1 – Integrated HTC-AD

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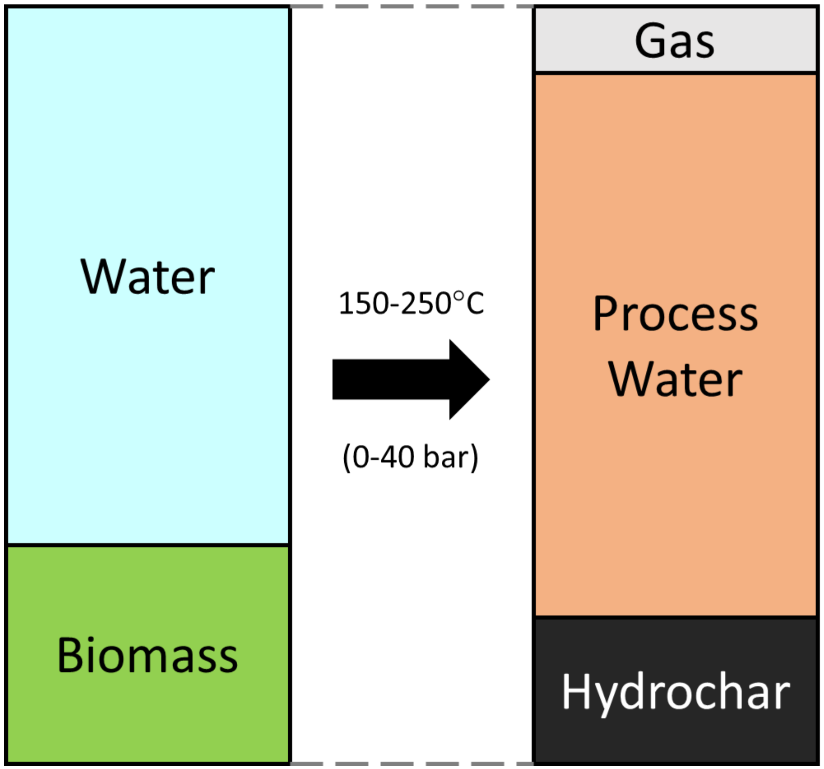
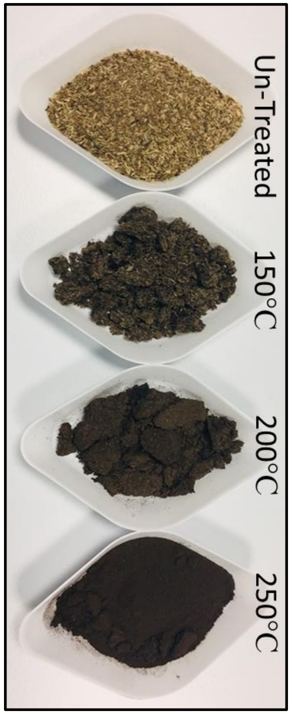
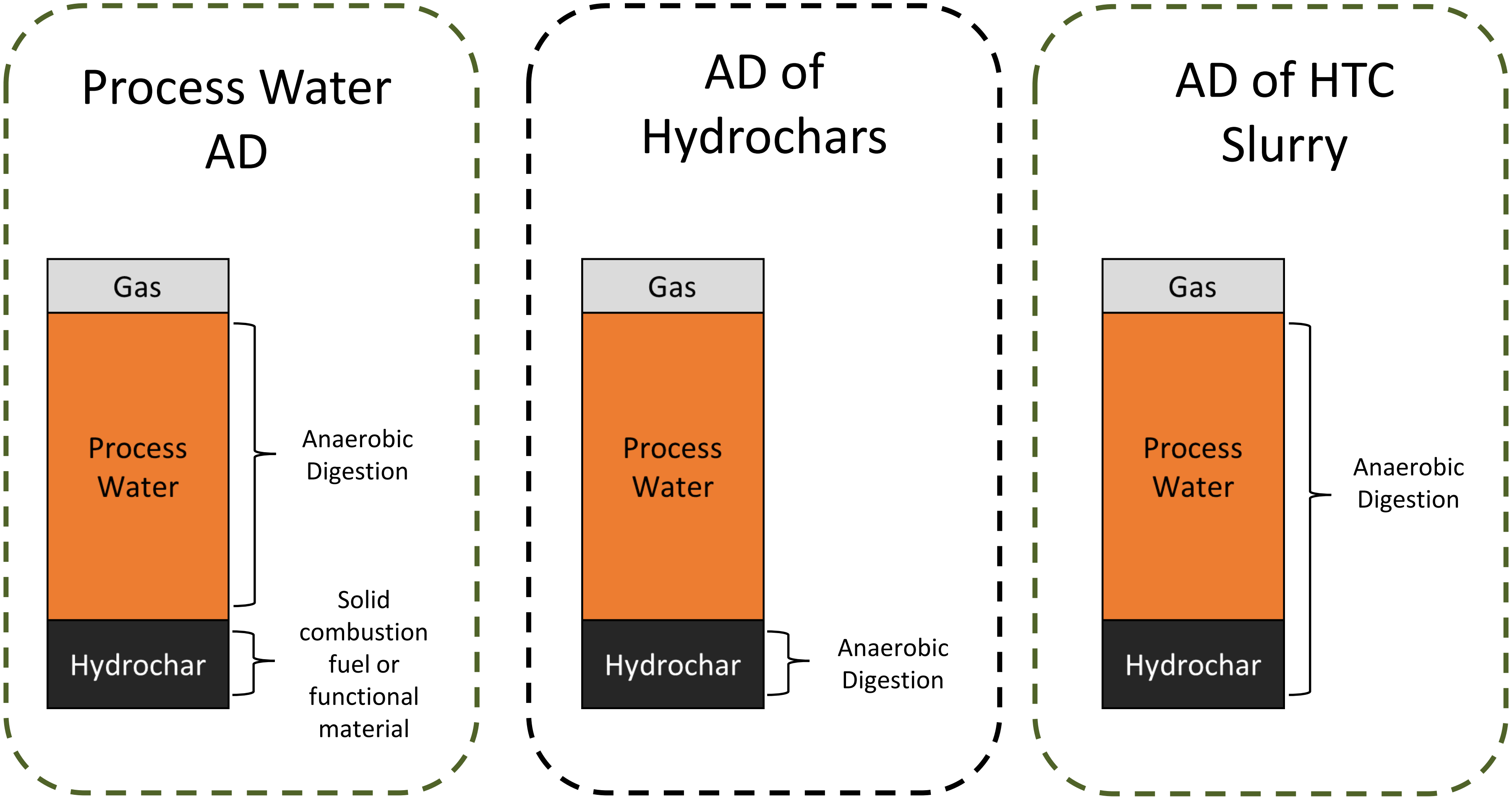




Session 1 – Integrated HTC-AD



Session 1 – Q+A

Thank you for listening

Any Questions?

Session 2
Setting up a BMP Test

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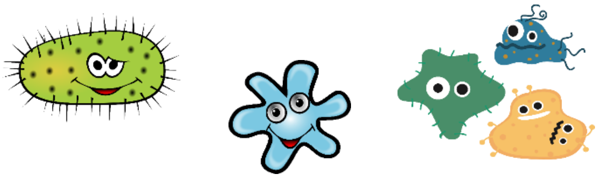
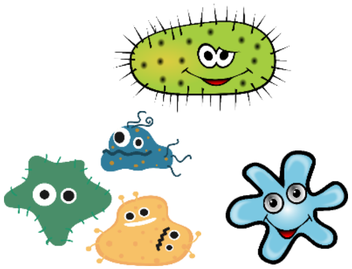
Session 2- Setting up a BMP Test



This session will cover:

- Processing of inoculum
- Establishing the parameters of a BMP Test
- Loading up a BMP Reactor
- Guidelines for a ‘gold standard’ BMP Test

Session 2- Inoculum



Collection

- Collect as fresh as possible
- Ideally, collect from an active anaerobic digester

Processing

- Homogenise by passing through a screen (E.g. 1-mm) to remove large particulate matter

Storage

- Store in a fridge (4°C) for a maximum of 1-month
- Or incubate (37°C) and 'feed' inoculum regularly to keep it active

De-gassing

- Incubate inoculum (37°C) for around 2-days before setting up BMP test to reduce residual methane emissions.

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Session 2- BMP Parameters

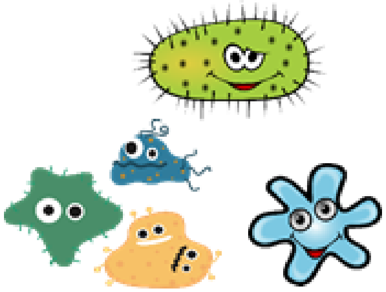
Parameter	Notes
Temperature	Mesophilic (35-42°C) or Thermophilic (45-60°C)
pH Adjustment	Optimal pH range is between 6.8-7.2
Nutrient Addition	Nutrients should not be limited Trace elements and vitamins can be added, if required
Replicates	Triplicate repeats (n=3) are preferred
Reactors	Tests should include [1] Sample [2] Blank [3] Positive Control
[1]ISR	ISR >2 recommended. Although this is feedstock dependent.

[1]Inoculum-to-substrate ratio.

Session 2 – ‘Our’ BMP Parameters

The biomethane potential of water hyacinth was measured using batch laboratory-scale digestions:

- AMPTS II
- Mesophilic conditions (37°C)
- 30-day incubation period
- 2:1 inoculum-to-substrate ratio
- Inoculum sourced from a waste water treatment plant
- Automatic mixing
- BMP was measured on a ‘volatile solid’ basis (mL CH_4/g VS) for solids
- BMP was measured on a ‘chemical oxygen demand’ basis (mL CH_4/g COD) for aqueous samples (process waters)

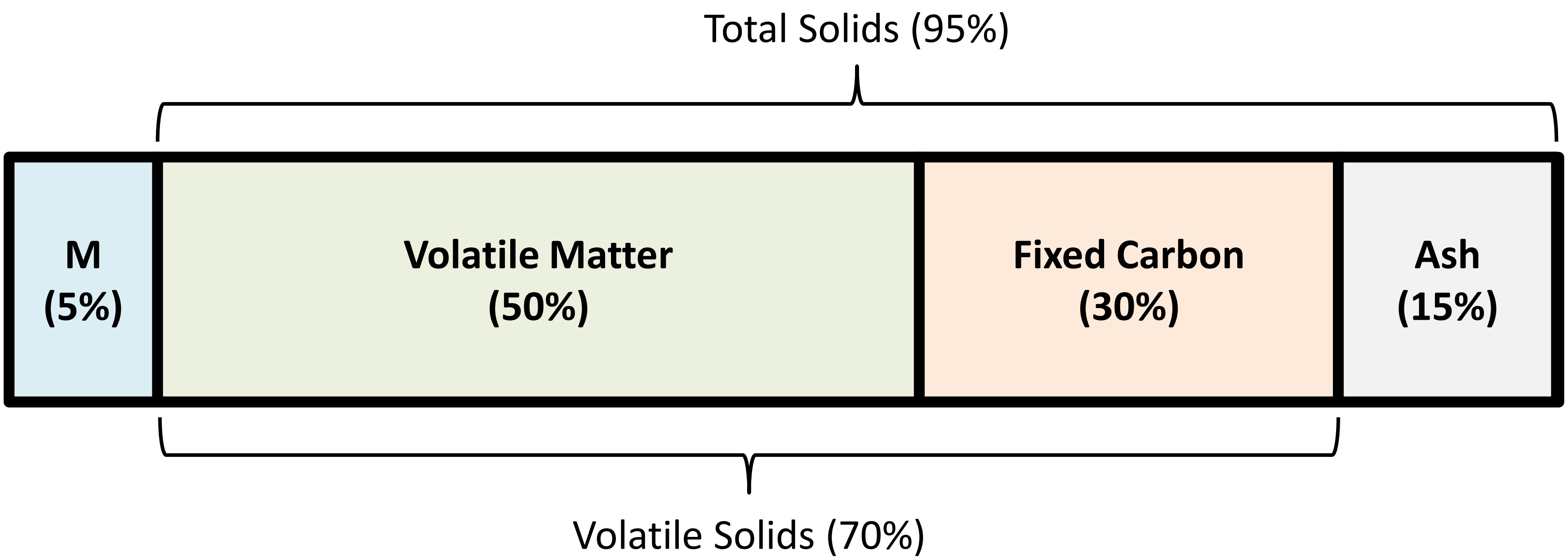


Session 2- TS/VS Methodology

Volatile solid content is a measure of the organic fraction of a feedstock:

- **Total** Solids = [Volatile Matter + Fixed Carbon + Ash]

- **Volatile** Solids = [Volatile Matter + Fixed Carbon]

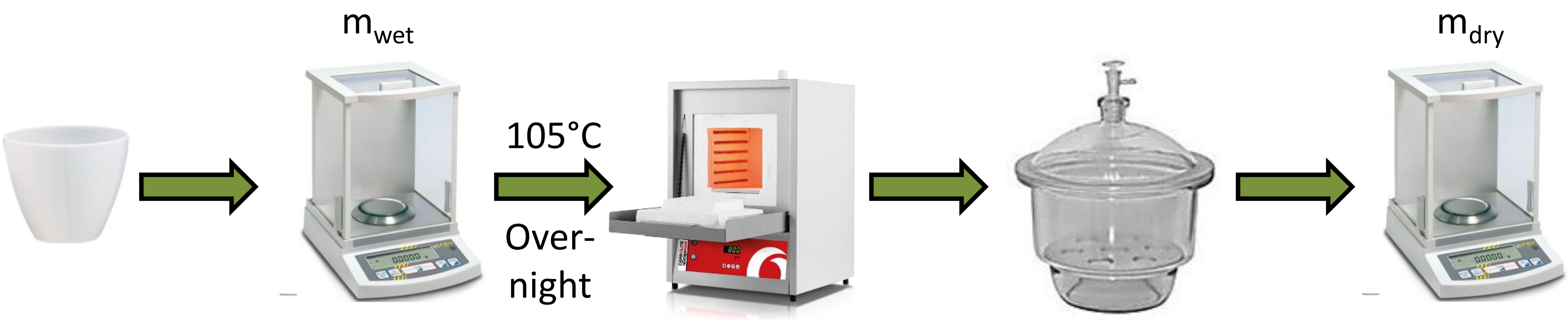


Session 2- Total Solids (TS)

Total solids are measured through heating a sample at <u>105°C:</u>

1. Weigh a clean crucible
2. Add approx. 1g of sample to the crucible and record the sample mass (m_{wet})
3. Place crucible in a pre-heated oven at 105°C and leave overnight (~24-hours)
4. Cool the crucible in a desiccator and weigh the crucible and calculate the sample mass (m_{dry})

$$TS\ (\%) = \frac{m_{dry}}{m_{wet}}$$

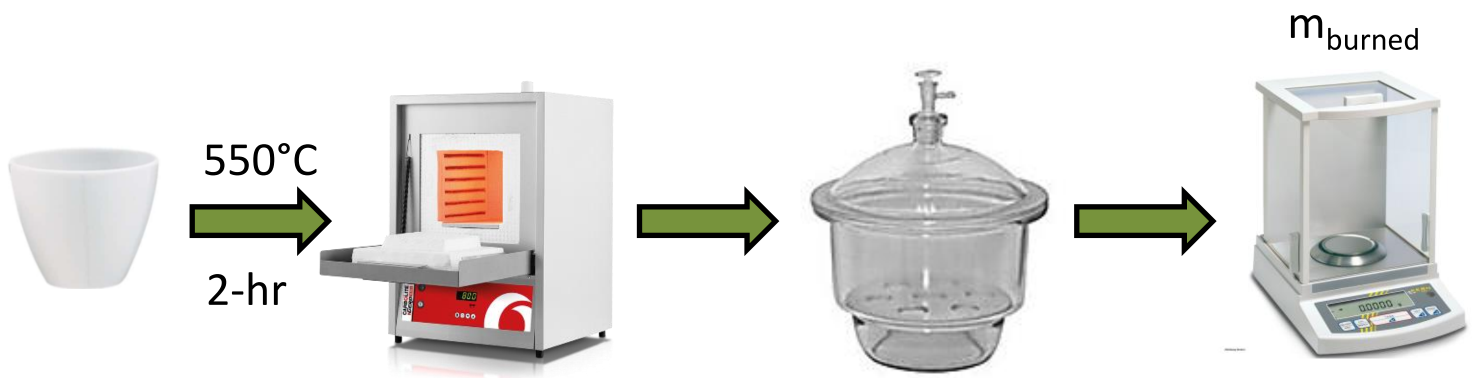


Session 2- Total Solids (VS)

Total solids are measured through heating the residue from TS analysis at 550°C:

1. Transfer the crucible with the remaining residue from TS analysis to a pre-heated furnace at 550°C and leave for 2-hours.
2. Cool the crucible in a desiccator and weigh the crucible and calculate the sample mass (m_{burned})

$$VS\ (\%) = \frac{m_{dry} - m_{burned}}{m_{wet}}$$



Session 2- Loading a BMP Reactor

100mL
Headspace

400mL
Working Volume

200mL
Inoculum → **20g VS/L**

200mL
Sample → **10g VS/L**

2:1
Inoculum-to-substrate ratio

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Session 2- COD Method

- Chemical oxygen demand (COD) is considered indirect measure of the organic matter within a liquid sample – for example HTC process water
- COD analysis can be conducted on solid samples, but this is not recommended
- COD can be determined using HACH cuvette kits (LCK014), however a manual method also exists (BS 6068-2.34).
- Oxidizable substances react with sulphuric acid and potassium dichromate solution in the presence of a silver sulphate catalyst. The green colouration of Cr_3^+ is evaluated using UV-Vis spectrophotometry.

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Session 2- Loading a BMP Reactor

100mL
Headspace

400mL
Working Volume

200mL
Inoculum → **20g <u>COD</u>/L**

200mL
Sample → **10g <u>COD</u>/L**

<u>2:1</u>
Inoculum-to-substrate ratio

Session 2- Loading a BMP Reactor

Blank	Sample	Positive Control
200mL 20g VS/L Inoculum	200mL 20g VS/L Inoculum	200mL 20g VS/L Inoculum
200mL Distilled Water	200mL 10g VS/L Sample	200mL 10g VS/L Positive Control

Session 2- Positive Control

- A positive control confirms sufficient microbial activity from the inoculum, which validates the BMP test.
- Microcrystalline cellulose is the most widely reported positive control used across studies.
- Cellulose should yield between 352-414 mL CH_4/g VS to validate the BMP test.
- Recent reports indicate the use of common supermarket products as positive controls. Although microcrystalline cellulose is the most extensively studies.

Session 2- Loading a BMP Reactor

- Once loaded, the reactor is sealed and fitted with an electronic agitator.
- Reactors are flushed with N_2 to ensure anaerobic conditions.
- Reactor motors are connected together to ensure simultaneous mixing.
- Reactors are placed in the water bath.
- The BMP test can begin.

Session 2 – A ‘Gold Standard’ BMP Test

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Defining the biomethane potential (BMP) of solid c
wastes and energy crops: a proposed protocol for
assays

I. Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J. L. Campo
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frontiers in Environmental Science
HYPOTHESIS AND THEORY
published: 01 November 2019
doi: 10.3389/fenvs.2019.00178

thane potential tests

laki, Irini; Astals, S.; Baier, U.; Bougrier, C.; Buffiere, P.;
ernandez, B.; Ficara, E.; Fotidis, Ioannis; Frigon, J.-C.; de
artel, M.; Heerenklage, J.; Horvath, I. S.; Jenicek, P.; Koch, K.;
ger, L.; Nistor, M.; Oechsner, H.; Oliveira, J. V.; Paterson, M.;
oso, F.; Ribeiro, T.; Rusch Pfund, F.; Stromberg, S.; Torrijos,
a, H.; Wierinck, I.

Identification of Critical Problems in Biochemical Methane Potential (BMP) Tests From Methane Production Curves

Konrad Koch[1*], Sasha D. Hafner[2], Sören Weinrich[3] and Sergi Astals[4,5]

water

Review

Biochemical Methane Potential (BMP) Assay Method for Anaerobic Digestion Research

Jameson Filer, Huihuang H. Ding and Sheng Chang *

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Received: 16 March 2019; Accepted: 28 April 2019; Published: 1 May 2019

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Article

Improving Inter-Laboratory Reproducibility in Measurement of Biochemical Methane Potential (BMP)

Sasha D. Hafner [1,*,†], Hélène Fruteau de Laclos [2], Konrad Koch [3] and Christof Holliger [4,*]

Session 2 – 'Gold Standard' BMP

A 'gold standard' BMP test includes the following:

- Active, homogenised inoculum – used as freshly as possible
- Flush reactors with a mixture of CO_2 & N_2
- Total reactor contents recommended between 20-60 g VS/L
- Inoculum-to-substrate ratio of between 2:1-4:1 recommended
- Inclusion of a positive control – E.g. microcrystalline cellulose
- The duration of the BMP test should not be fixed – and should be finished when cumulative gas production is <1% across three consecutive days
- Report gas values under standard conditions (1 atm, 0°C, zero moisture)

Session 2 – Q+A

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Any Questions?

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Session 3
Data Handling and Interpretation

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Session 3 –

This session will cover:

- Interpreting raw BMP Data
- Calculating the biodegradability of a biomass
- Modelling the digestion kinetics of BMP curves
- Calculating the energy balance of integrated HTC-AD

Session 3 – Initial Data Output

$$\mathrm{BMP_{ex}} = \frac{(V\mathrm{CH_4Sample} - V\mathrm{CH_4Blank})}{VS\mathrm{Sample}}$$

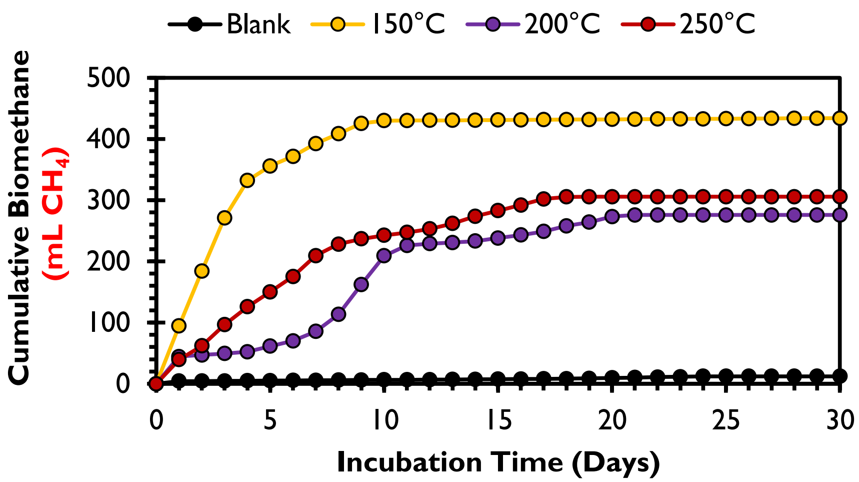
$V\mathrm{CH_4}$Sample = Volume of biomethane from the sample reactor (mL)
$V\mathrm{CH_4}$Blank = Volume of biomethane from the blank reactors (mL)
*VS*Sample = Mass of sample VS in reactors (2g)

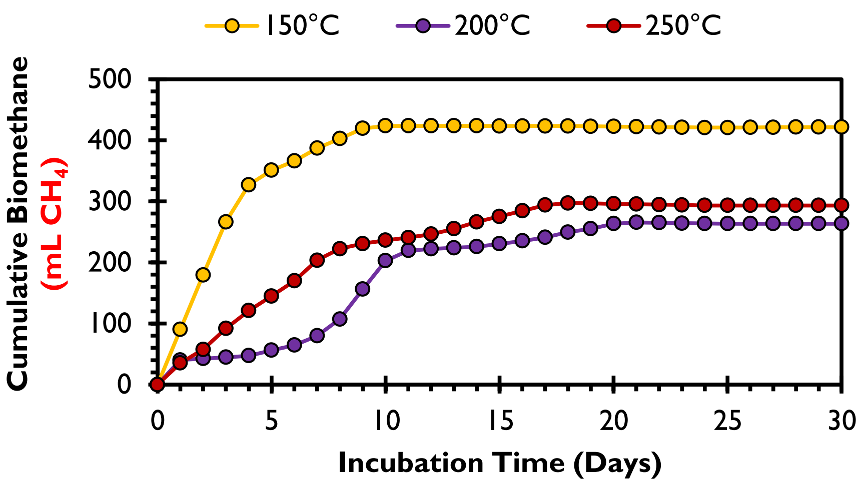
Session 3 – Initial Data Output

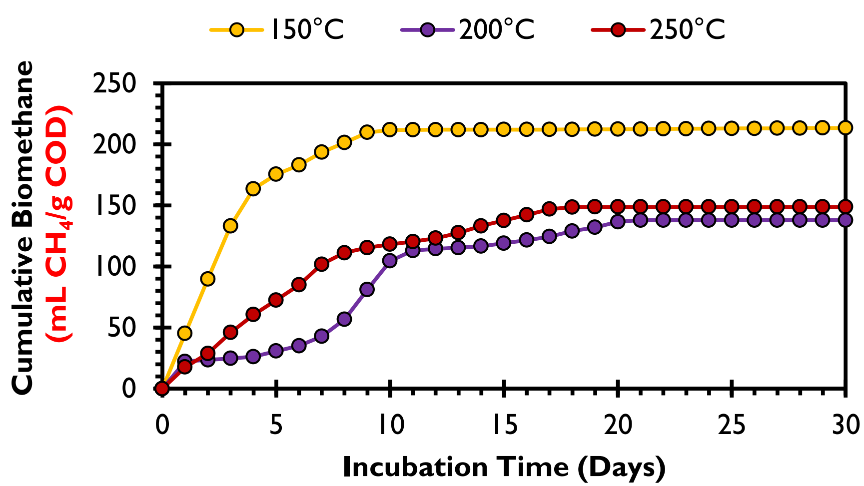
$$\mathrm{BMP_{ex}\ Aqueous\ Residues} = \frac{(V\mathrm{CH_4Sample} - V\mathrm{CH_4Blank})}{COD\mathrm{Sample}}$$

$V\mathrm{CH_4}$Sample = Volume of biomethane from the sample reactor (mL)
$V\mathrm{CH_4}$Blank = Volume of biomethane from the blank reactors (mL)
*COD*Sample = Mass of sample COD in reactors (2g)

Session 3 – Initial Data Output







Session 3 – Theoretical BMP

Theoretical biomethane potential (BMP_{th}) can be calculated using the elemental (CHNS-O) composition of a sample.

Food Waste	C	H	N	S	O
Wt%	50.9	3.0	7.2	0.1	38.8
Atomic mass (g/mol)	12	1	14	32	16
Molar Fraction	4.2	7.2	0.2	-	2.4

$$BMP_{th}\ \text{Buswell} = \frac{22\,400\left(\frac{c}{2}+\frac{h}{8}-\frac{o}{4}\right)}{12c+h+16o}$$

$$BMP_{th}\ \text{Boyle's} = \frac{22\,400\left(\frac{c}{2}+\frac{h}{8}-\frac{o}{4}-\frac{3n}{8}\right)}{12c+h+16o+14n}$$

The Boyle's Equation is considered more accurate, due to the consideration of the Nitrogen-fraction.

Session 3 – BI Example

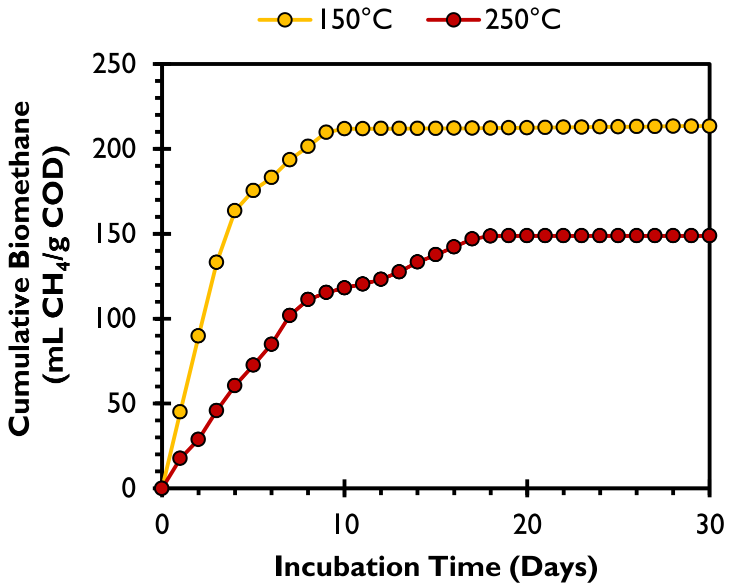
Food Waste	
Theoretical Biomethane Potential (Boyle's BMP_{th})	523 mL CH_4/g VS
Experimental Biomethane Potential (BMP_{ex})	478 mL CH_4/g VS
Biodegradability Index (%)	91%

$$BI = \frac{BMP_{ex}}{BMP_{th}} \times 100$$

Session 3 – Digestion Kinetics

The digestion kinetics of cumulative BMP_{ex} curves can be described by fitting the curves.

One of the most common methods of describing the process kinetics is by using the **Modified Gompertz Model**

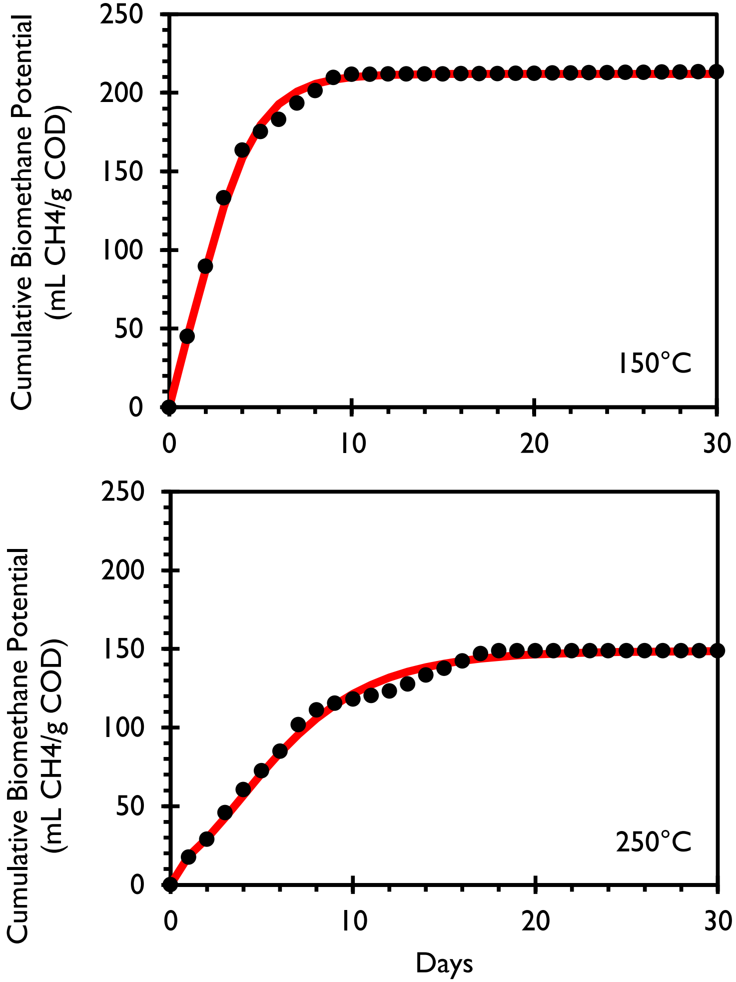


Session 3 – Modified Gompertz Model

$$Gompertz = H_m \exp\left[-\exp\left(\frac{R_m e}{H_m}(\lambda - t) + 1\right)\right]$$

Symbol	Meaning	Unit
H_m*	Maximum biomethane yield	mL CH_4/g COD
Exp	Exponential function	-
R_m*	Peak methane production rate	mL CH_4/g COD/d
e	Constant	2.71828
λ*	Lag time	d
t	time	d

*Calculated using by the sum of least squares using MS Excel or SPSS



Session 3 – Modified Gompertz Model

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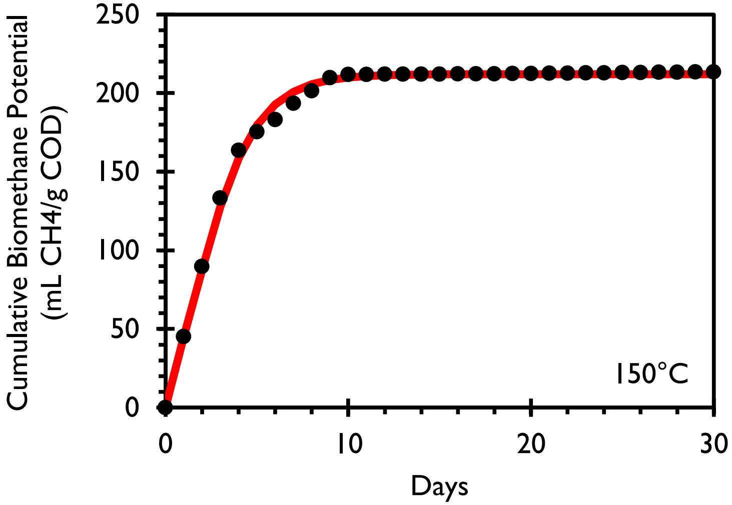
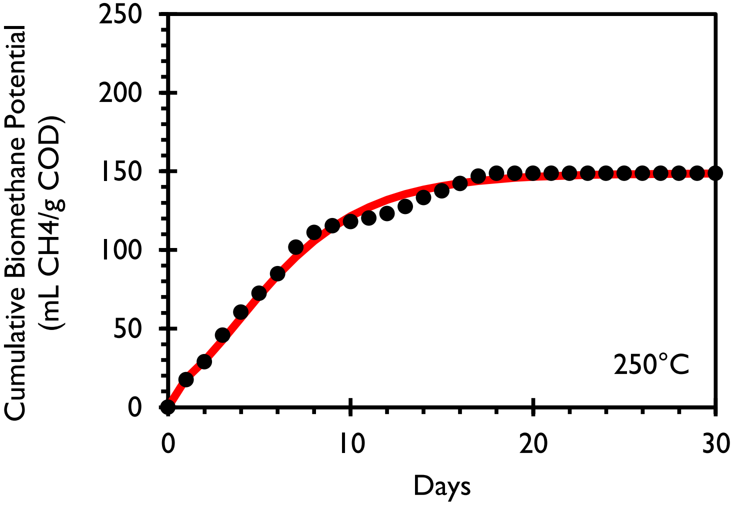
Sample	BMP_{ex}	H_m	R_m	λ	R^2
	mL CH_4/g COD	mL CH_4/g COD	mL CH_4/g COD/d	d	-
150°C	213.4	212.1	43.6	0.0	0.99
250°C	148.8	148.7	14.2	0.0	0.99

BMP_{ex}=experimental biomethane potential. H_m=maximum biomethane production. R_m=peak biomethane production rate. λ=lag phase.





Session 3 – Energy Balance Calculations

- Integrating HTC-AD allows for a greater energy recovery efficiency, compared to AD alone.

- The energy balance (energy output vs energy input) can be calculated for the different HTC-AD integration strategies.

- The following slides work through an example of calculating the energy balance of HTC, where the hydrochars are used as a combustion fuel and the process waters used as a feedstock for AD.

- In this instance, water hyacinth is used as an example biomass – although the equations are universally applicable to any biomass.

Session 3 – Energy Input Calculations

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$$\text{Energy Input HTC (MJ/kg)} = \frac{(VwCw + Mb\,Cb) \times (Treac - Tamb)}{Mb}$$

Parameter	Description	Units	Example
*V*w	Volume of water in HTC reactor	kg	0.88
*C*w	Specific heating capacity of water	KJ/kg/K	4.2
*M*b	Mass of biomass in HTC reactor	kg	0.096
*C*b	Specific heating capacity of water	KJ/kg/K	1.5
*T*reac	HTC reaction temperature	°C	250
*T*amb	Ambient temperature	°C	25

9.00 MJ/kg

Session 3 – Energy Output Calculations

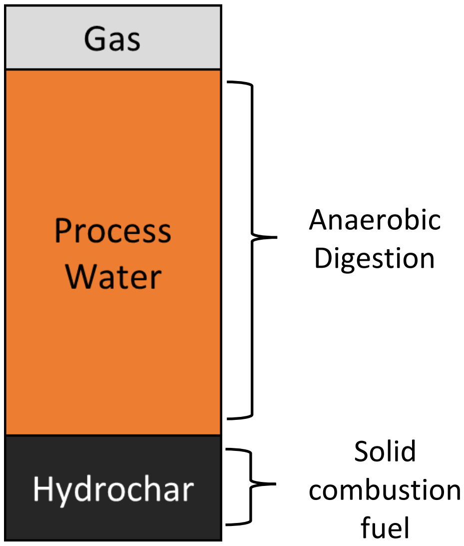
$$\text{Energy Output Process Water AD (MJ/kg)} = \frac{M\text{pw} \times \text{COD} \times \text{BMP}_{ex}}{1{,}000{,}000} \times 39.8$$

$$\text{Energy Output Hydrochar Combustion (MJ/kg)} = M\text{hc} \times \text{HHV}$$

Parameter	Description	Units
*M*pw*	Mass of residual process water*	kg
COD	Chemical oxygen demand	g/L
BMP_{ex}	Experimental biomethane potential	mL CH_4/g COD
1,000,000	Conversion of mL to m^3	-
39.8	HHV of methane	(MJ/m^3)
*M*hc*	Mass of residual hydrochar*	kg
HHV	HHV of residual hydrochar	(MJ/kg)

*based on a starting point of 1-kg dry biomass

Process Water AD



Session 3 – Energy Balance

Parameter	Energy Input (MJ/kg)	Energy Output (MJ/kg)			EROI*
		Hydrochar Combustion	Process Water Digestion	Combined	
WH	-	-	3.02	3.02	-
WH HTC-150°C	5.00	10.23	1.50	11.73	5.21
WH HTC-200°C	7.00	9.11	1.44	10.55	3.35
WH HTC-250°C	9.00	7.83	1.80	9.63	2.37

*assumed 55% energy recovery efficiency.

energies
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Article

An Assessment of Different Integration Strategies of Hydrothermal Carbonisation and Anaerobic Digestion of Water Hyacinth

Aaron E. Brown [1], Jessica M. M. Adams [2], Oliver R. Grasham [1], Miller Alonso Camargo-Valero [3,4] and Andrew B. Ross [1,*]

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Session 3 – Q+A

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