CORFU2022

15-18 JUNE

corfu2022.uest.gr

State-of-the-Art Technologies for Improved, Sustainable Energy and Resources Recovery from Sewage Sludge

Daniele Cecconet, Arianna Callegari, Andrea G. Capodaglio

University of Pavia, Italy

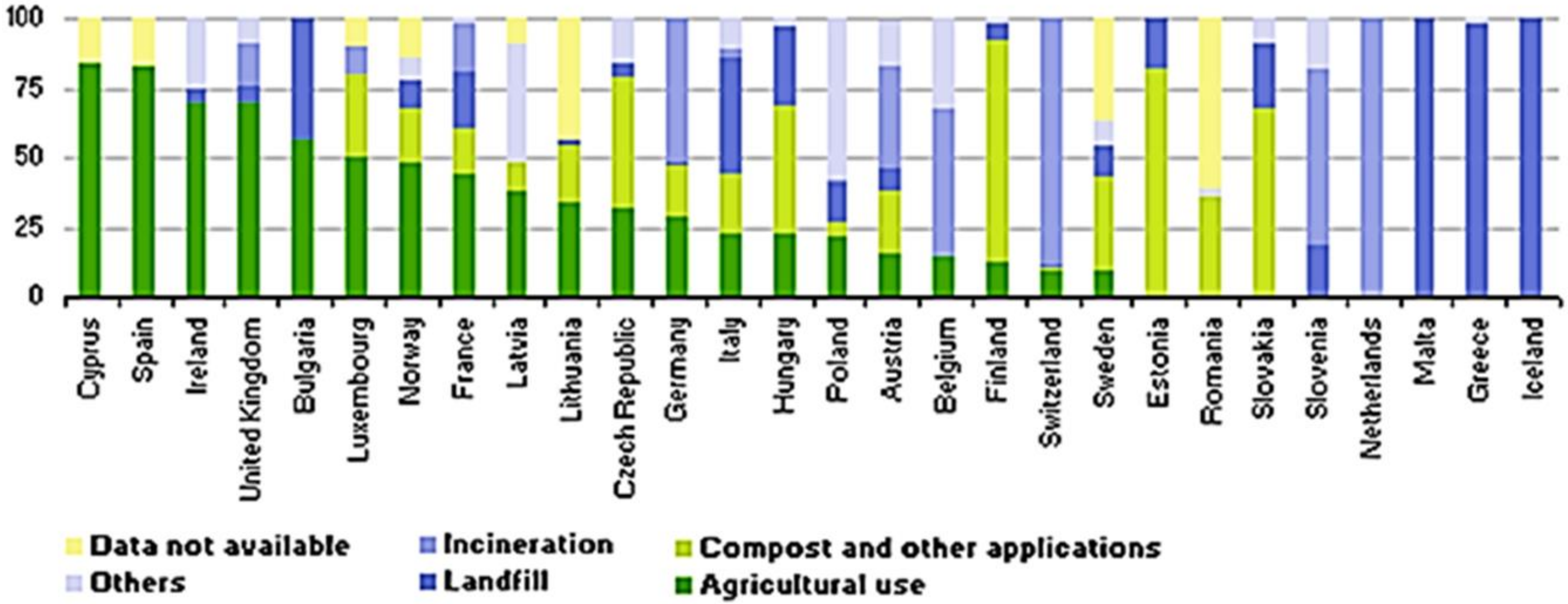
9th International Conference on Sustainable Solid Waste Management

Municipal WWTPs excess sludge production for the entire EU in 2020 was about 13 Mt.

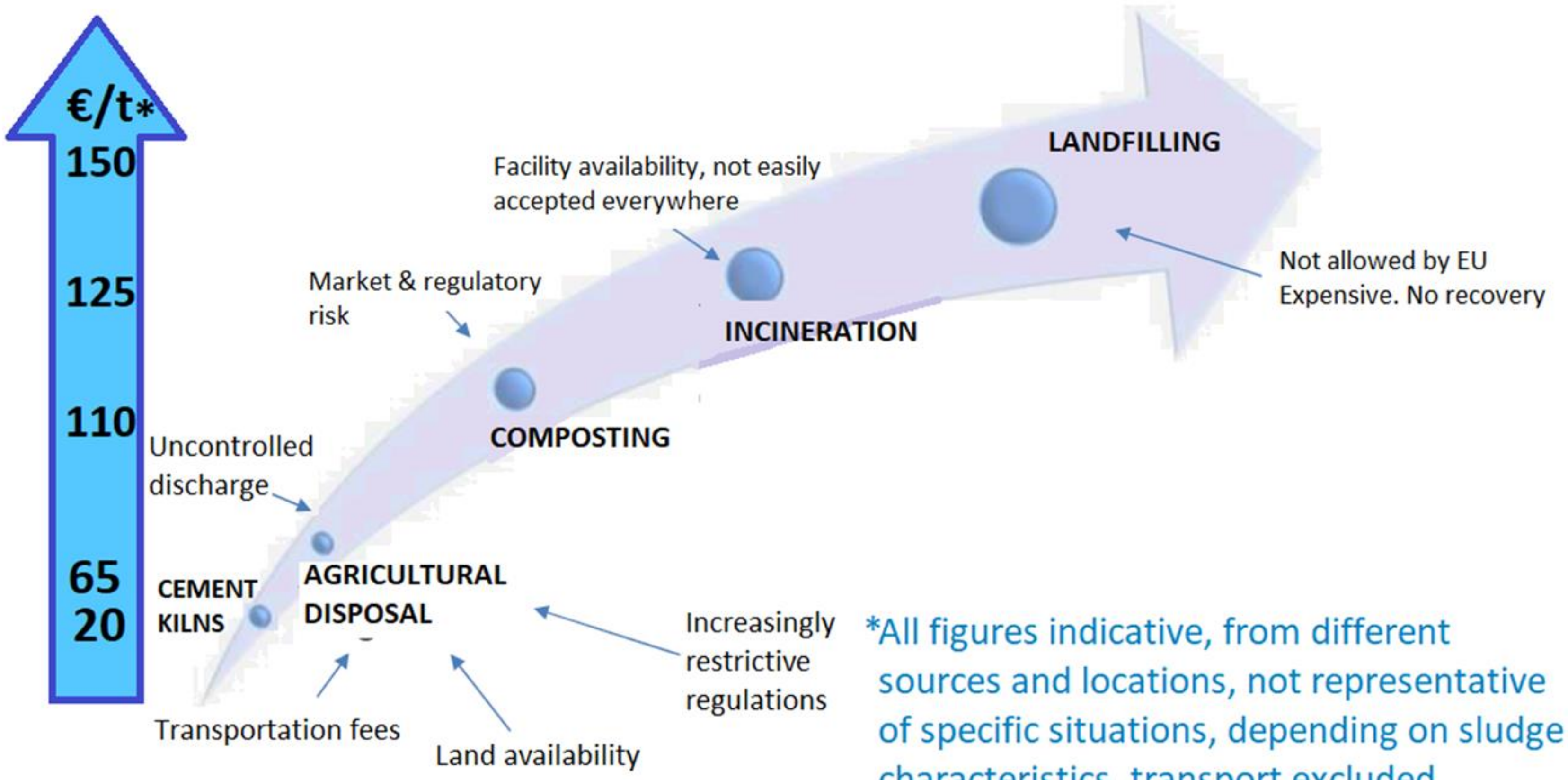
Assuming a dried sludge water content of 30%, the total volume of sludge to be disposed yearly would be just short of the volume of FOUR Cheope's PYRAMIDS!

NOT a wise solution…

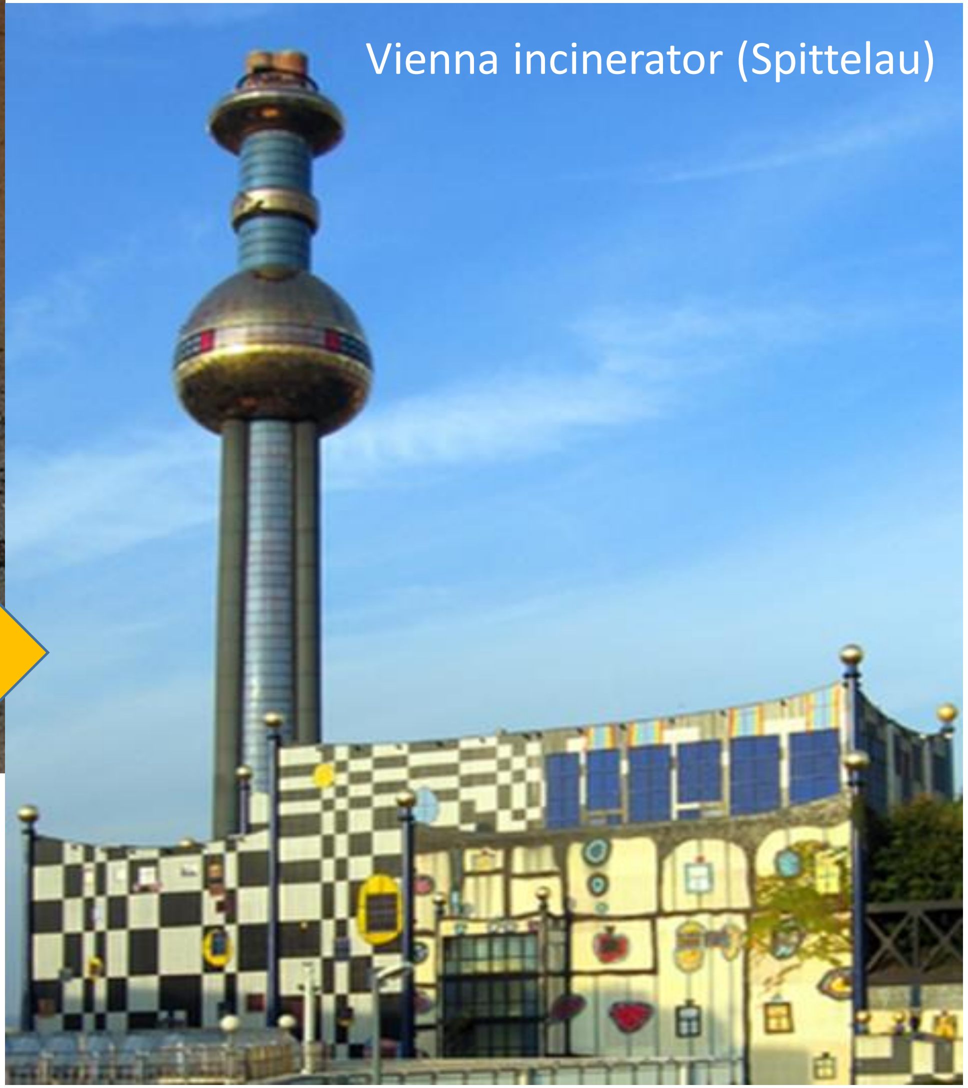
Main sludge disposal options in EU member states



Current sludge disposal costs in Italy (indicative only)
(Including accessory and transportation costs, the real figures are much higher!!!)



*All figures indicative, from different sources and locations, not representative of specific situations, depending on sludge characteristics, transport excluded



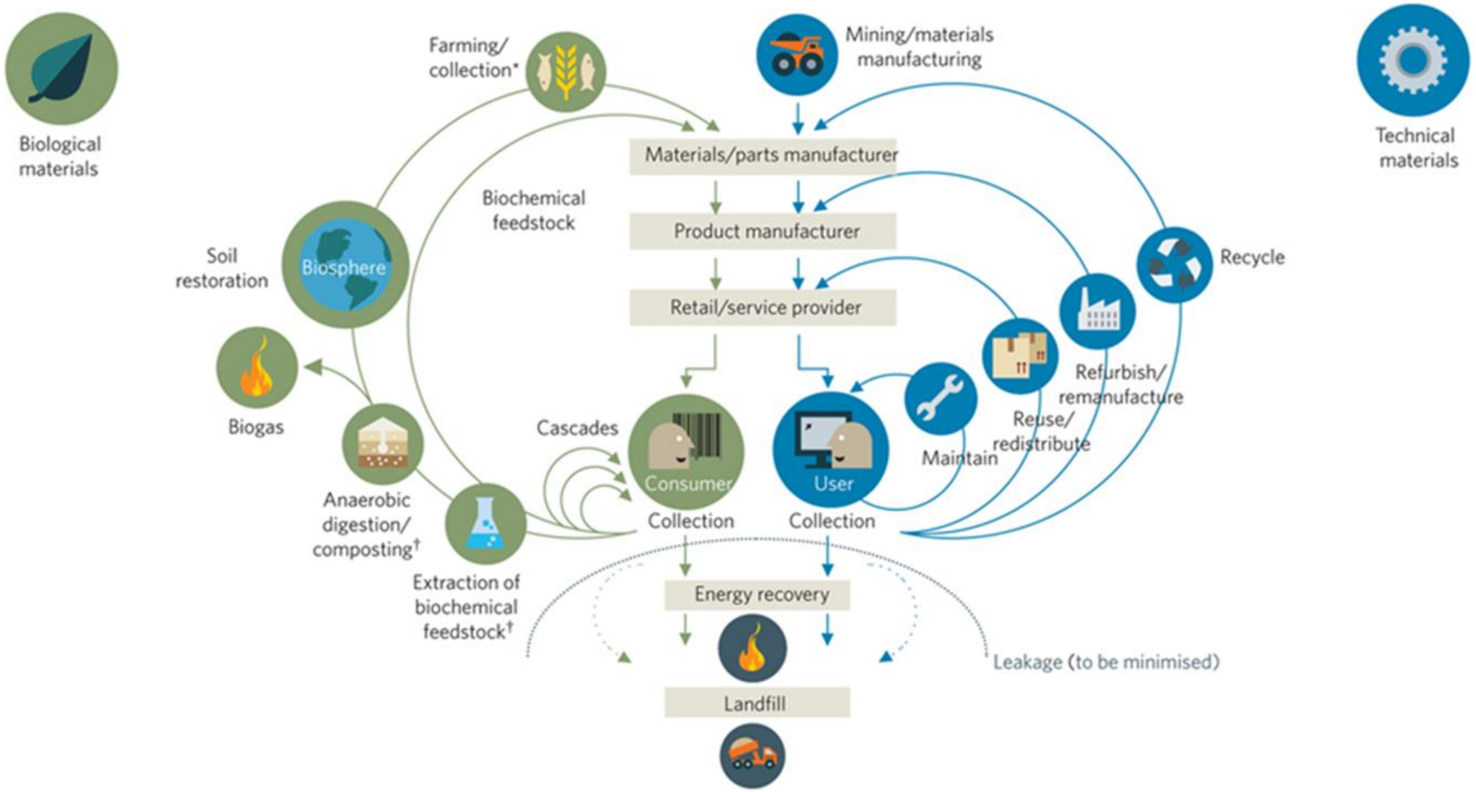
Source	Primary Sludge	Secondary Sludge	Anaerobically digested Sludge
Zanoni & Mueller (1982)	15.0	13.5	11.4
Vesilind & Ramsey (1995)			12.6
Shizaz & Bagley (2004)	15.9	12.4	12.7

Values in kJ/g d.w.

process is autothermal (sustained by the heat of combustion itself) only at sludge moisture contents below ≈ 30%
→ requires preprocessing!

CIRCULAR ECONOMY

most materials (and energy) remain in circle within the top part of the inverse pyramid



SLUDGE SHOULD BE PART OF AN ADVANCED C.E. CYCLE

through new/improved technologies

The new EU Sewage Sludge Directive (SSD) is under discussion and made necessary by the adoption of the EU Circular Economy Action Plan (2020)

- Minimization of excess biological sludge production reduces handling and disposal costs

- These solutions may be energy-intensive, and must be compatible with energy and materials recovery approaches

- Recoverable resources other than heat from combustion and biogas include liquid and solid end-products (e.g. biodiesel, biochar), phosphorus, high value-added products, such as polyhydroxyalkanoates (PHAs) and extracellular polymeric substances (EPS)

Anaerobic sludge digestion (ASD) optimization

Under standard technologies, only approximately 20–30% of organic matter in the sludge is mineralized, and as much as 70% of the organics remain within. ASD is hence not a complete solution to sludge management, and further treatment of digested sludge is necessary for recovery of remaining recoverable resources.

Increasing specific methane yield from ASD (1)

Hydrolysis was identified as the main rate-limiting step in AD, most studies focused on its improvement by physical, thermo-chemical, and biological pre-treatments

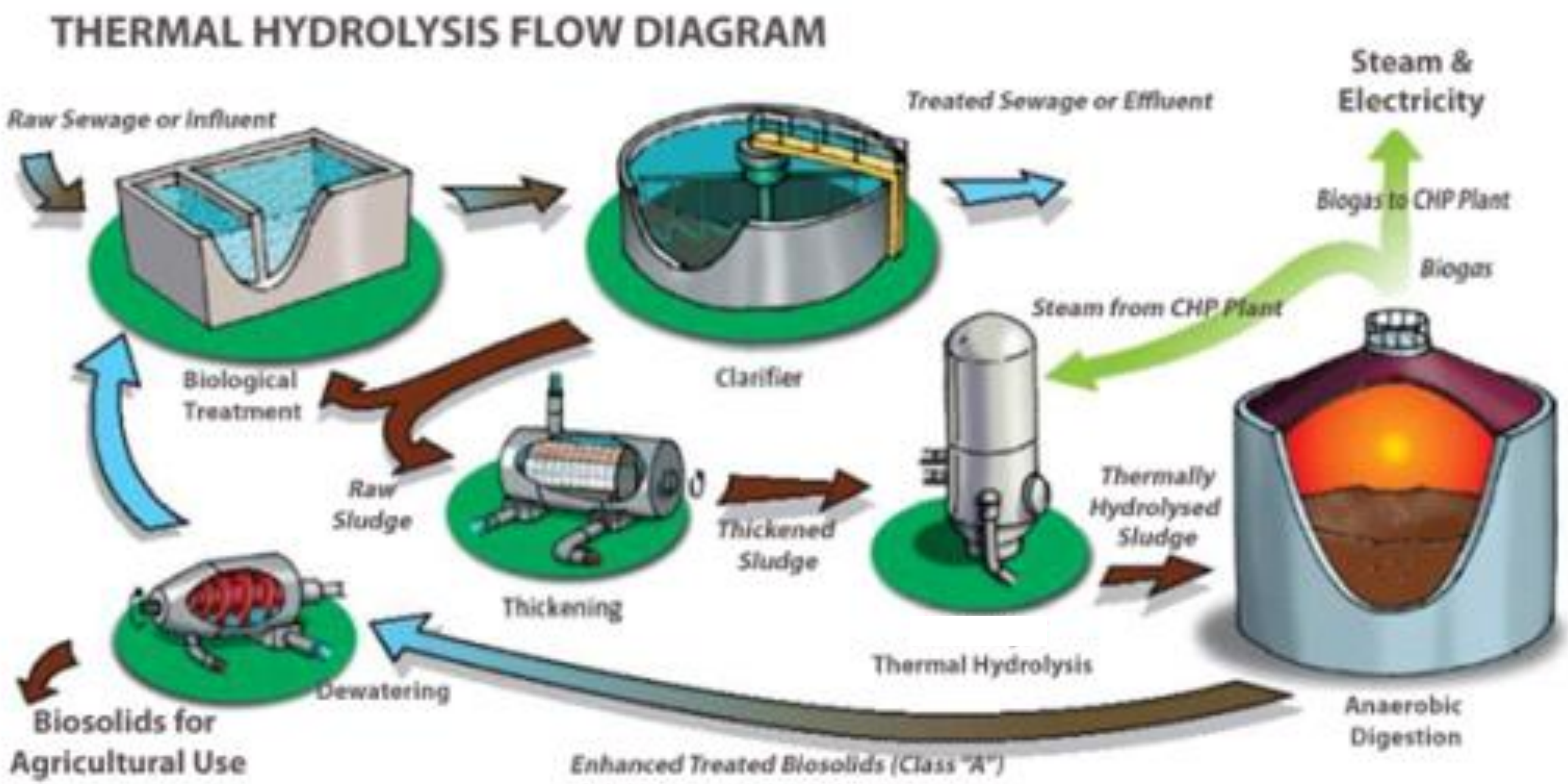
In hydrolysis smaller molecules are produced from large ones, then turned into VFAs and into methane

- **Thermal Hydrolysis** at high temperature (>100°C) and pressure (10 bar) requires large amounts of energy and special equipment, and may harm methanation
- Low temperature (60–100°C) TH showed optimal biogas yield after pre-treatment at 70°C for 9 hours
- **Mechanical disruption** of sludge cells structure can improve hydrolysis:

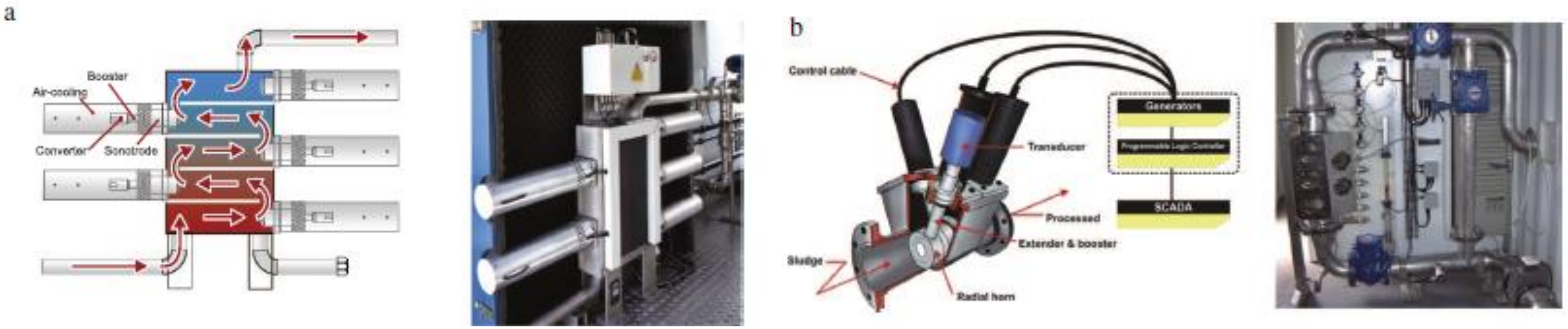
  -**ultrasonication** @20-40kHz with specific energy from 1000 to 16,000 kJ/kg TS increased biogas production from 24 to 140%

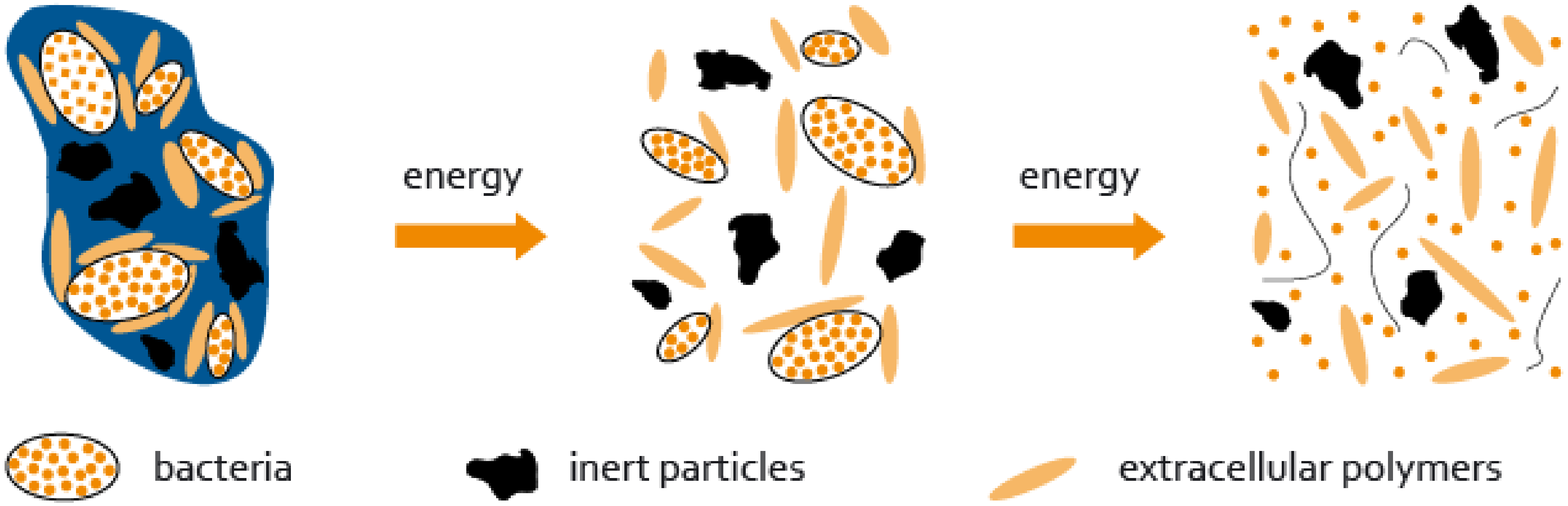
  -**pulse electric field** (PEF) technology has been reported to improve methane generation by up to 58%

  -other techniques are **ozonation**, dosage of **lipase enzymes** (can be extracted from sludge through biorefinery)

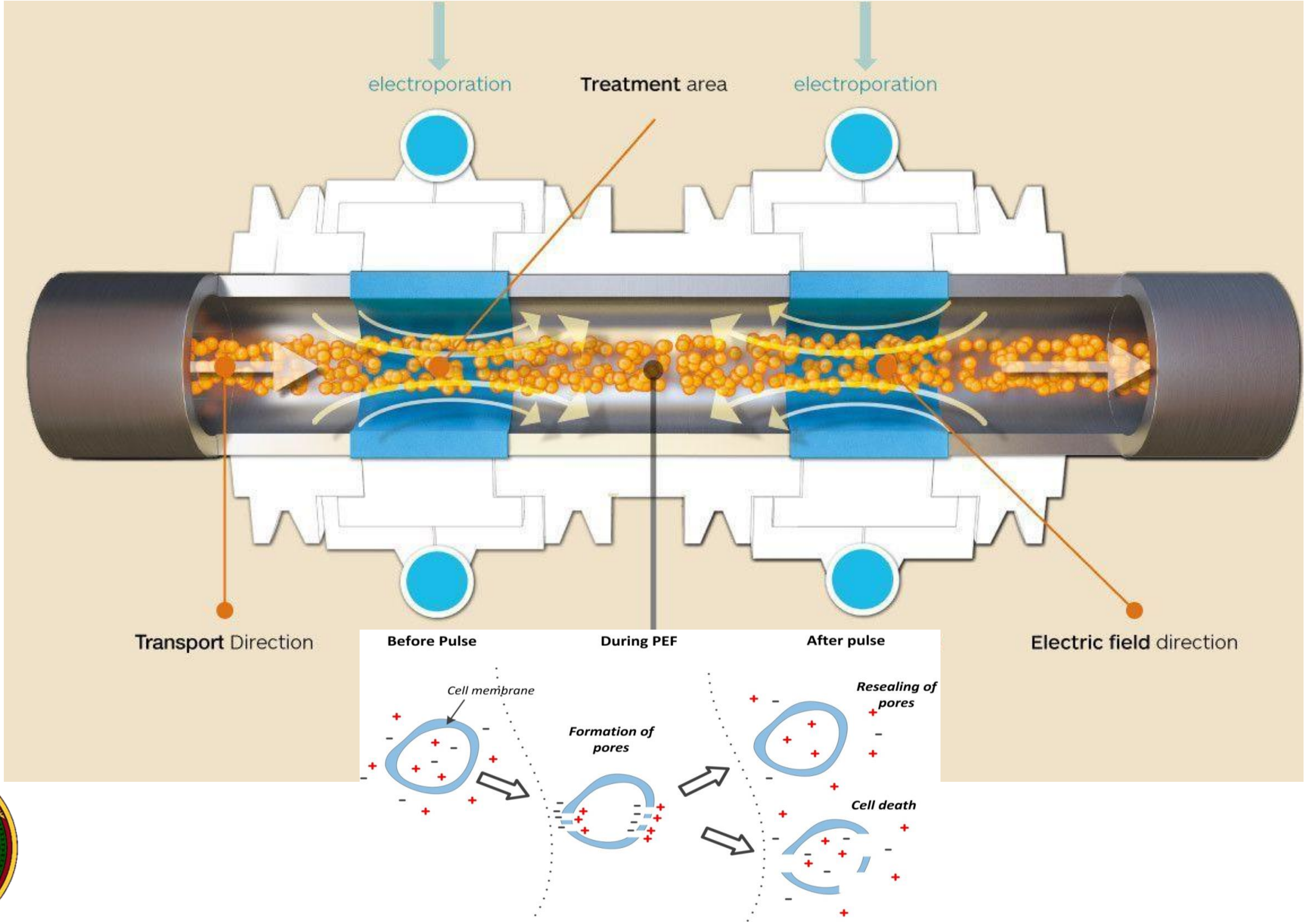

THERMAL HYDROLYSIS FLOW DIAGRAM
Raw Sewage or influent
Treated Sewage or Effluent
Steam & Electricity
Biogas to CHP Plant
Biogas
Steam from CHP Plant
Biological Treatment
Clarifier
Raw Sludge
Thickened Sludge
Thermally Hydrolysed Sludge
Thickening
Thermal Hydrolysis
Dewatering
Biosolids for Agricultural Use
Anaerobic Digestion
Enhanced Treated Biosolids (Class "A")

ULTRASONICATION





PULSE ELECTRIC FIELD



Increasing specific methane yield from ASD (2)

Electron transfer plays an important role in methanation. **Direct interspecies electron transfer** (DIET) between microorganisms plays a significant role in methane yield.

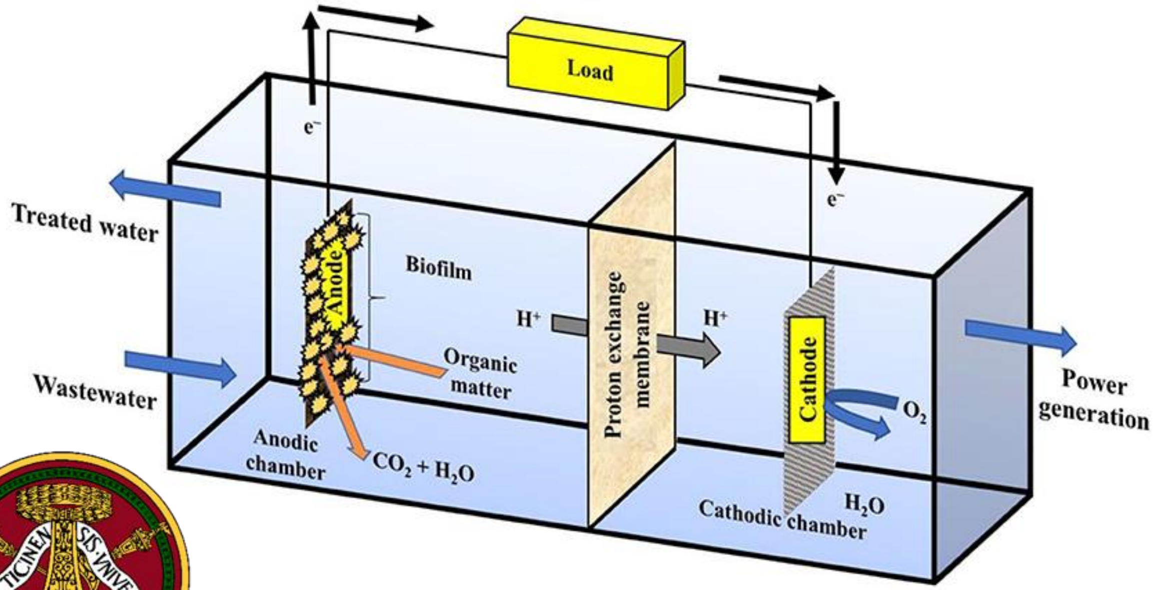
- **microbial electrolysis cell** (MEC) can enhance enzymatic hydrolytic activity in AD through Fe^{2+} release into the substrate, increasing methane production in the range 22-30%
- **electrically conductive carbon** (ECCs), such as activated carbon, biochar and electrically conductive micro (and nano) particles (ECMs) in AD reactors can enhance hydrolysis, acidogenesis-acetogenesis, and methanogenesis, and alleviate process inhibition.
- **Biochar** can be produced by thermal treatment of digested sludge, as part of a sludge-based Circular Economy cycle
- evidence suggests that synergy between bioelectrochemical systems and ECMs amplifies their effects: biochar can assist exoelectrogenic *Thermincola* organisms to promote DIET between exoelectrogen and methanogenic bacteria. MECs with 1.0 g/gDW sludge-based biochar increased methane by 24.7% and enhanced organics removal by 17.9%

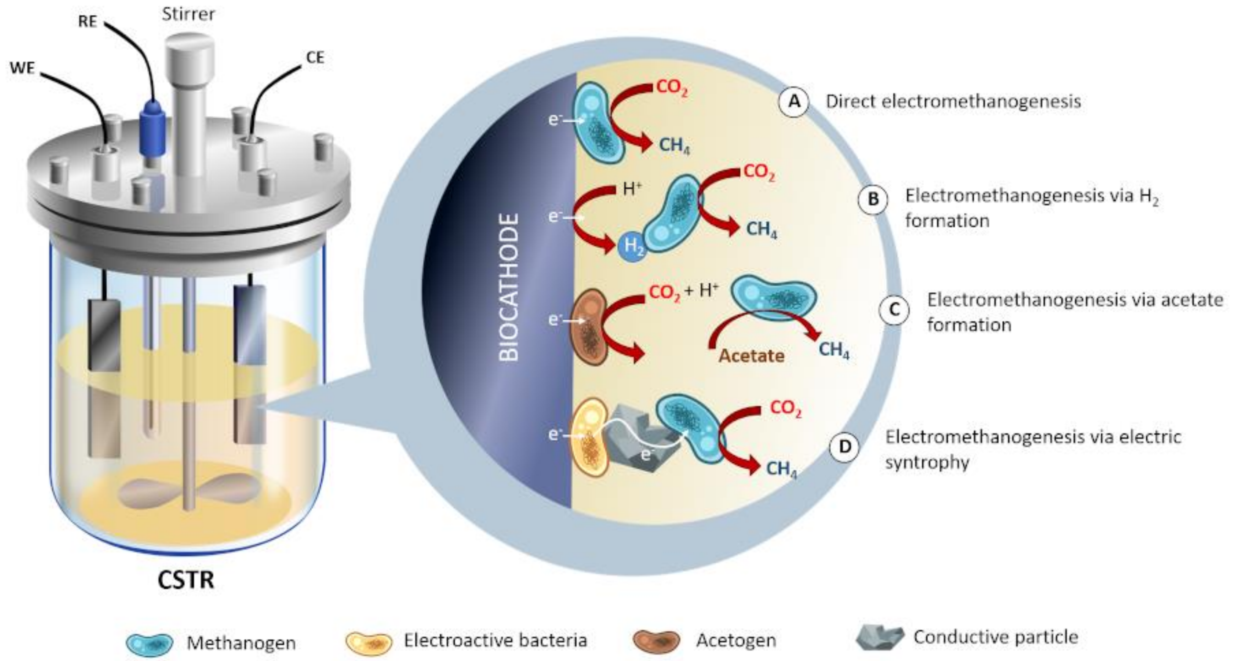
Increasing specific methane yield from ASD (3)

MFCs (Microbial Fuel Cells) coupled to AD in integrated recirculation loop result in methane production higher than from AD alone.

Improved biogas yield attributed to migration of ammonium ions from digester to the cathode of the MFC.

MFCs may not be suitable for direct sludge treatment, but may function as AD improvement and post-treatment to polish digested supernatant.





Effectiveness of different sludge preprocessing technologies

- pre-treatments improve biogas production: ozonation (0.10 to 0.16 g O_3/g TS) by 11-24%; sonication (6250 to 9350 kJ/kg TS), thermal hydrolysis (170 to 190°C) by 47-51%;
- thermal (80–121 °C), high pressure (600 bar) homogenisation and enzymatic (carbohydrase addition) pretreatment increase biogas production by >20% at low intensity treatment (90-121°C); by 16–17% at high pressure (80 ◦C); by 13%;
- thermal (121°C), chemical (7 g/L NaOH), ultrasonic (120 min @ 42 kHz) and thermochemical (121°C, 7g/L NaOH) preprocessing results: thermal (+35% CH_4), thermochemical (+34%);
- US and chemical pretreatments increase methane yield by 20 and 13%, respectively

All methods imply substantial capital costs (thermal hydrolysis highest). One main indicator of process efficiency is energy, hence any additional energy recovery due to higher biogas production, should exceed the input required by pre-processing!

Biogas enhancement (biomethanation) (1)

Biogas: 30–40% CO_2, traces of N and O (<5%) other gases (H_2S, organic S, siloxanes, ammonia, halogenated compounds, other VOCs) AND CH_4.

The type of substrate, as well as digester operating conditions, directly affect the type and amounts of these compounds.

Biogas onsite conversion into electrical and thermal energy by CHP generators:

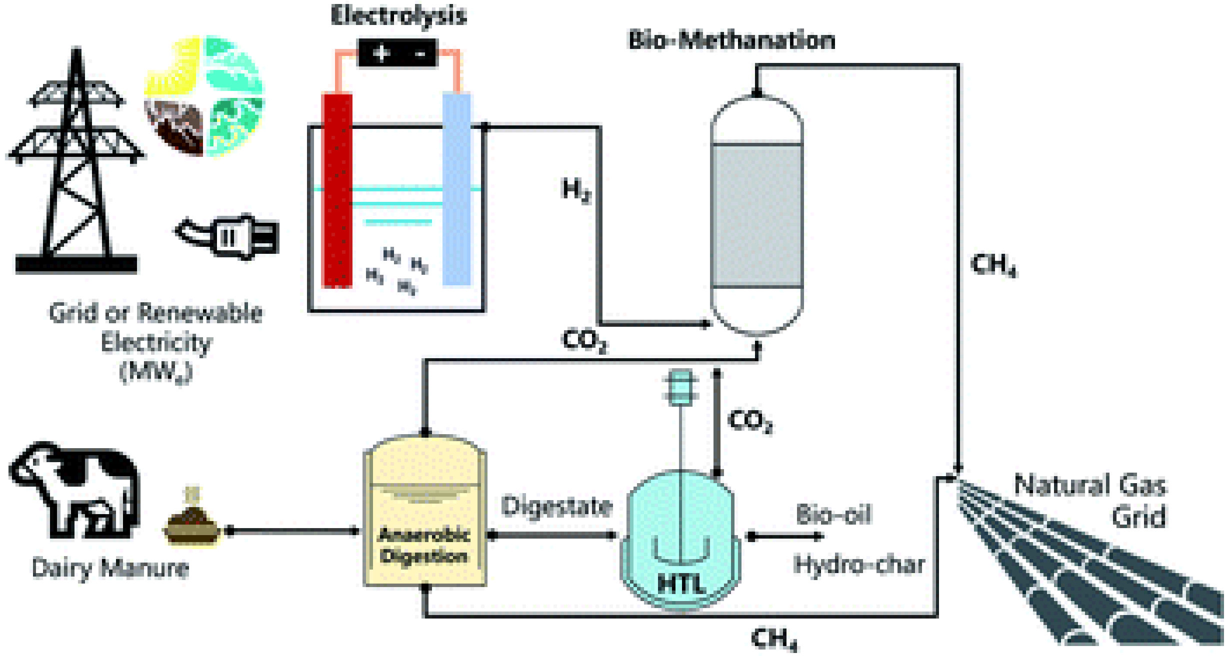
- recovered energy can offset ~50% of a WWTP energy consumption, however
- biogas conversion to biomethane (gas fuel with > 96% CH4 and H2 ≤ 2%, EN 16723) compatible with NG standards makes transportation and storage in gas networks possible

biomethane use is more flexible and efficient!!!

Biogas enhancement (biomethanation) (2)

- Compared to original biogas (calorific value 28–39 MJ/Nm), biomethane calorific content up to 51 MJ/Nm.
- Biomethanation occurs by converting biogas CO_2 to CH_4 by means of catalytic addition of H_2, allowing to **increase final volume of biomethane by ≈80% from the same quantity of biomass**.

- Cost of biomethanation decreases with decreasing CO_2 in original biogas → preliminary AD optimization should be addressed

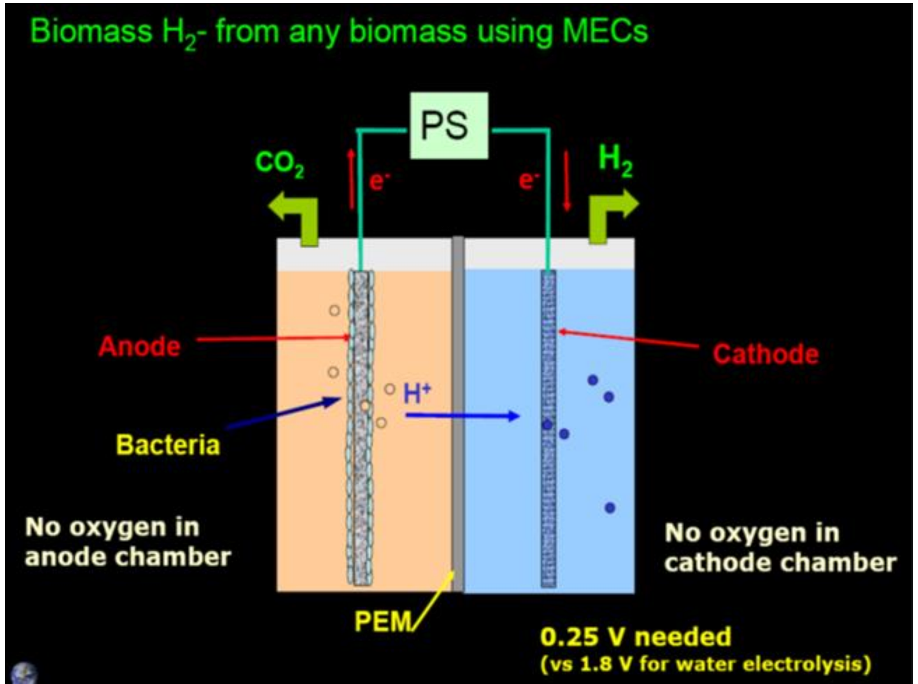


Biogas enhancement (biomethanation) (3)

- Investment costs for biomethanation units range from approximately 775 to 1000 €/kW CH_4 processed, depending on technology.
- Operating costs mainly due to electricity consumption for electrolysis (≈ 75% of OCs).
- CO_2 concentration in original biogas influences process sustainability.
- Electrolysis is the most common process for H_2 production, H_2 can be produced also by plasma reformation, steam reforming of natural gas, pyrolysis, etc.
- ≈95% of commercial H_2 is produced from natural gas (CH_4) by steam reforming, however this makes little sense in case of biomethanation!

Biogas enhancement (biomethanation) (4)

- H_2 can be produced by **wastewater electrolysis** with considerable energy savings, though use of MECs: bio-H_2 is produced from organic wastewater by biocatalyzed electrolysis through the supply of external current
- Wastewater bioelectrolysis takes advantage of the embedded chemical energy in organic matter, reducing energy needed for H_2 recovery compared to clean water processing
- Domestic wastewater can yield 0.154 L_{H2}/g_{COD} at applied voltage = 0.25 V, water electrolysis requires 1.8 V for H_20 molecule splitting!



Biogas enhancement (biomethanation) (5)

- Biomethanation is an exothermic catalytic process according to Sabatier's reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + 165\ kJ/mol$$

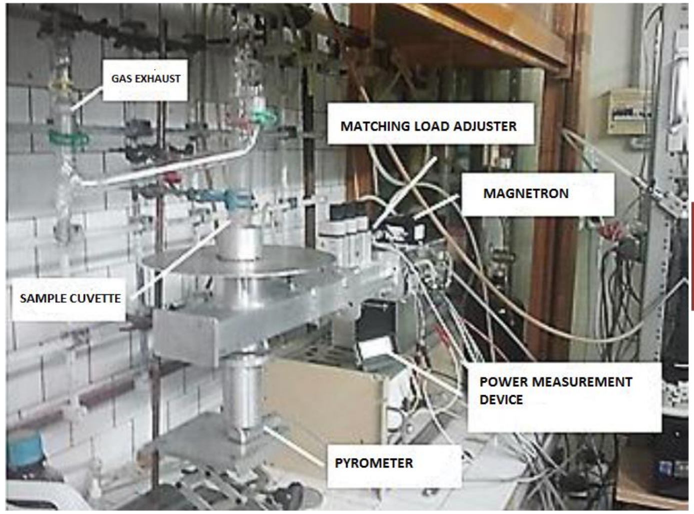
it produces 1.4-1.7 kW/Nm^{3}h of processed biogas of recoverable excess heat.

- At market price of (bio)methane = 0.10 €/kWh, process cost using H_2 from water electrolysis is economically sustainable at maximum electric energy prices between 0.053 - 0.075 €/kWh$_{el}$
- Considering additional revenues from recovered heat and O_2 (from water electrolysis), process economic margin could increase by about 0.015€/kWh$_{el}$
- For each 10% CO_2 (vol.) decrease in original biogas, economic margin increases by 0.025 €/kWh biomethane generated.

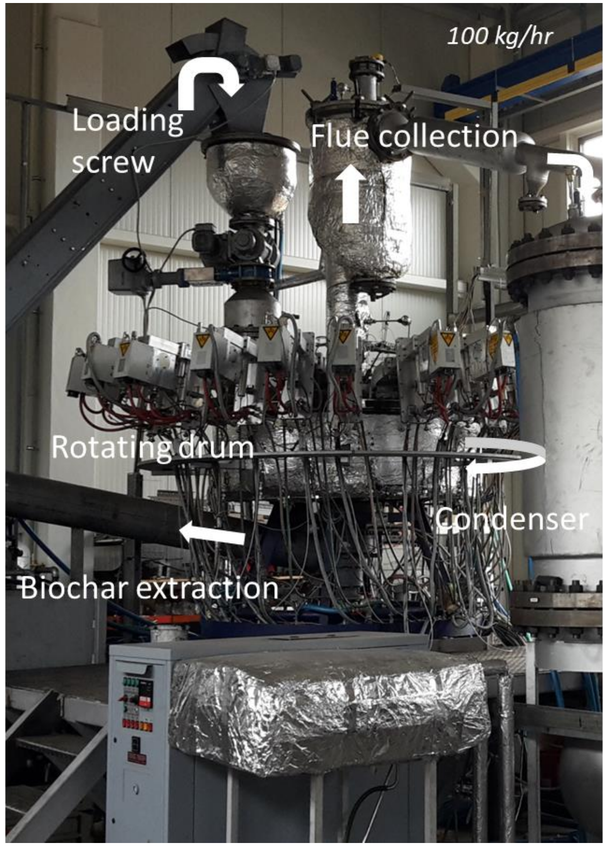
Sludge Gasification/Pyrolysis

Gasification converts sludge into gaseous fuel at temperatures between 700-1100°C under limited O_2 presence (reducing atmosphere). Higher energy recovery and lower atmospheric emissions compared to combustion.

From LAB…



15-25 g/test



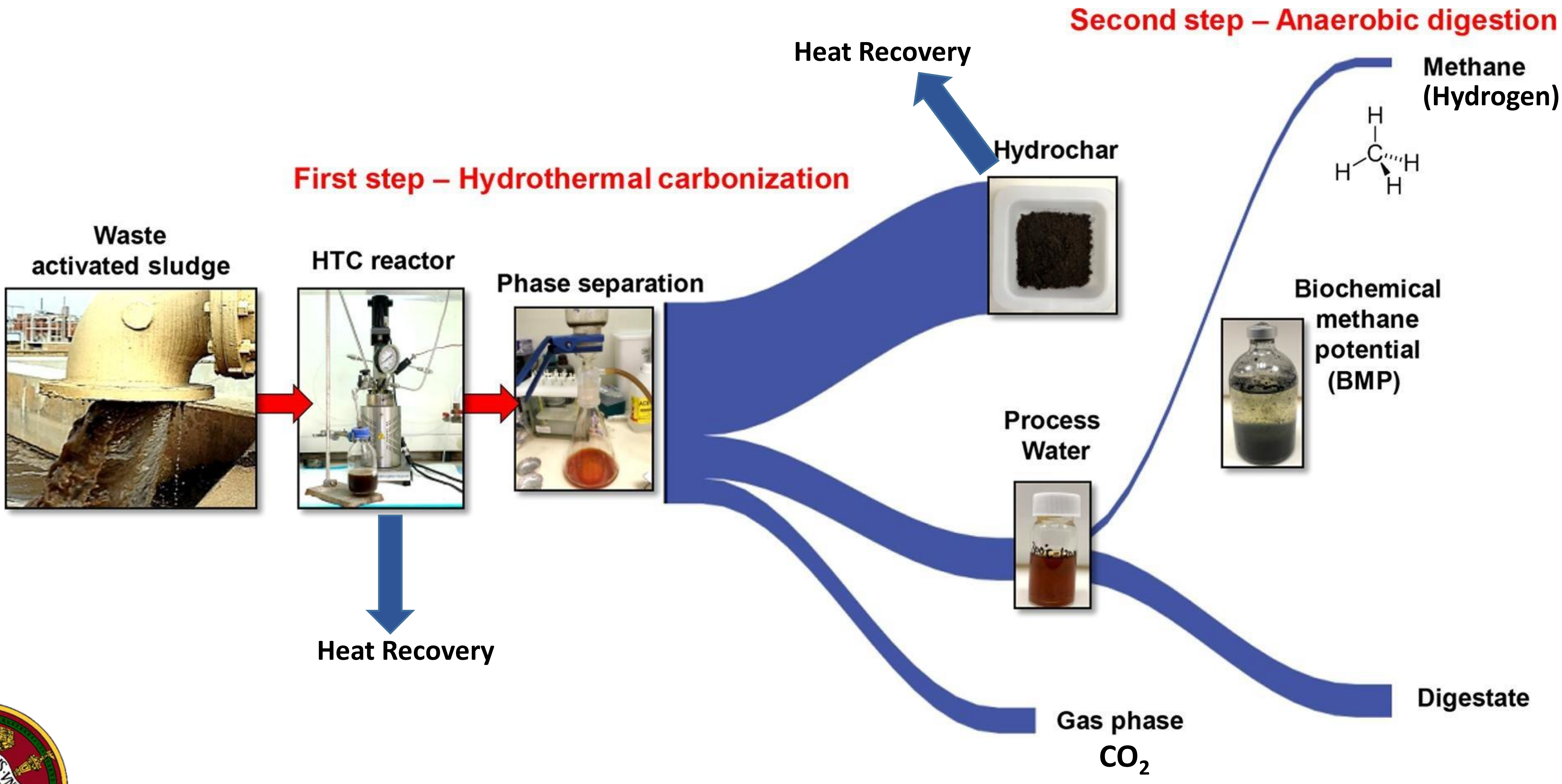
…..to full scale

Pyrolysis: sludge subject to high temperature (350–600 °C) in the absence of O_2. Converted into biochar, pyrolysis oils, water vapor, and combustible gas in varied proportions.

50% or more reduction in waste volume, stabilization of organic matter, recovery of valuable end products.

Hydrothermal carbonization (HTC)

- Environmentally friendly thermochemical process for high moisture biomass under pressure (2-6 MPa) at temperature 180-350°C for up to a few hours.
- Simulates in few hours biomass to coal conversion in geological times, producing solid (hydrochar, 50-80% wt), liquid (bio-oil and water mix, 5-20% wt) and gas (mainly CO2, 2-5% wt) by-products.
- Predominant presence of nutrients (N, P, K, others) in hydrochar rather than liquid fraction makes hydrochar amenable as soil amendment, especially when produced at low temperature (preventing N loss as volatilized ammonia).
- Liquid fraction (COD = 10 and 40 g/L) can be separated (e.g. filtration or centrifugation) from hydrochar and returned to the WWTP, with potential for additional biogas production by AD
- Excess exothermic heat of HTC reactions, and heat from slurry cooling can be recovered, exceeding energy invested in the process

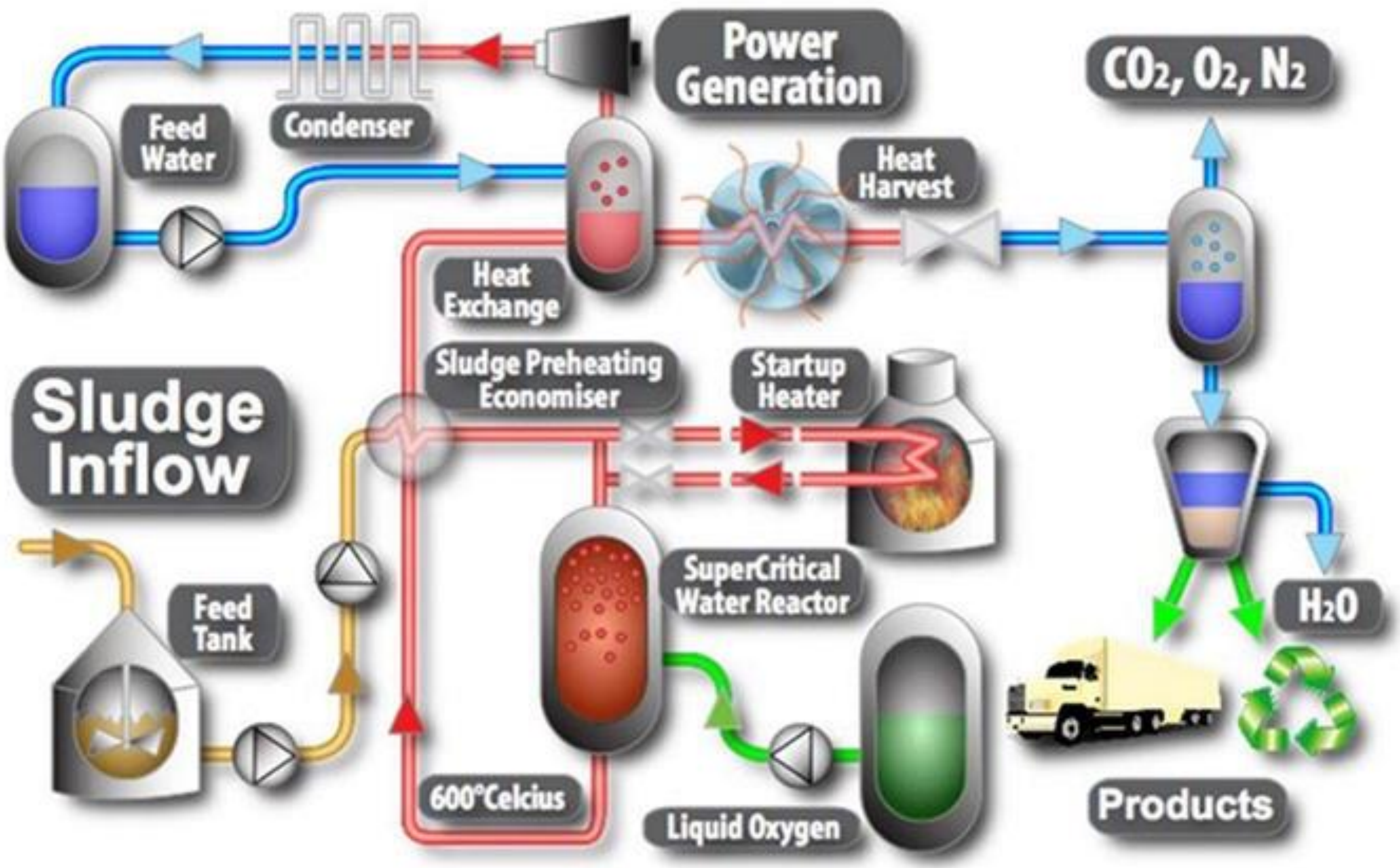

Second step – Anaerobic digestion
Heat Recovery
Methane
(Hydrogen)
Hydrochar
First step – Hydrothermal carbonization
Waste
activated sludge
HTC reactor
Phase separation
Biochemical
methane
potential
(BMP)
Process
Water
Heat Recovery
Digestate
Gas phase
CO_2

Supercritical wet oxidation (SCWO) (1)

- Temperature and pressure above supercritical point of water: 374.2°C, 22.1MPa
- water special properties: superior ability to dissolve O_2 and organics, low solubility of minerals
- O_2 (25 to 50% excess) and sludge heated to about 250°C and injected in the reactor at high pressure (25 MPa)
- conversion rates in SC conditions much faster than normal: process HRT is few seconds to a minute.
- organic compounds (including toxics) completely oxidized, ammonia and amino acids converted into nitrogen gas
- energy recovery occurs from effluent's heat: enthalpy for sludge preheating (10% solids d.w.) about 1500 kJ/kg, from post-recovery in heat exchanger over 2500 kJ/kg. Process would be less costly than incineration, even at low capacities

Supercritical wet oxidation (SCWO) (2)

- preliminary sludge dewatering need is minimal.
- off-gas contains mainly CO_2, N_2 and O_2: its treatment cost is minimal
- process solid residual consists of a slurry of inorganic ash in pure water phase: free of organic contaminants. Phosphates, iron, aluminium, and heavy metals can be recovered.
- SCWO shows high potential to sustainably address sludge disposal and resources recovery in an economically competitive way, however
- required use of pure oxygen, high-pressure vessels, and potential equipment corrosion problems still limit its large scale development.


Power Generation
CO_2, O_2, N_2
Feed Water
Condenser
Heat Harvest
Heat Exchange
Sludge Preheating Economiser
Startup Heater
Sludge Inflow
Feed Tank
SuperCritical Water Reactor
H_2O
600°Celcius
Liquid Oxygen
Products

Biorefinery

- defined as “sustainable processing of biomass into a spectrum of marketable products and energy” (IEA).
- embraces a range of technologies to separate biomasses into their building blocks and convert them to value added products, biofuels and chemicals.
- carbohydrates, proteins and lipids represent 80% of organic matter in sludge, mostly as extracellular polymeric substances (EPSs: complex high molecular weight polymers originated from secretion and lysis of microbial cells).
- thermochemical processes yield oil, gas and char according but polymers or enzymes in ESS are lost.

- Enzymes

(e.g. lipases, dehydrogenase, glycosidase, peroxidase, and aminopeptidases): employed as biological catalysts for applications in the pharmaceutical, food, and fine chemicals industries.

Enzymes attached to cell surfaces or embedded in EPS must be extracted for reuse. Cation exchange resins and nonionic detergent alone or in combination with EDTA are used for extracellular enzyme extraction. Release of microbial enzymes is achieved by disrupting sludge cells by US/PEF.

- Polyhydroxyalkanoates (PHAs)

Poly-beta-hydroxybutyric acid and its co-polymer poly (3-hydroxybutyrate-co-hydroxyvalerate [P(3HB-co-HV)]) are common PHAs (linear polyesters) produced by microorganisms that use C as substrate. They properties are comparable to petroleum-based plastics. PHA accumulation has been observed from 0.30 to 22.7 mg polymer/g sludge. At the moment extraction is affected by high production costs

- Bio-pesticides

i.e. *Bacillus thuringiensis,* widely used in agronomy as less impacting on environment compared to conventional chemical pesticides (no toxic residues).

Conventional fermentation medium for production of BT-based bio-pesticides involves significant portion (40–60%) of total production cost. Waste sewage sludge appears to be a cost-effective medium for BT production. Its use could reduce industrial production cost of BT by 50%.

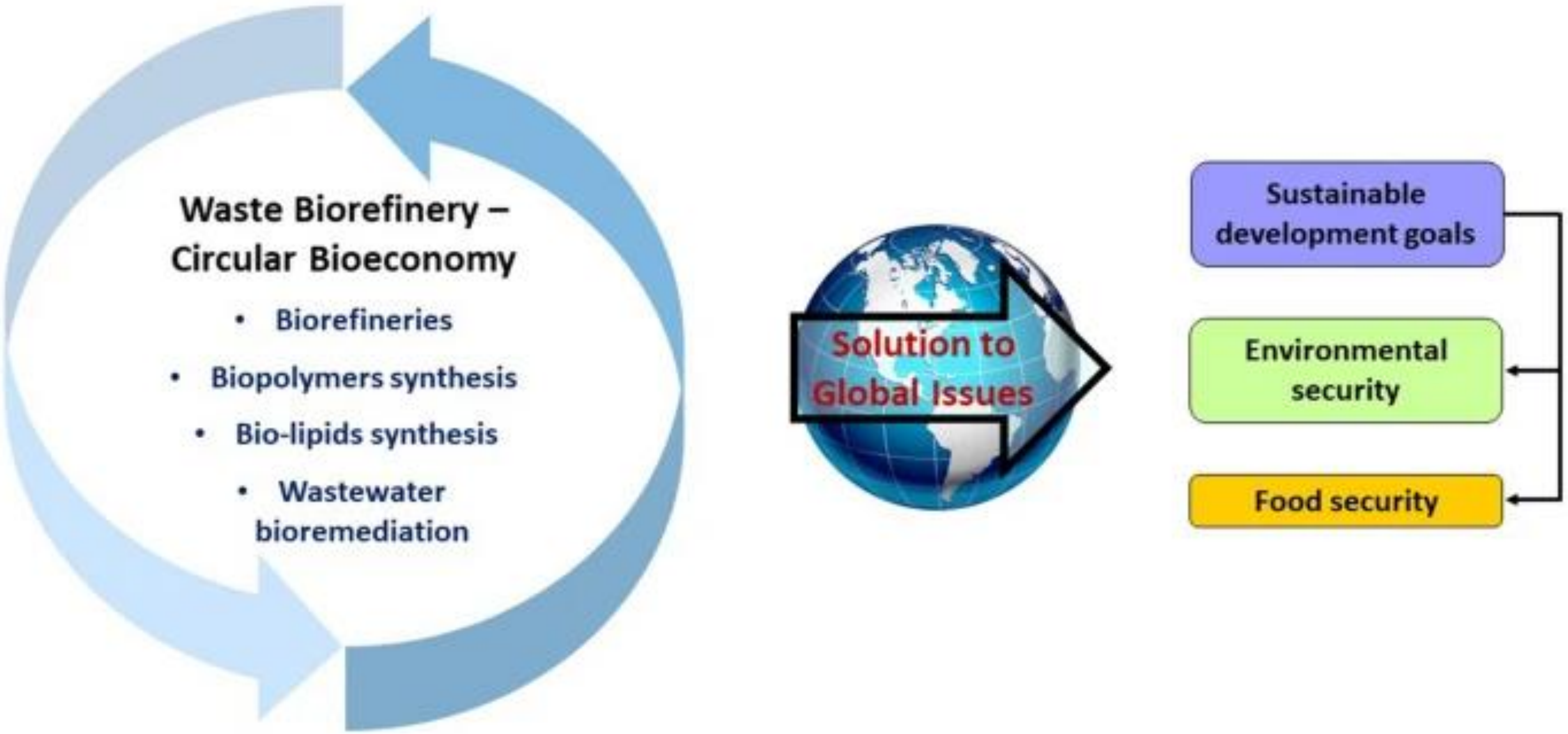
- Protein recovery

proteins (~50% cell d.w.) in sludge make it a potential source for recovery. Proteins as components of animal feed supply energy and nitrogenand can be achieved by cell disintegration or enzymatic methods.

Biorefinery is not an exclusive sludge process, but it may precede others.

As an example, high moisture content in sludge renders it unsuitable for direct application of thermochemical treatments.

- Biochemical (biorefinery) processing leads to volume reductions of up to 90%.
- Biorefined sludge can be directed to the thermochemical pathway with greater efficiency.



LAST, BUT NOT LEAST…

Science alert

Sewage Sludge Contains Millions of Dollars Worth of Gold

21 JAN 2015

Engineers have analysed the contents of sewage sludge to discover that in a city of a million people, there's as much as $13 million worth of valuable metals, including gold and silver, annually, at a value of US $280/ton of sludge. A new study has estimated that if you take all the sewage sludge produced by a population of 1 million you'll find over $2.5 million worth of gold and silver, plus other metals worth millions more.

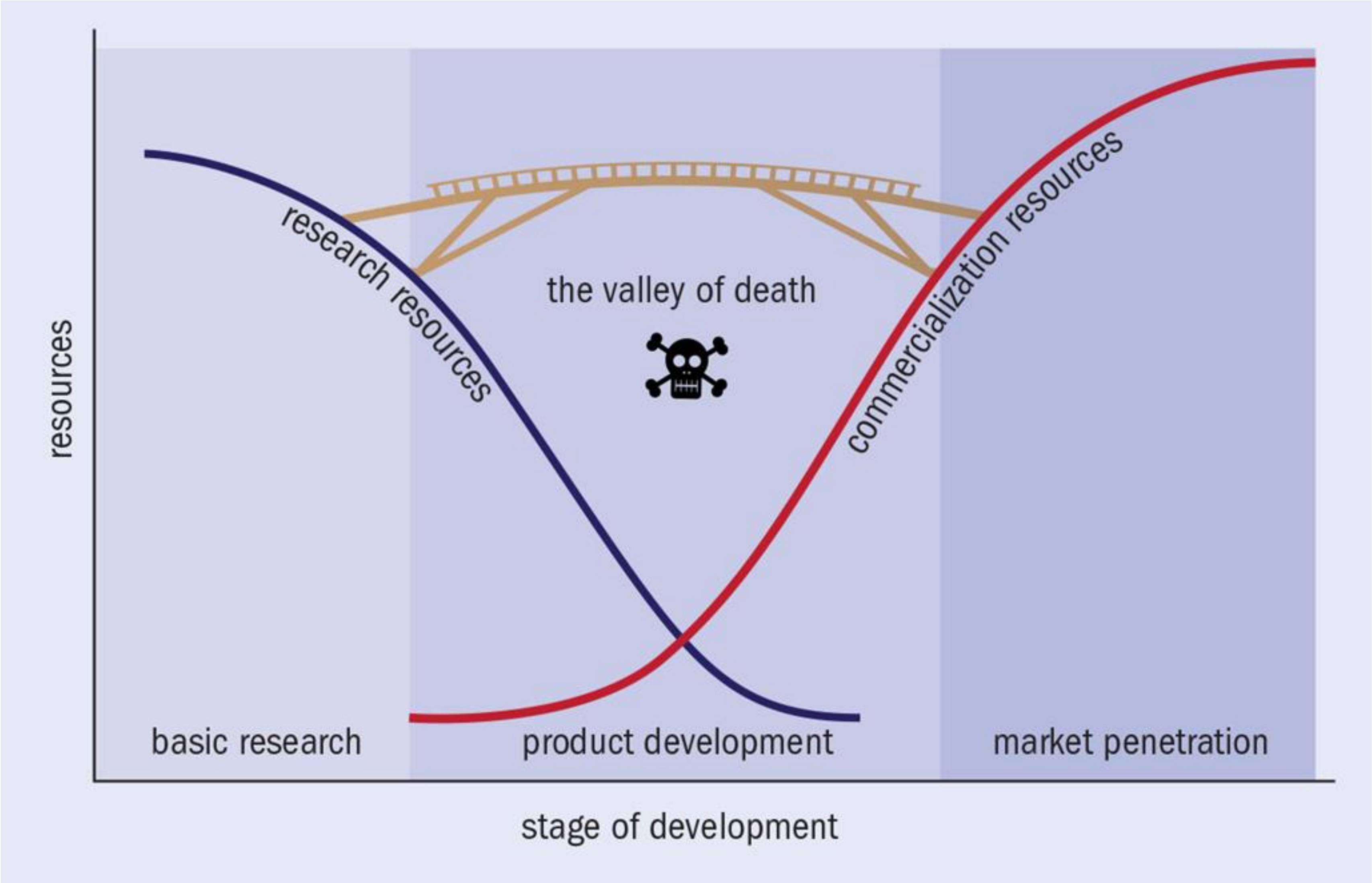
Westerhoff P., Lee S., Yang Y., Gordon G.W., Hristovski K., Halden R.U., Herckes P. (2015) Characterization, recovery opportunities, and valuation of metals in municipal sludges from U.S. wastewater treatment plants nationwide. Environ. Sci. Technol.

JUST

AND ALL IS NOT GOLDEN THAT GLITTERS, AND NOT ALL THAT GLITTERS IS GOLD.

Aloysius Charles Swinburne

The main problem……



Thank you, and …….

One at a time, please!!!

(Uno alla volta, uno alla volta, peeer carità… - Rossini, The barber of Seville, Act 1)