Food waste to H_2
Biorefineries as a tool for environmental innovation

Joana R. Ortigueira

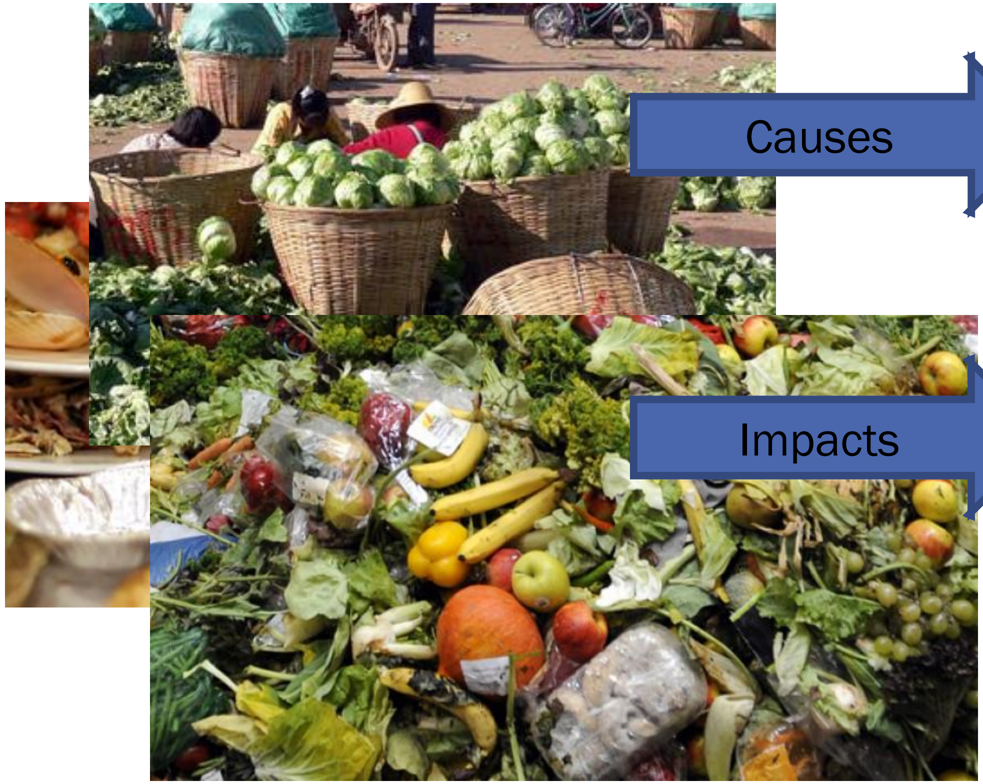
1.

Context & Introduction

The problematic of food waste

Food Waste

Raw or cooked food lost before, during or after meal preparation, as well as food discarded in the manufacturing/production, distribution, wholesale/retail and food service sectors



Causes

1. Overproduction & faulty production
2. Inadequate marketing rules and strategies
3. Deficient stock management
4. High appearance standards

Impacts

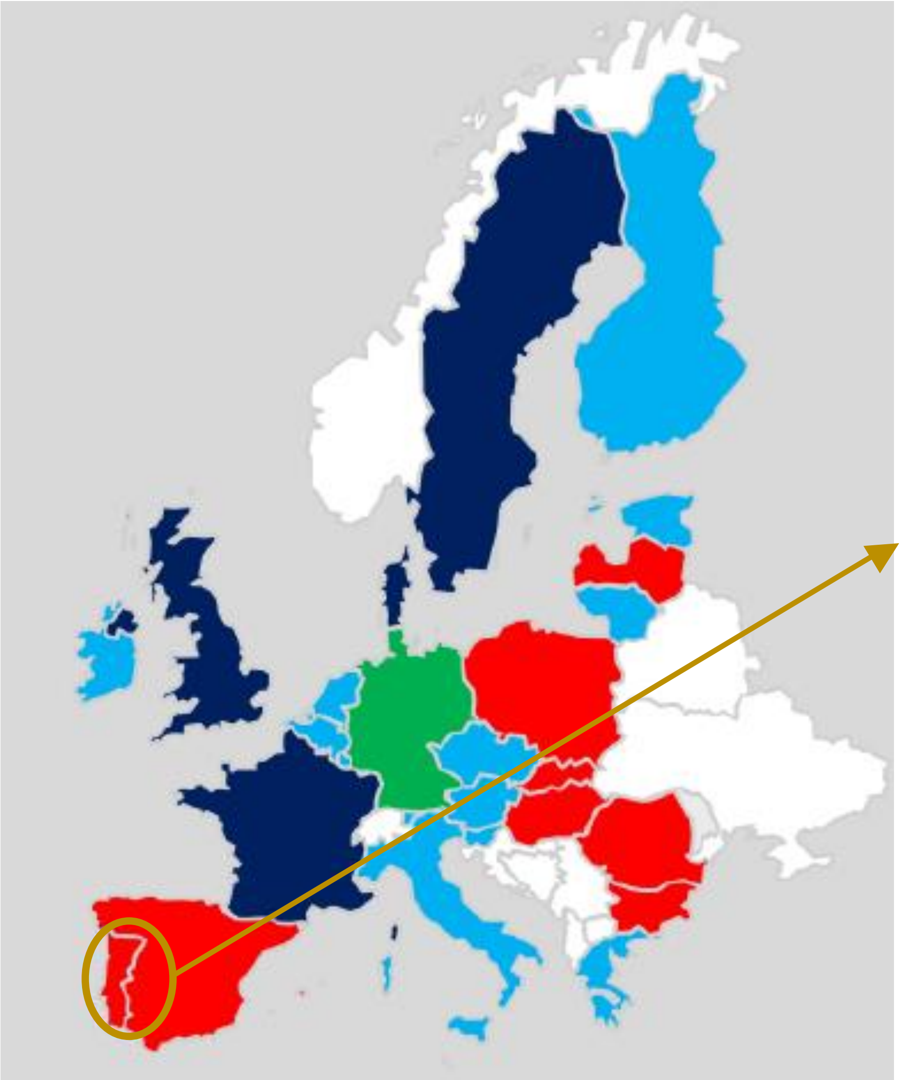
A. Waste of resources
B. Environmental impact
C. Cost of treatment and disposal

Directly affects food security and availability

- Less variable chemical characterisation
- Generally with set valorisation/disposal methods
- Highly dependent of cultivated cultures

- Highly dependent of the local diet, culture and territory
- Chemical characteristics dependent of seasonality
- High water content (>70-80%)
- Extremely heterogenous

Food waste quantification and disposal



FUSIONS, Reducing food waste through social innovation, 2016

At the EU-28 level (*per year*):

1.031

Mt of food waste produced in the Portuguese territory

kg CO_2 eq. *per capita*

143 billion €

Economic loss

In 2017, 39% of the portuguese urban residues were classified as bioresidues

42% of the biodegradable urban residues were valorised

58% of biodegradable urban residues

Anaerobic digestion

Biological conversion of residue into methane and compost in anaerobic environment

Composting

Biological conversion of residue into compost in aerobic environment

Landfill

Deposition of residue in between layers of soil

1 830 000 t
of biodegradable urban residues

980 000 t
were disposed of in *landfill*

Relatório Anual de Resíduos Urbanos, 2017

Biological process disadvantages

- Production of CO_2 and H_2S
- Release of CH_4
- Extensive process duration (2-10 weeks)

Biogas conversion disadvantages

- Production of NO_x and CO_2
- Release of non-converted fuel (CH_4)
- Low efficiency of fuel combustion (20-30%)

Waste management guidelines

"Member States shall not accept the following waste in landfills for non-hazardous waste by 1 January 2025, recyclable waste including plastics, metals, glass, paper and cardboard, and other biodegradable waste."

Ammendment to 1999/31/EC on the landfill of waste

ERL codes (European residue list): ERL 010203, ERL 020203, ERL 020304, ERL 020501, ERL 020601

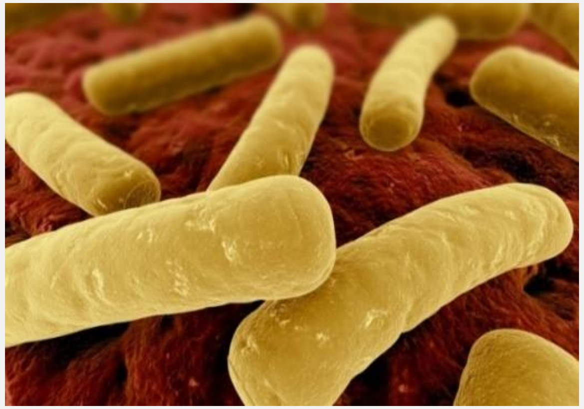
Material degradable through biological decomposition → FOOD WASTE

- Carbohydrates
- Proteins
- Fat
- Assorted funcionalised compounds

2.

Acidogenic fermentation as valorisation system

Dark fermentation as valorisation system



Anaerobic bacteria

H_2

Organic acids

- Highly functionalised compounds
- Industrial building block for polyhydroxyalkanoates production
- Drop-in biofuel: butyl-butyrate
  n-butanol

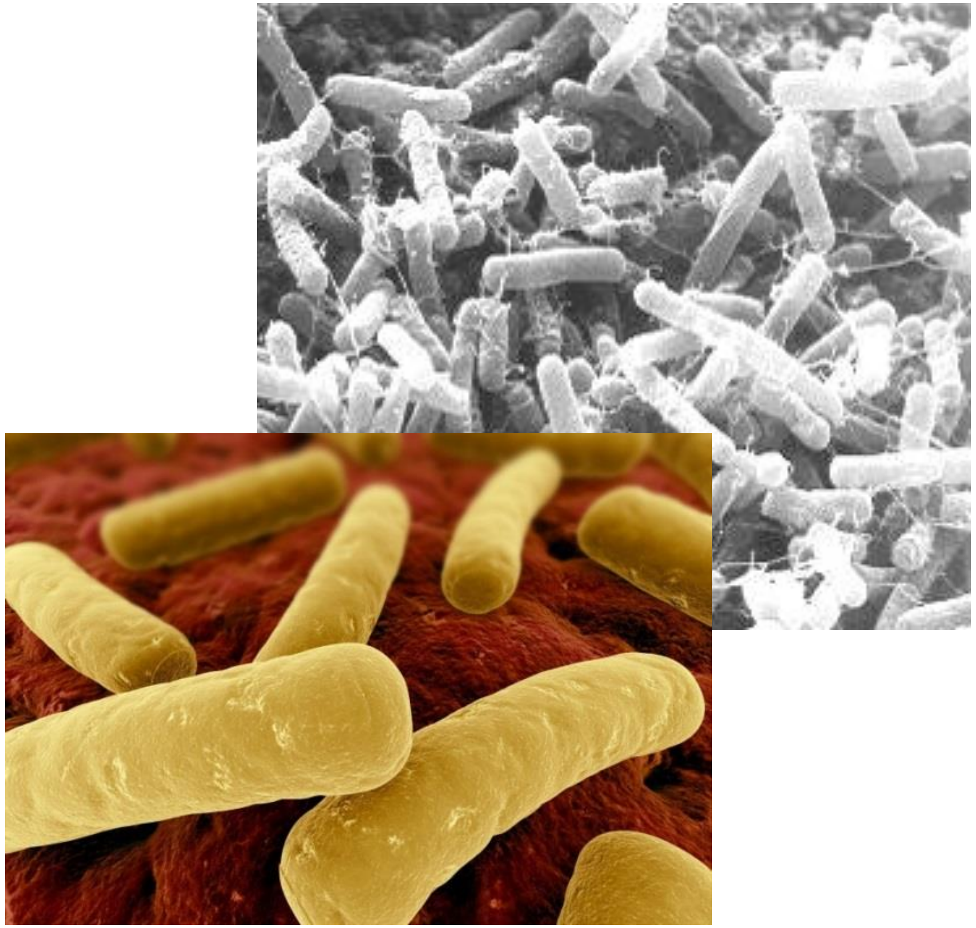
High heat

Easily converted into

No CO_2 or NO

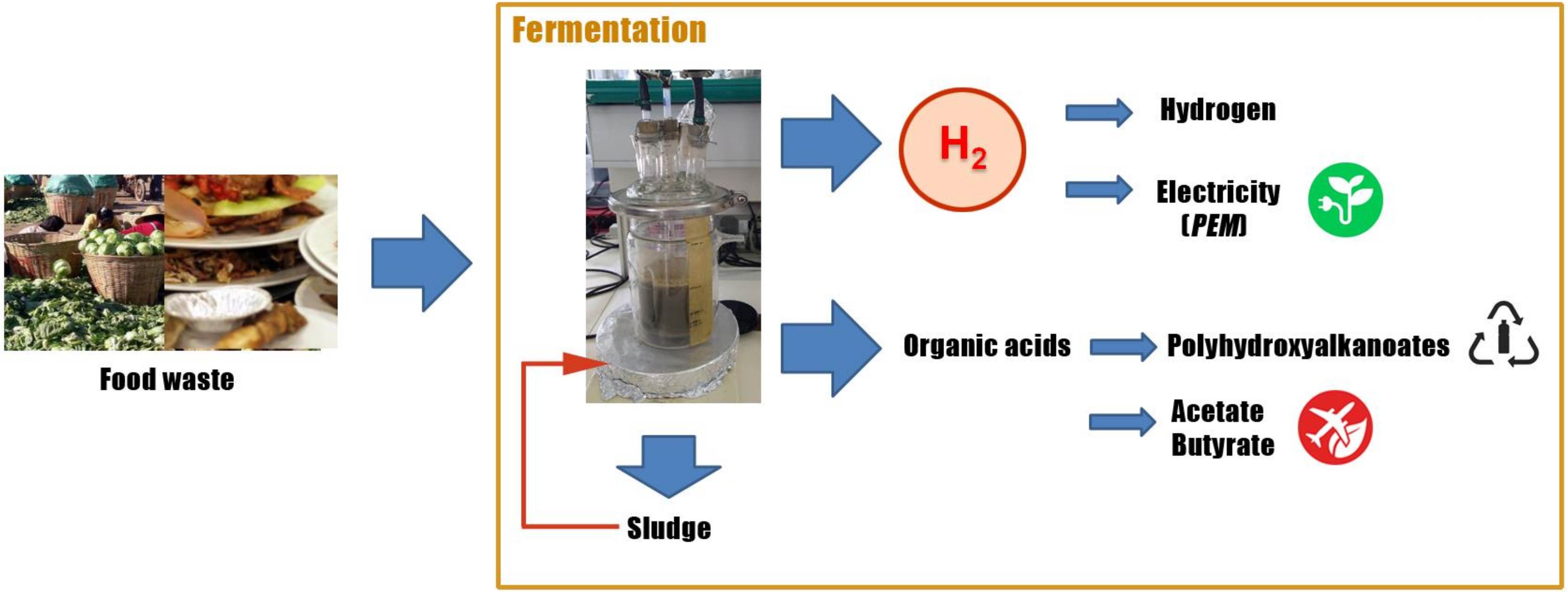
2. Acidogenic fermentation of food waste

Clostridium butyricum as vector for energy production

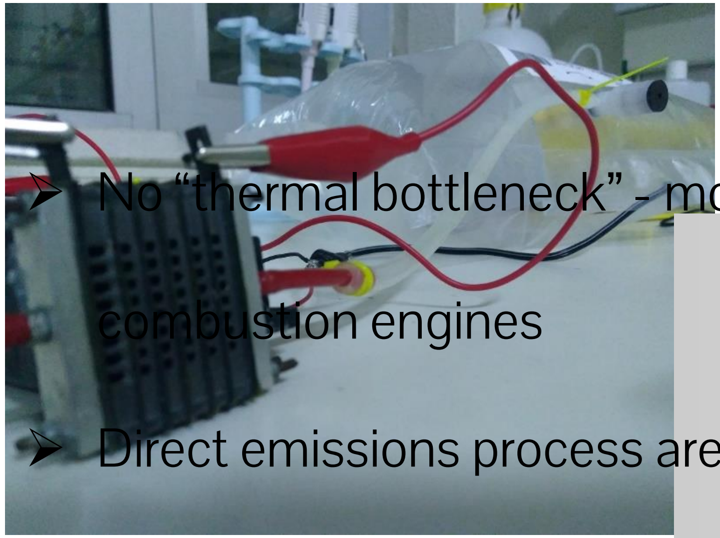


- Strict anaerobic bacteria.
- Extensive characterisation and subject to variated strain improvements
- Good H_2 producer.
- Capable of converting a wide range of substrates with high yields.
- Optimal pH 5.2-6.0

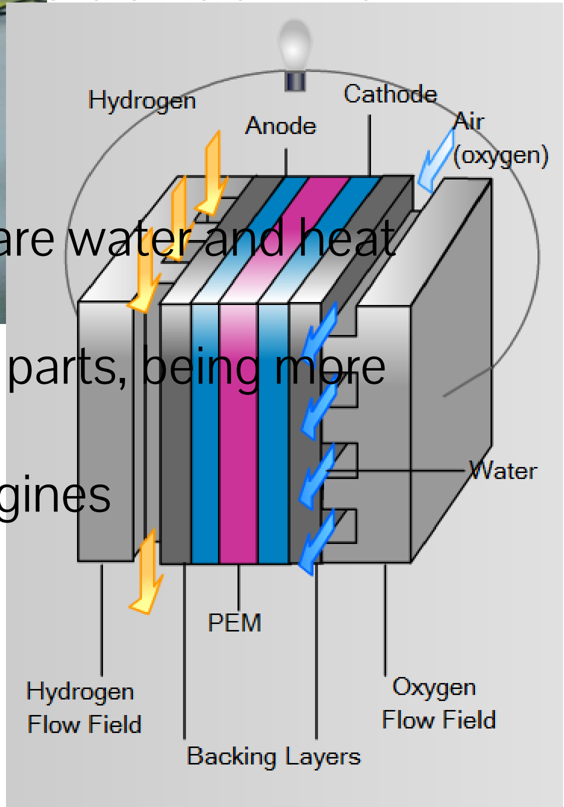
Proposed food waste biorefinery



Main product: H_2 to electricity

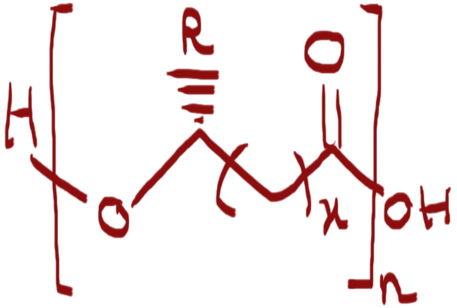


- No "thermal bottleneck" - more efficient than combustion engines
- Direct emissions process are water and heat
- Fuel cells have no moving parts, being more reliable than traditional engines

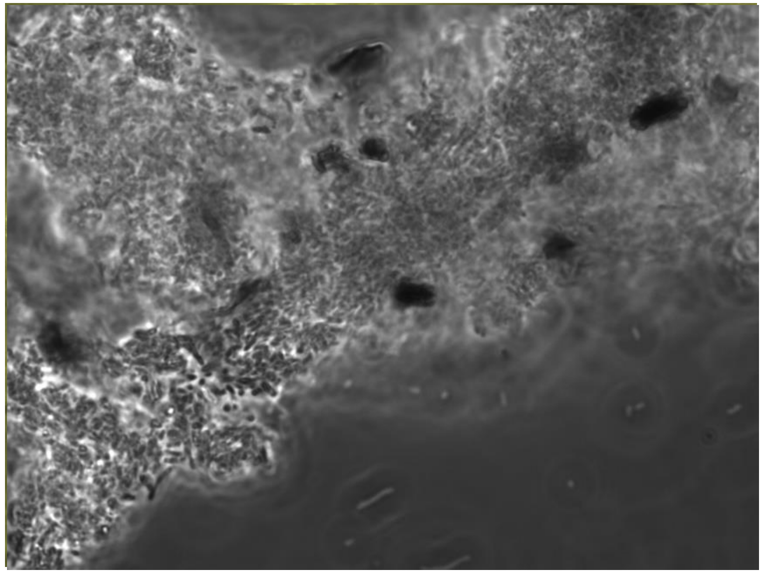


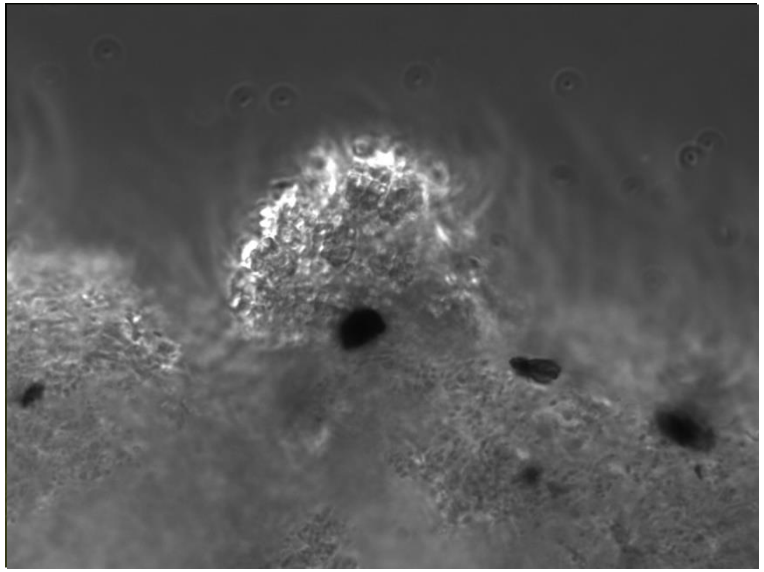
http://www.hydrogenics.com/technology-resources/hydrogen-technology/fuel-cells/

Byproduct: polyhydroxyalkanoates



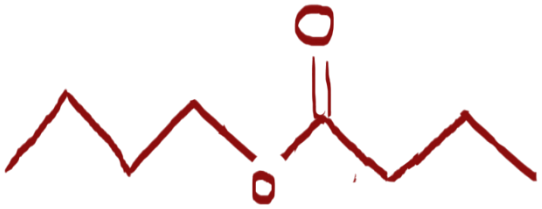
- Polyesters of R-hydroxyalkanoates
- Produced as carbon storage
- 100% biodegradable
- Highly variable structure and thermochemical characteristics





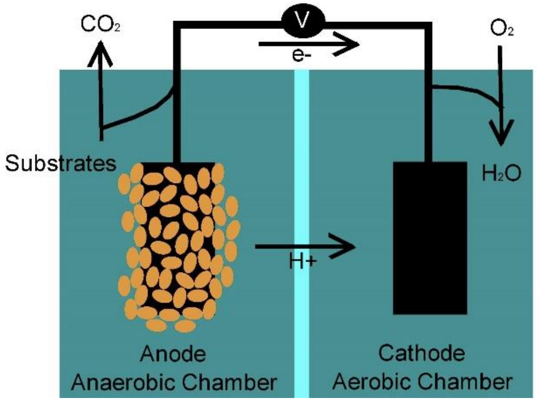
Adapted from Moita et al., 2013

Byproduct: butyl-butyrate



- Esterified form of butyrate and butanol
- Thermochemical characteristics similar to fossil fuels
- Lower melting point
- Reduced hydrocarbons, sulfur and nitrogen oxides emissions
- Low aromatic content

Byproduct: electricity



Adapted from https://www.labroots.com/trending/earth-and-the-environment/6010/methane-electricity-bacteria

- High conversion efficiency from substrate to energy
- Low temperature functioning
- Reduced hydrocarbons, sulfur and nitrogen oxides emissions
- No energy required for aeration of cathode
- Highly versatile system

Substrate collection and processing

Seafood restaurant kitchen waste

Removal of bones and other foreign materials

Mashing and homogenisation

Fermentable FW biomass

Winter sampling ($\%_{d.w}$)

- 42% total sugars
- 24% crude protein
- 22% fat
- 2% ash

Summer sampling ($\%_{d.w}$)

- 62% total sugars
- 10% crude protein
- 26% fat
- 1% ash

Experimental set-up

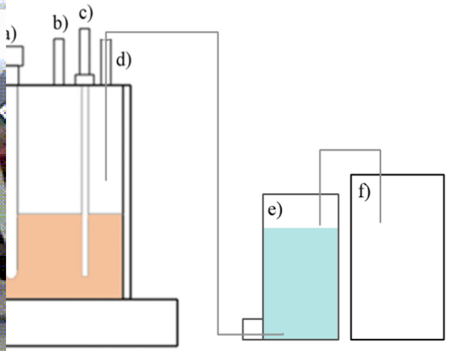
- Small scale, no pH c
  6.8

  37 ºC, 20 mL medium

- Bench scale, batch

  37 ºC, pH = 5.5

  500 mL medium, 1.1

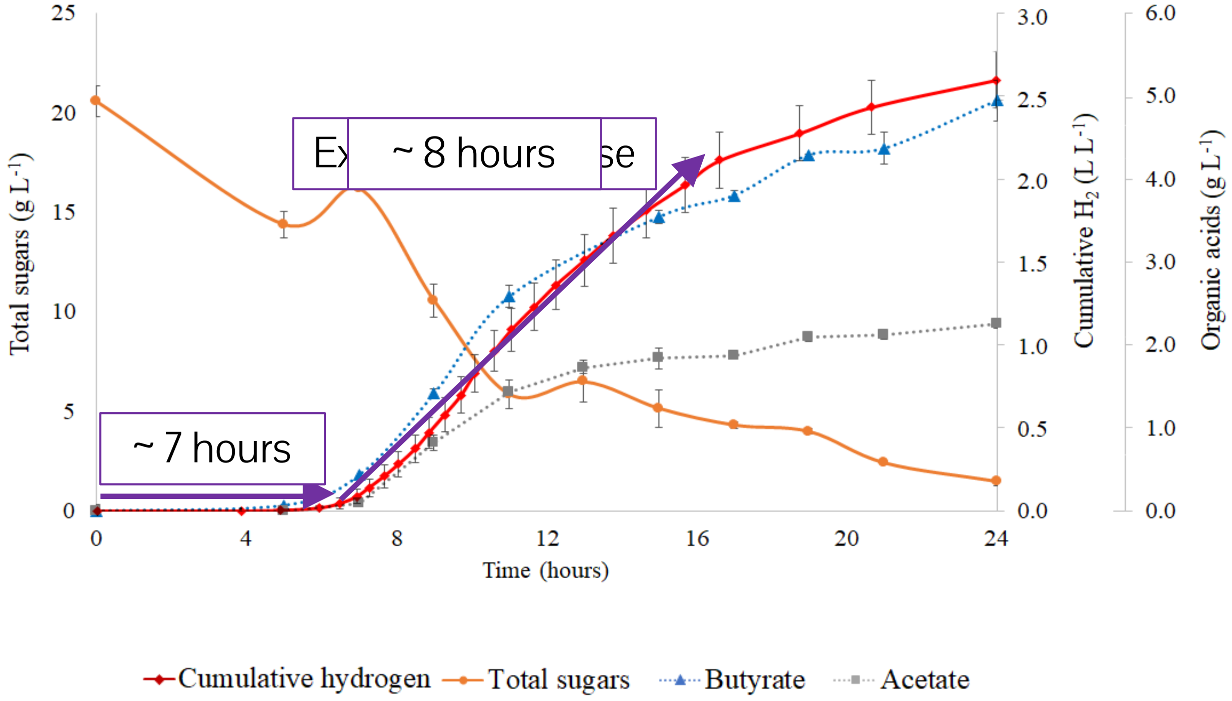


l electrode
oculum inlet
trogen inlet

d) Gas sampling exit
e) CO_2 scrubber
f) Sampling bag

Quantification: H_2, C ... ration, ash and H_2O

Food waste fermentation in bench-scale assay



Parameters	
Total H_2 production [L L^{-1}]	4.1
H_2 yield [mL H_2 $g_{d.w.}^{-1}$]	78.4
H_2 productivity [ml $(L\ h)^{-1}$]	250
Final % H_2 in the sample (% vol)	77
Sugar consumption (%)	86.5

	Food waste	
	Sterile	Non-sterile
H_2 yield [L H_2 kg_{VS}^{-1}]	78	32
H_2 productivity [mL H_2 $(L\ h)^{-1}$]	250	128

59 %

51 %

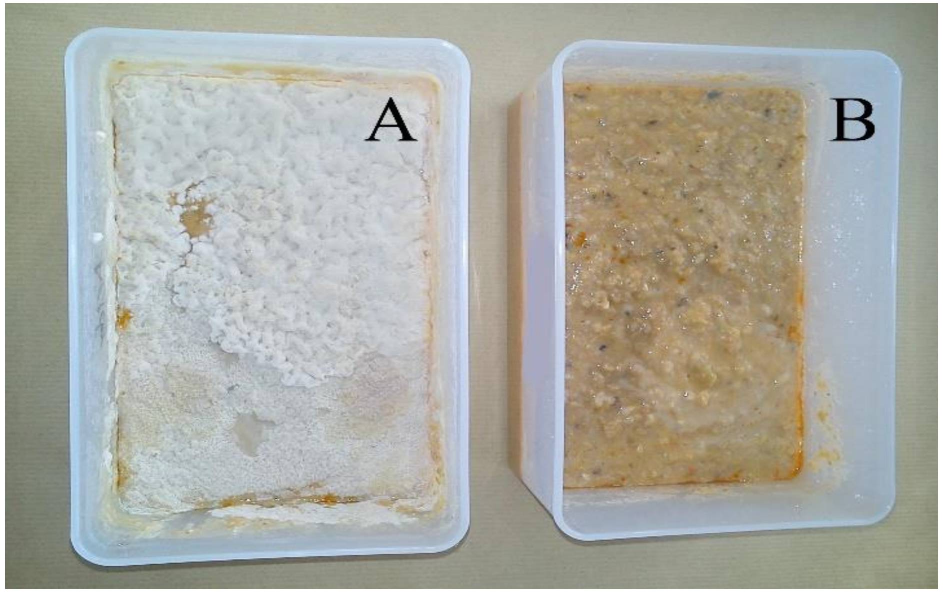
Contamination control

- Contamination control
- Avoid further contamination - **Storage**

A – crude ground biomass

versus

B – Microwave pretreated biomass



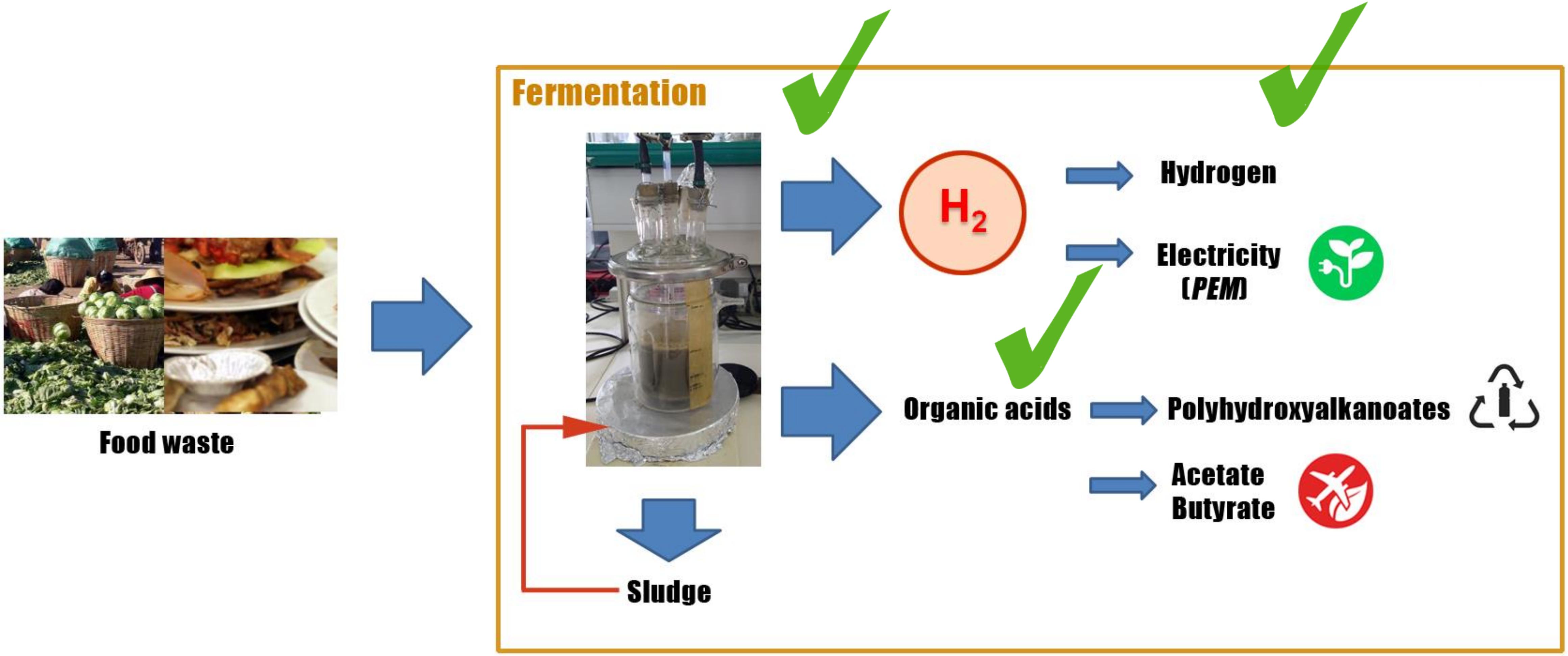
In comparison with the non-sterile condition

Increase in H_2 yield	Increase in H_2 productivity
177 %	216 %

In comparison with the sterile condition

Increase in H_2 yield	Increase in H_2 productivity
14 %	63 %

Proposed food waste biorefinery



Nitrogen source optimisation

Residual nitrogen in fermentate

- Limits polyhydroxyalkanoate (PHA) accumulation
- Nutrient waste

Nitrogen source reduction

Reduction by 66% of initial NH_4Cl concentration

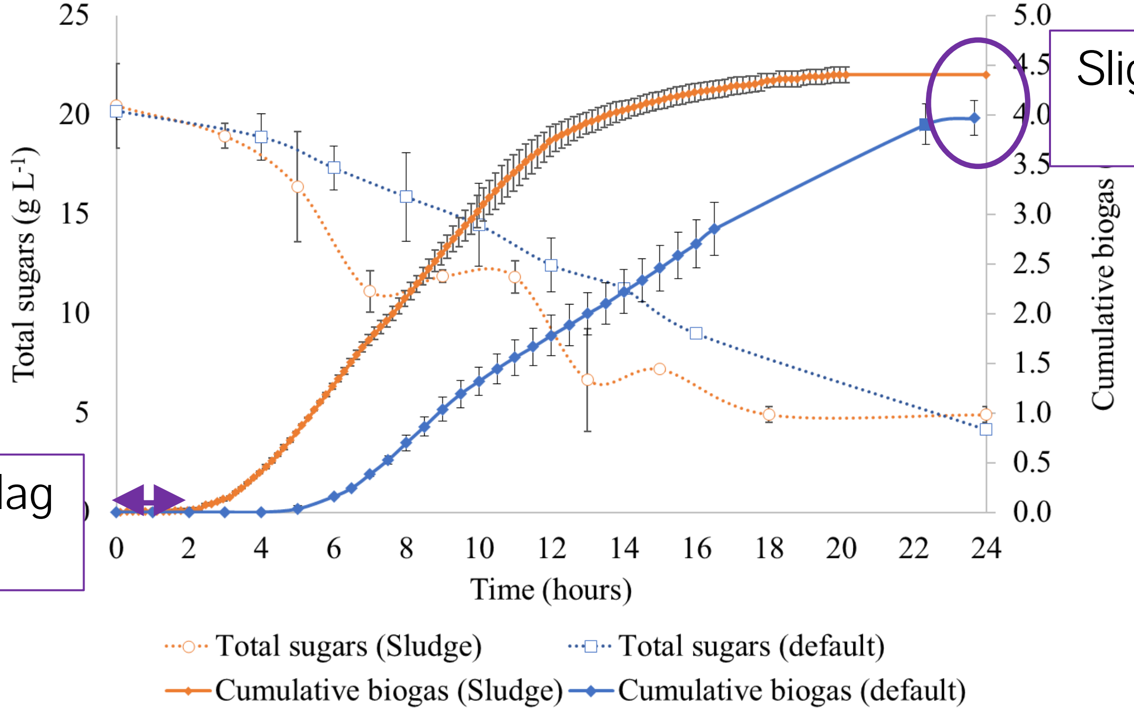
Dark-fermentation sludge ($\%_{d.w}$)

14% total sugars
58% crude protein

Nitrogen source replacement

Replacement of NH_4Cl with DF-sludge

Food waste fermentation with nitrogen source replacement



Shortest lag phase

Slight increase H_2 production

Parameters	
Total H_2 production [L L^{-1}]	4.4
H_2 yield [mL H_2 $g_{d.w.}^{-1}$]	111.9
H_2 productivity [ml $(L\ h)^{-1}$]	433.3
Final % H_2 in the sample (% vol)	41
Sugar consumption (%)	75.9

66% reduction assay in comparison with the original nitrogen condition

Increase in H_2 yield
82 %

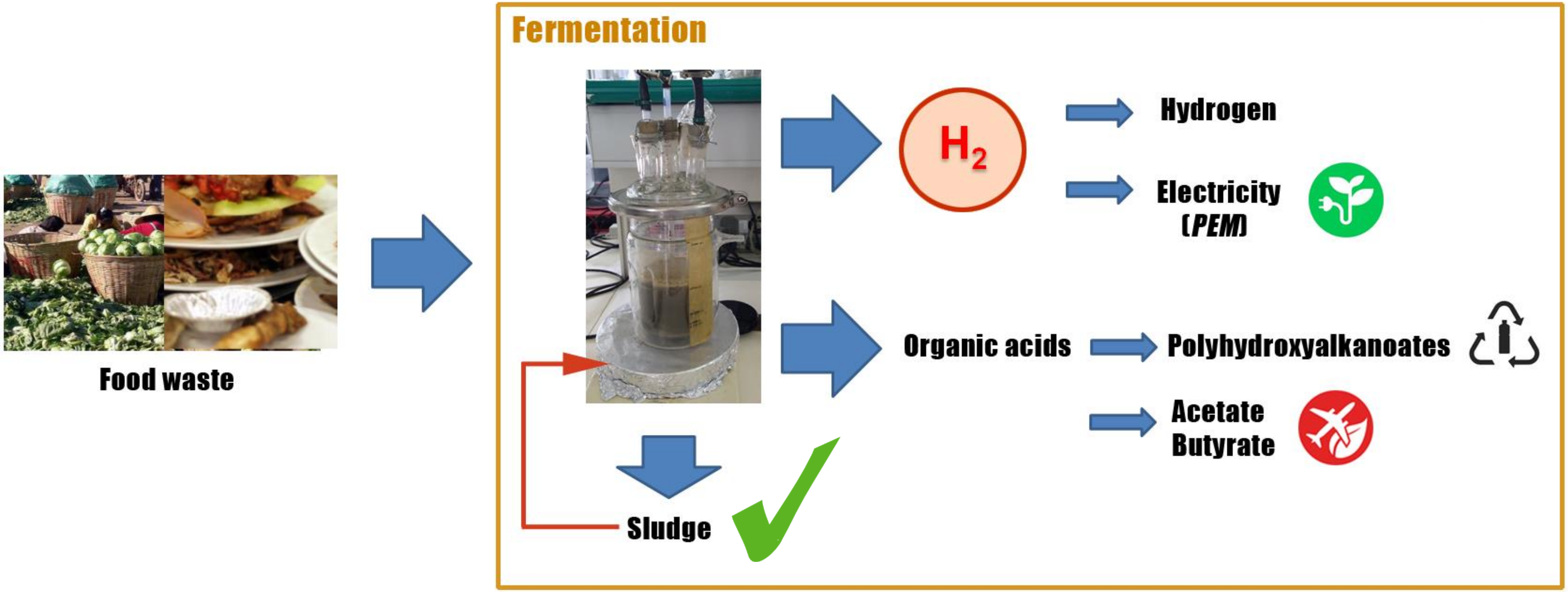
Increase in H_2 productivity
59 %

Sludge assay in comparison with the original nitrogen condition

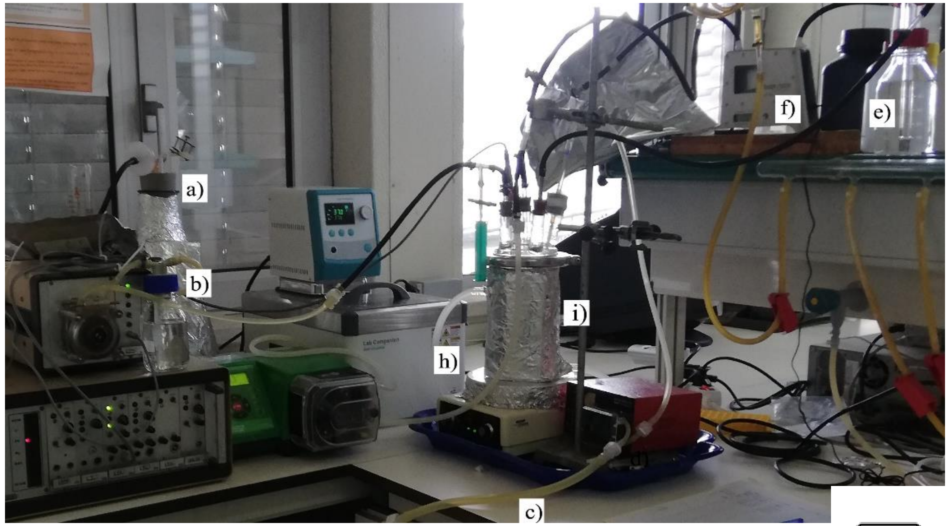
Increase in H_2 yield
40 %

Increase in H_2 productivity
64 %

Proposed food waste biorefinery



Experimental set-up



a) Fermentation medium feed
b) NaOH solution for pH control;
c) Effluent
d) Sampling port;
e) CO_2 scrubber
f) Flowmeter;
g) PEMFC;
h) Water bath
i) Biorreactor

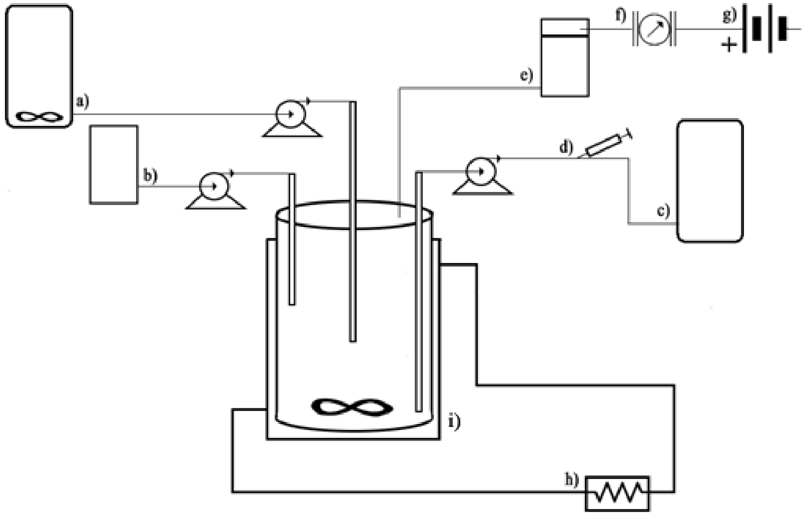
Bench scale,

Optimum conditions for *C. butyricum*

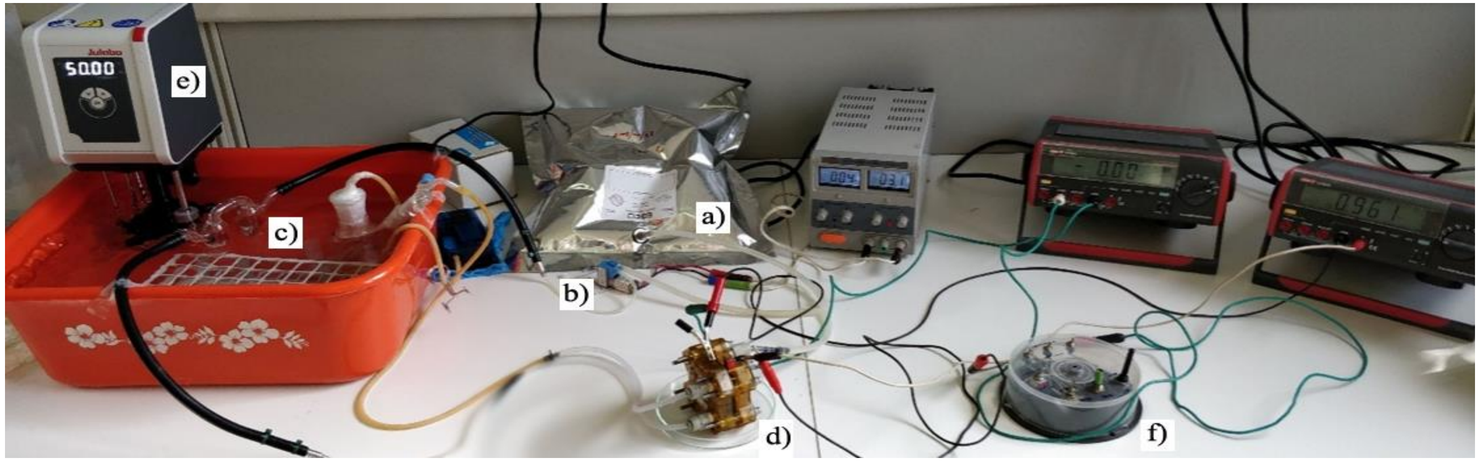
37 ºC, pH = 5.5, 1.1 g sugars L^{-1} h^{-1}

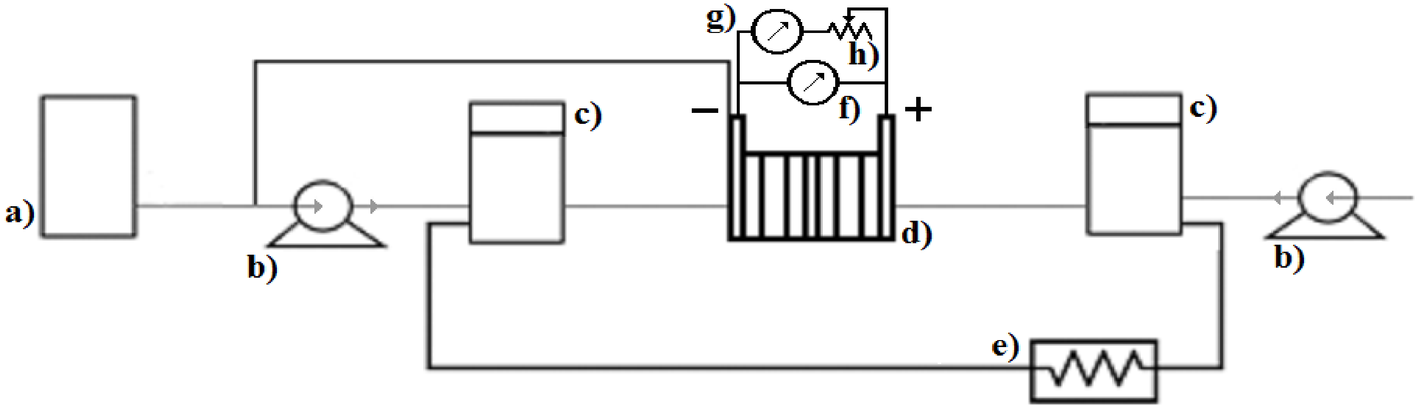
500 mL medium, 1.1 L headspace

FW Summer sampling



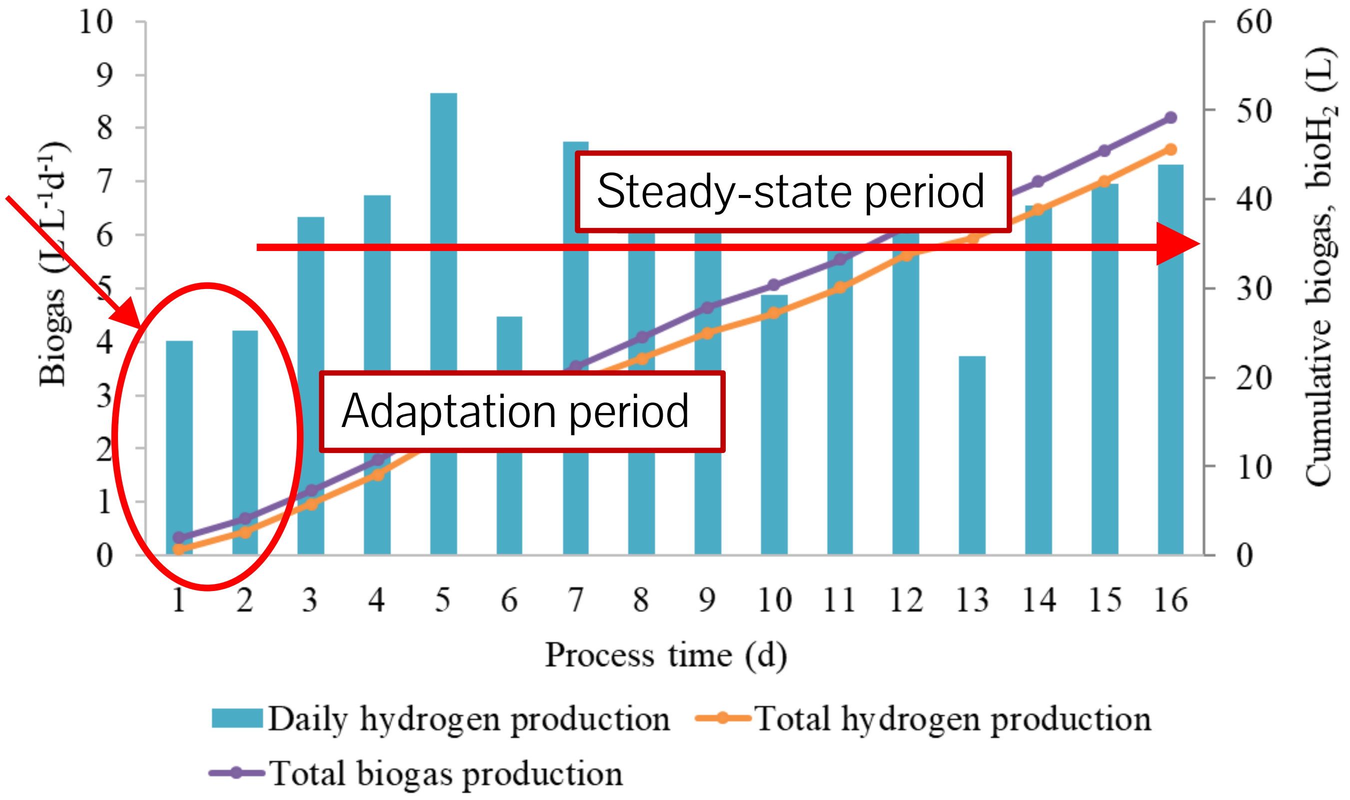
Quantification: H_2, CO_2, total sugars, organic acids, nitrogen concentration, ash and H_2O



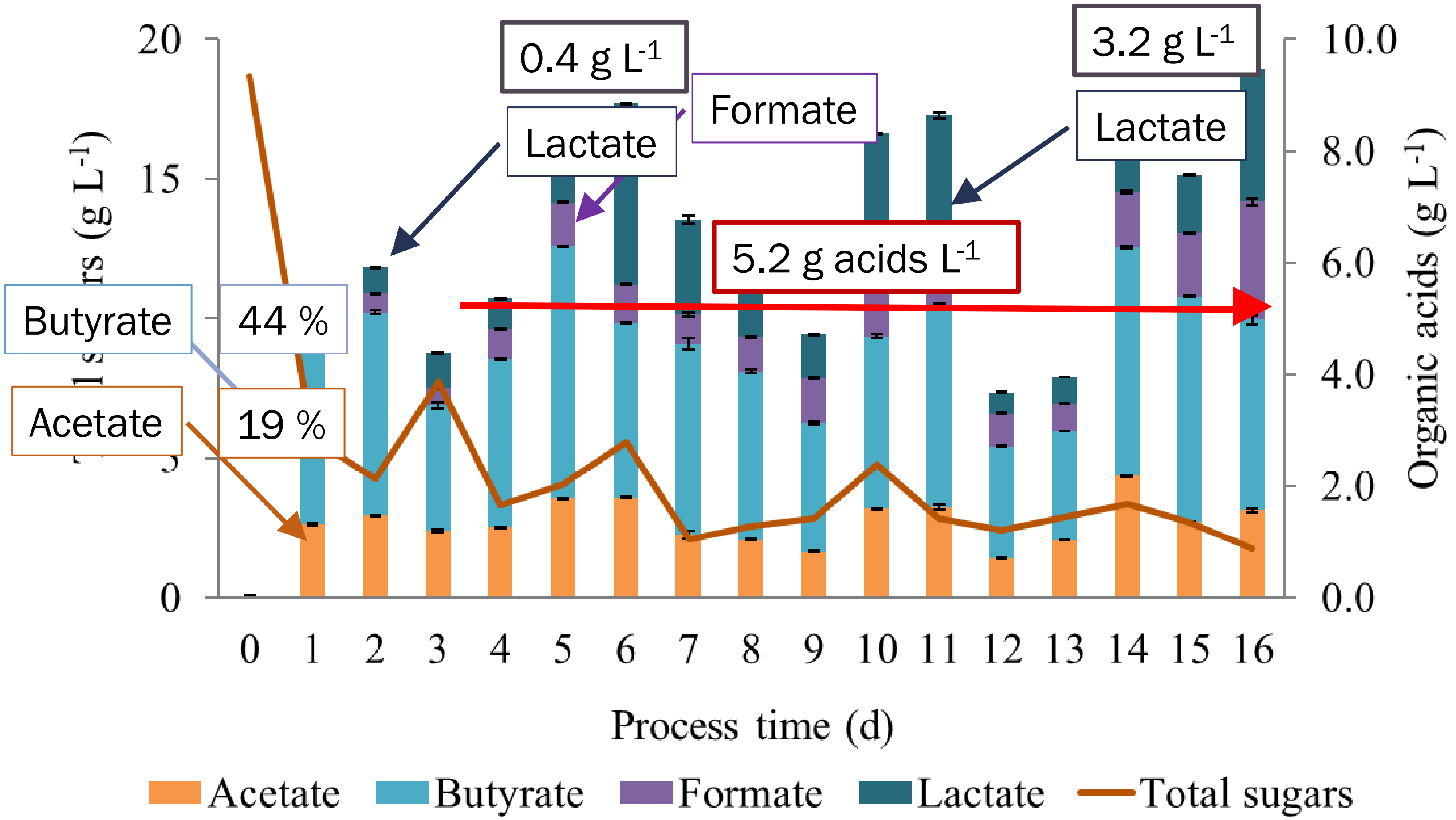


a) BioH_2 sample;
b) Gas pump;
c) Gas washing bottle;
d) Fuel cell;
e) Water bath for temperature control;
f) Voltmeter;
g) Ammeter;
h) Potentiometer

Food waste fermentation in CSTR mode



Parameters	
Total H_2 production [L L^{-1}]	45.6
H_2 yield [L H_2 $kg_{d.w.}^{-1}$]	74.9
H_2 productivity [L $(L\ d)^{-1}$]	6.1
Average % H_2 in biogas (% vol)	95.8
Sugar consumption (%)	94.1

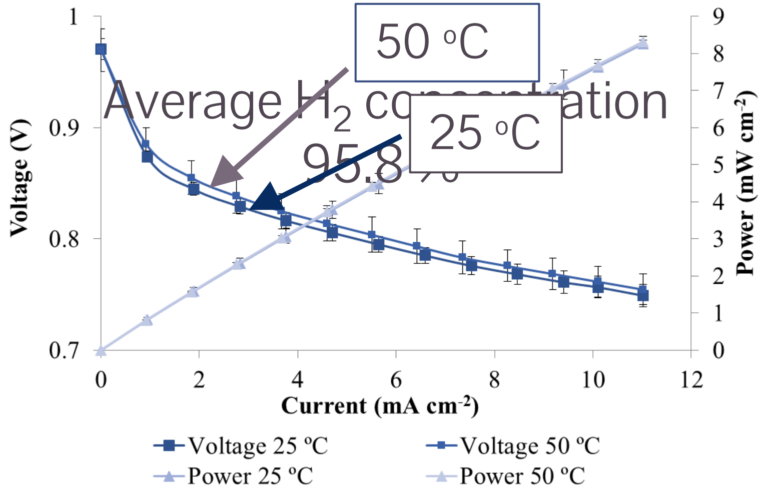


Parameters	
Average organic acid concentration [g L^{-1}]	5.2
Butyrate-to-acetate ratio [mol mol^{-1}]	1.9

Electricity generation from bioH_2 with a PEMFC

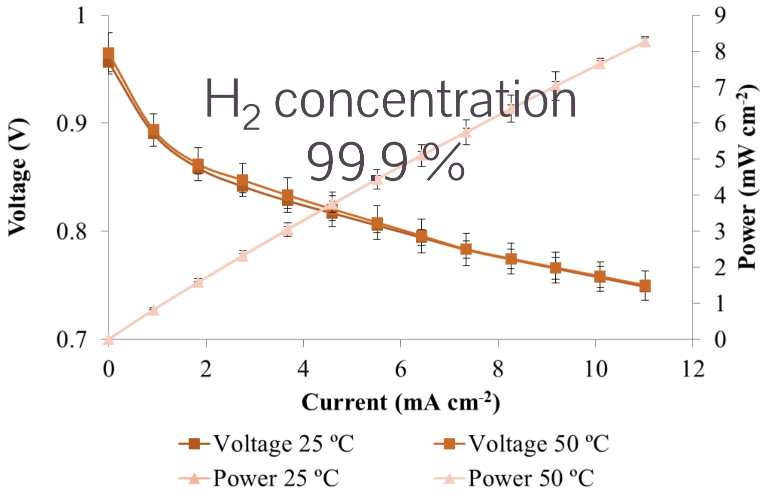
BioH_2

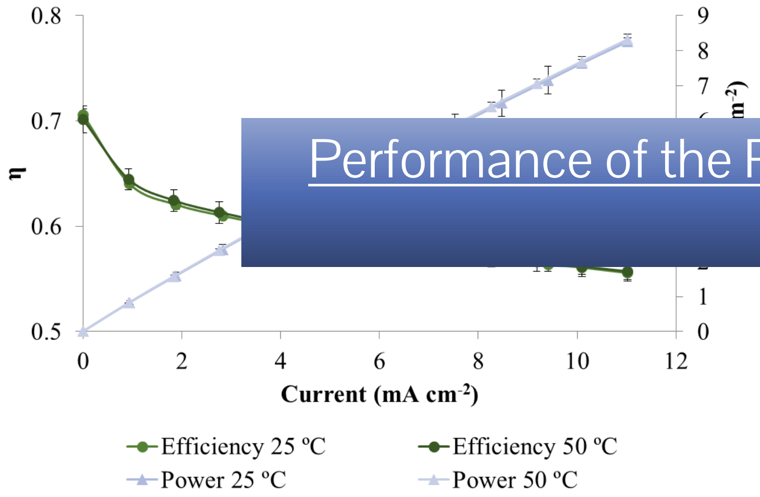
Average H_2 concentration 95.8 %

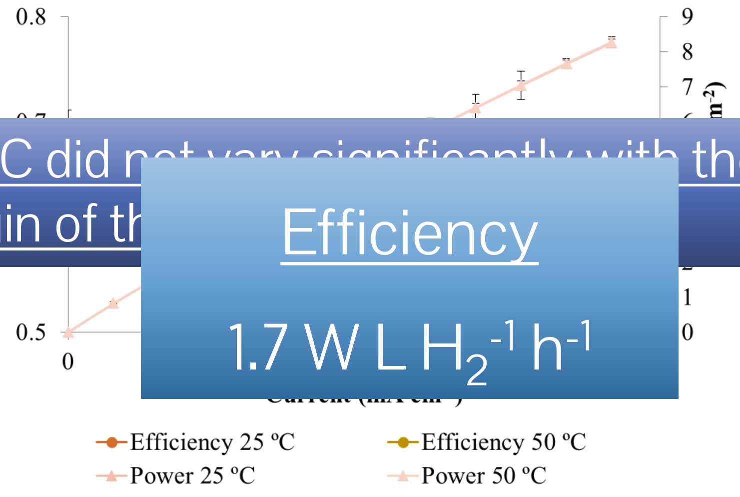


Commercial H_2

H_2 concentration 99.9 %





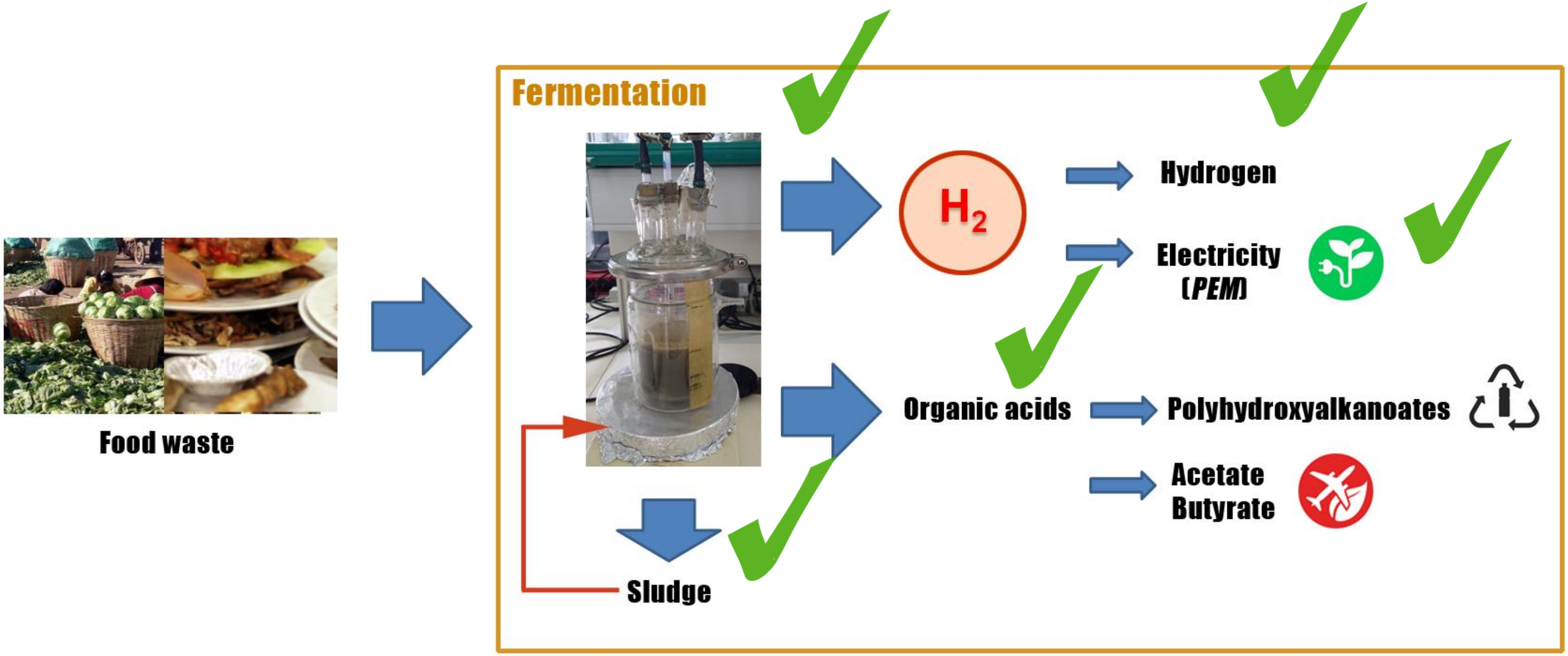


Performance of the PEMFC did not vary significantly with the origin of th

Efficiency

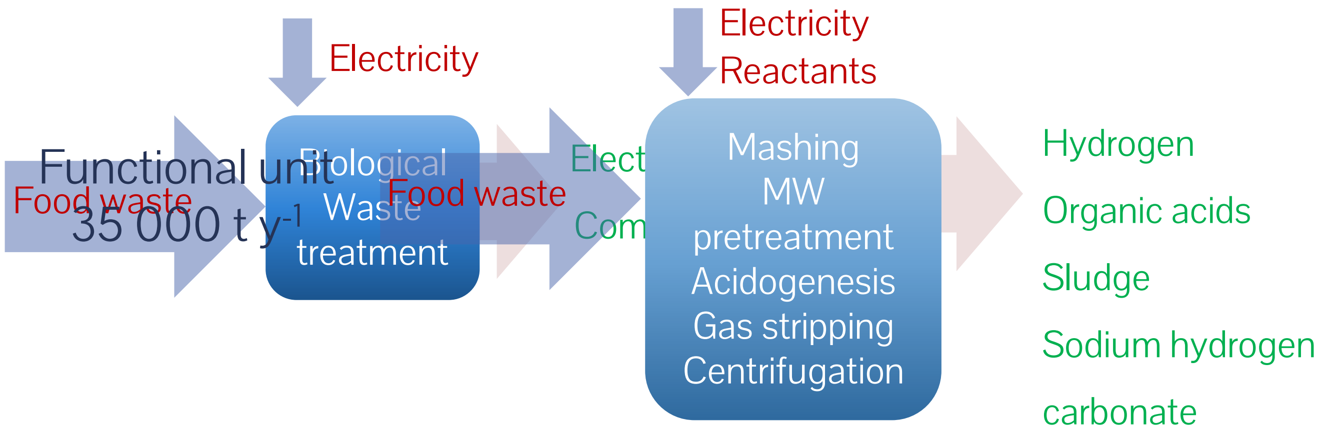
$1.7\ W\ L\ H_2^{-1}\ h^{-1}$

Proposed food waste biorefinery



Process scale-up and scenario analysis

ValorSul reference *Alternative system*



Global warming potential through consequential LCA

Sc#1: Proposed FW biorefinery to H_2

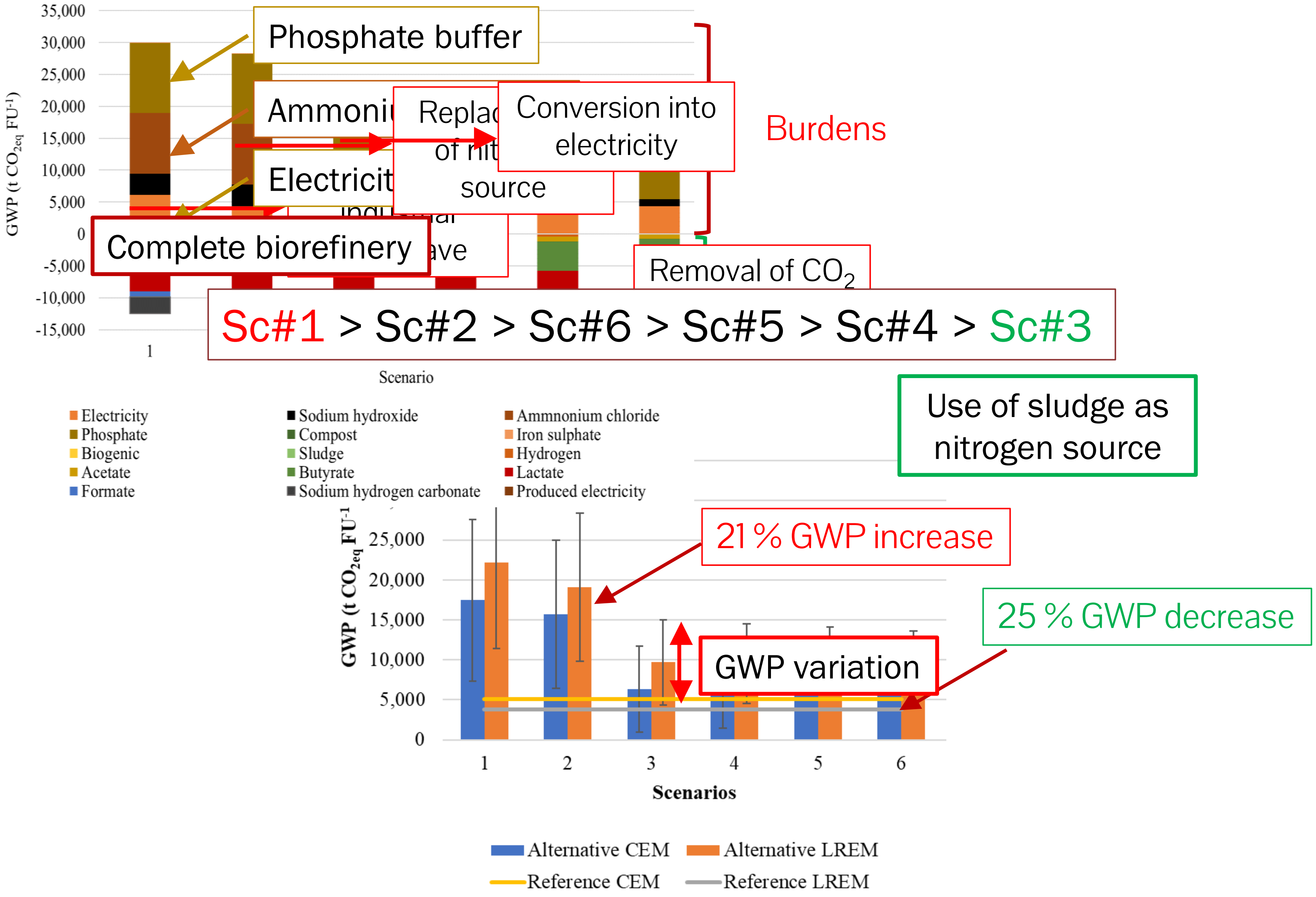
Sc#2: Microwave at household level

Sc#3/4: Use of sludge as nitrogen source

H_2 or electricity as final product

Sc#5/6: Removal of carbon sequestration

H_2 or electricity as final product


Phosphate buffer
Burdens
Conversion into electricity
Complete biorefinery
Removal of CO_2
Sc#1 > Sc#2 > Sc#6 > Sc#5 > Sc#4 > Sc#3
GWP (t CO_{2eq} FU^{-1})
Scenario
Electricity
Phosphate
Biogenic
Acetate
Formate
Sodium hydroxide
Compost
Sludge
Butyrate
Sodium hydrogen carbonate
Ammnonium chloride
Iron sulphate
Hydrogen
Lactate
Produced electricity
Use of sludge as nitrogen source
21 % GWP increase
25 % GWP decrease
GWP variation
Scenarios
Alternative CEM
Alternative LREM
Reference CEM
Reference LREM

6.

Conclusions

Conclusions

- The restauration FW sampled was efficiently converted into H_2, attaining a maximum productivity of 250 mL $(L\ h)^{-1}$ and a conversion yield of 78.4 mL $g_{d.w.}^{-1}$.
- The removal of nutrient supplementation and sterilisation stage caused a decrease in all fermentation kinetic parameters, particularly the H_2 yield by 41 and 59% respectively.
- Microwave procedure was chosen as the most appropriate method for control of sample contamination prior to fermentation and possibly increase substrate biodegradability.
- Microwaved-FW fermentation was the most efficient of the four tested conditions:
  - Total H_2 production: 4.6 L L^{-1}
  - H_2 yield: 89.4 mL $g_{d.w.}^{-1}$
  - H_2 productivity: 406 mL $(L\ h)^{-1}$

- The two tested conditions for nitrogen optimisation impacted positively fermentation performance, increasing productivity by 49 and 64% for the reduction and replacement assays, respectively.
- H_2 yield obtained with DF-sludge was 111.9 mL H_2 $g_{d.w.}^{-1}$, which represents a 40% increase when compared to the default assay.
- The recycling of nutrients in non-sterile FW fermentations for H_2 production increases the overall process efficiency and reduces the need for additional nitrogen source.

- Acidogenic FW-fed CSTR was undertaken successfully under non-sterile conditions, with the predominance of the biocatalyst facilitated by the MW preatreatment, low HRT and optimum pH and temperature.
- During the 16 days of process time:
  - Average H_2 productivity: 6.1 ± 1.3 L H_2 L^{-1} d^{-1}
  - H_2 % in biogas: 95.8 ± 1.0 %
  - H_2 yield: 74.9 ± 15.8 L H_2 kg^{-1}
  - Acetate + butyrate concentration: 5.2 ± 0.8 g L^{-1}
- Biogas was fed into PEMFC and its use compared with commercial H_2 at two temperatures. No significant difference was obtained at all tested conditions.
- Theoretical scale-up of the alternative system underlined that the replacement of ammonium chloride with acidogenic sludge for H_2 production was the best of the analysed scenarios.

Research papers and additional information

- Ortigueira J, Silva C, Moura P. Assessment of the adequacy of different Mediterranean waste biomass types for fermentative hydrogen production and the particular advantage of carob (Ceratonia siliqua L.) pulp. Int. J. Hydrogen Energy. 2018;43(16), 7773-7783.

- Ortigueira J, Martins L, Pacheco M, Silva C, Moura P. Improving the non-sterile food waste bioconversion to hydrogen by microwave pretreatment and bioaugmentation with *Clostridium butyricum*. Waste Manage. 2019;88:226-235.

- Ortigueira J, Moura P, Silva C. Dark fermentation sludge as nitrogen source for hydrogen production from food waste. In Wastes: Solutions, Treatments and Opportunities III: Selected Papers from the 5th International Conference Wastes 2019, September 4-6, 2019, Lisbon, Portugal (p. 301). CRC Press. 2019. ISBN: 9780429289798

- Ortigueira J, Pacheco M, Trancoso A, Farrancha P, Ferreira J, Silva C, Moura P. Food waste biorefineries: Stability of an acidogenic fermentation with carbon dioxide sequestration and electricity generation. J. Cleaner Prod. 2020.

Development and evaluation of an acidogenic biorefinery for food waste valorisation

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