Plasma und Ultraschall – ein synergistischer Ansatz für die Vorbehandlung von Biomasse

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FROM IDEA TO PROTOTYPE

Behandlung von Gärresten

Motivation

- 25 % der organischen Inhaltsstoffe bleiben in sogenannten Gärresten ungenutzt
- Ammoniakemissionen

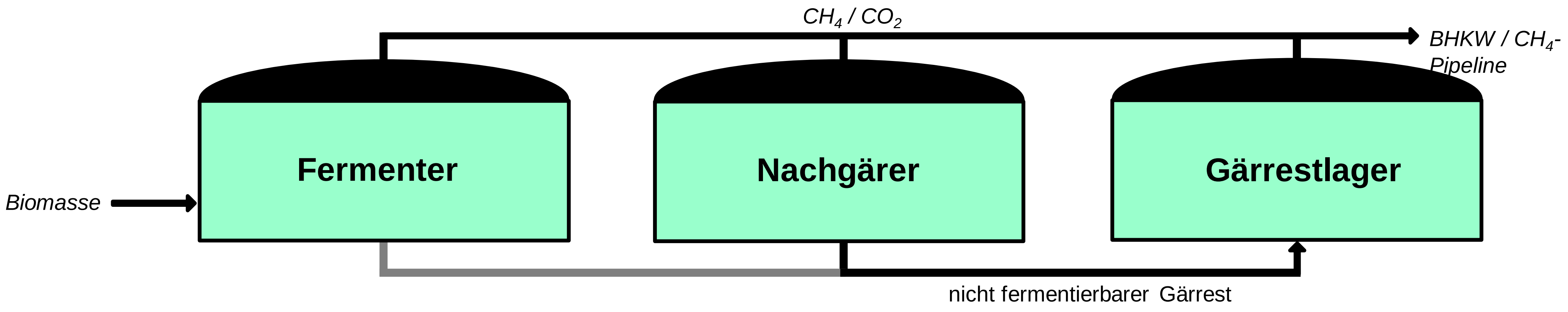
Projektziel

- **Effizienzsteigerung von Biogasanlagen** durch die Erschließung bislang ungenutzter Potentiale von Fermentationsresten aus dem Biogasprozess
- Emissionsreduktion

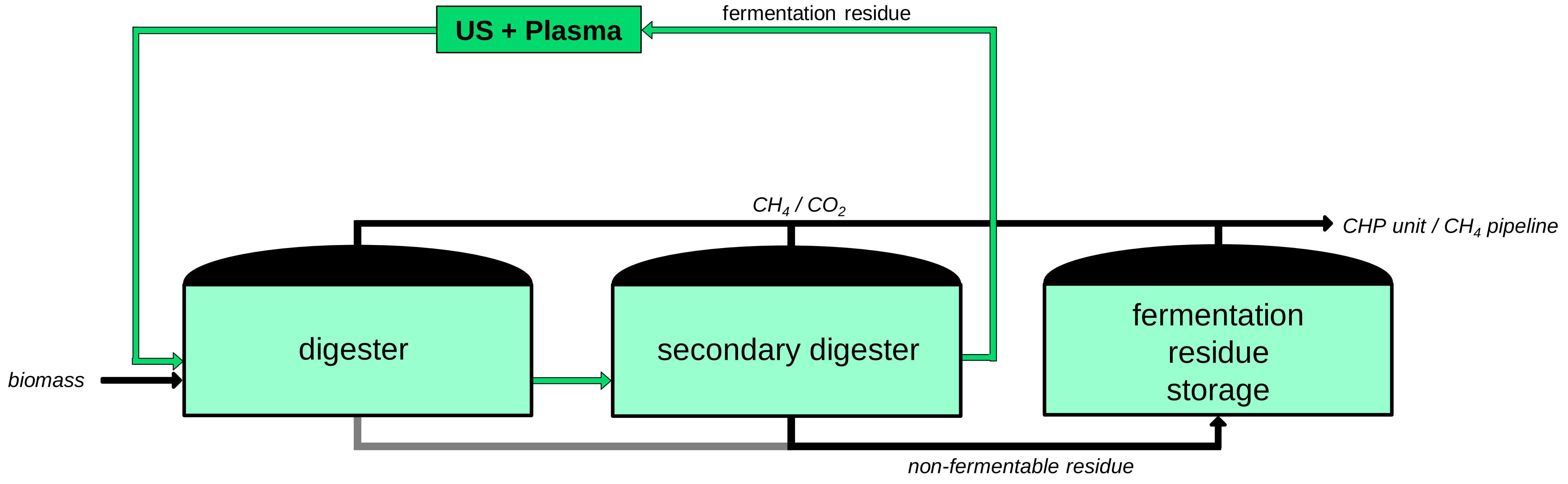
Lösungsweg

- Entwicklung eines modular aufgebautes **emissionsfreies Ultraschall/Plasma-Aufschlussverfahrens** für die Aus- oder Nachrüstung von Biogasanlagen

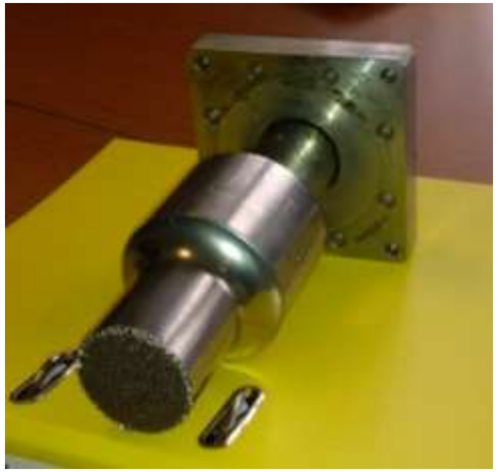
Biogasanlage



Biogasanlage mit Verfahren zur Behandlung der Gärreste



Ultraschallbehandlungsgerät



1. increase of electrical power by 17 - 18 % by operating the Wave-Box (using approx. 3.5 kW of electrical power)
2. increase of biogas production by 14 %
3. ratio of energy input to additional energy yield is 1 : 12.5 (4 kW energy input: 50 kW additional electrical yield)

Current microwave arrangement

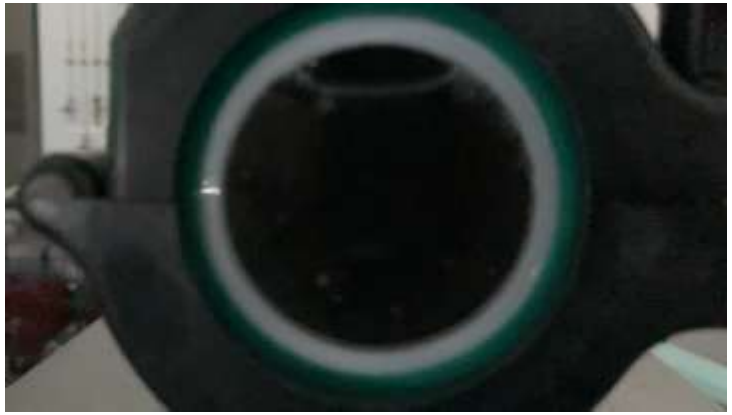
Reactor for biomass treatment

Stub tuner

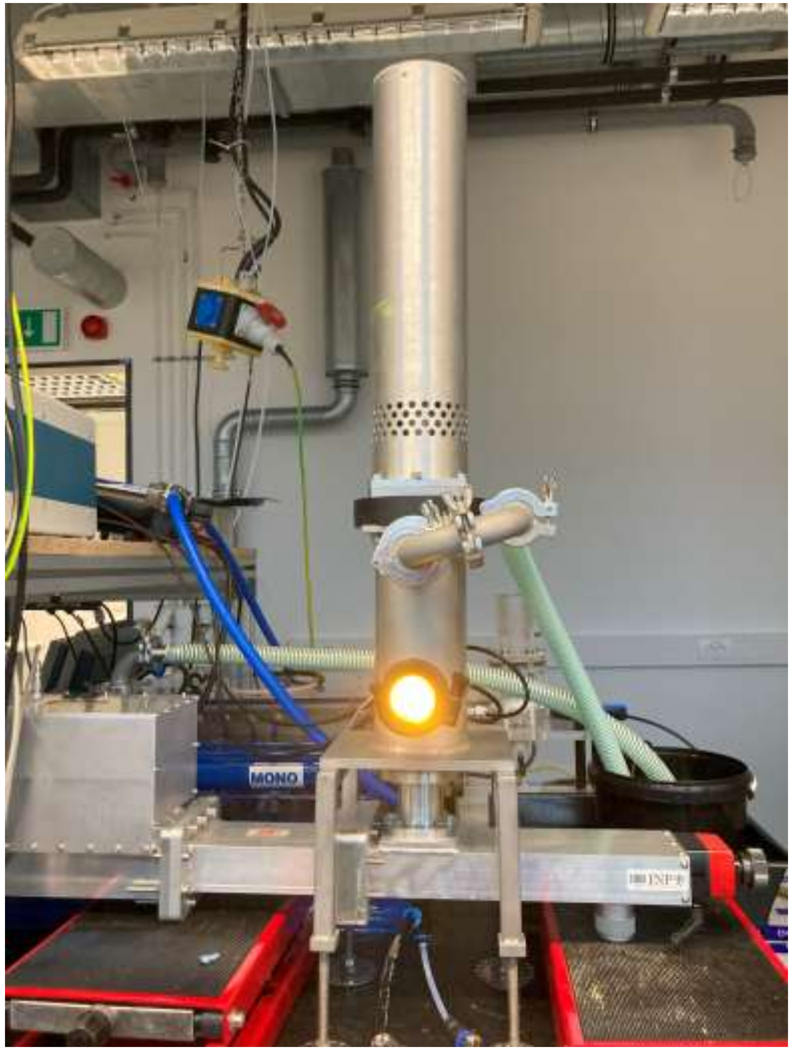
Sliding short circuit

Microwave antenna

Microwave generator

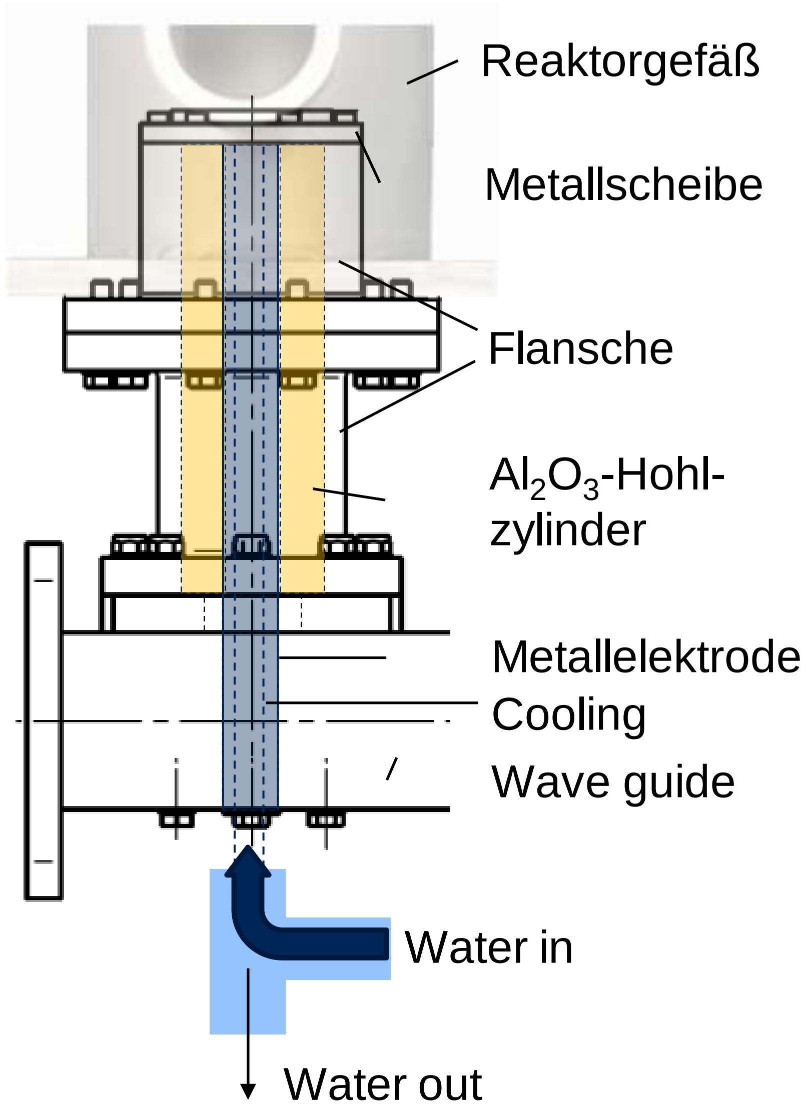


Current microwave arrangement

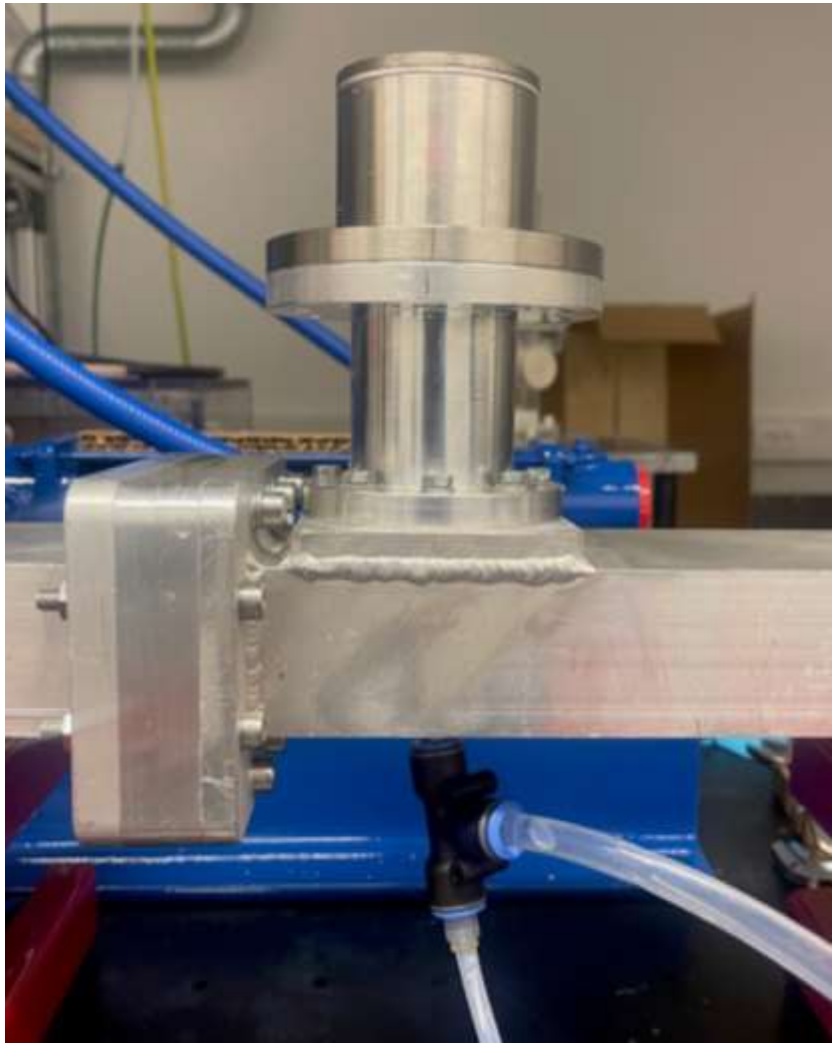


New microwave antenna with integrated a **cooling system** inside the metal rod

a)



b)



a) Schematic of the new antenna implemented by cooling system

b) Picture of the new antenna implemented by cooling system

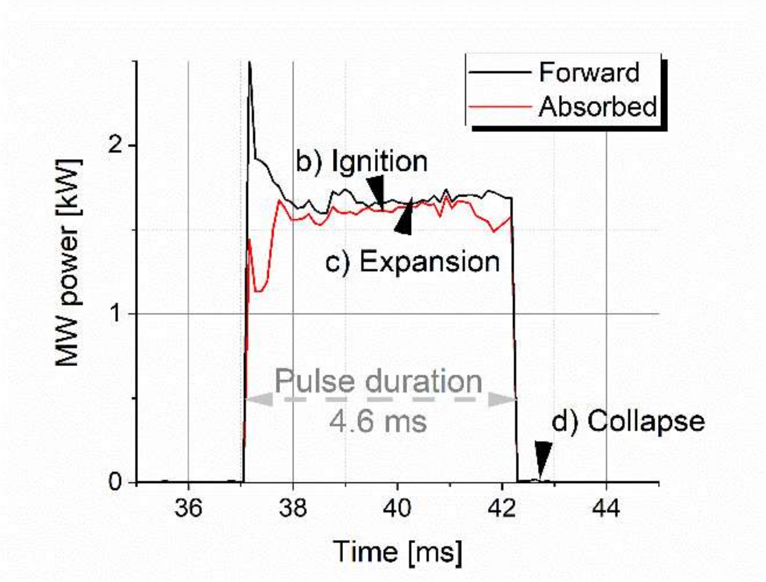
Ignition Behavior

One MW pulse:

1. Heating + vapor bubble formation
2. Discharge + bubble growth
3. Collapse of the vapor bubble

- ➢ Ignitability: Elapsed Time (applied energy) till ignition

Fast framing recording (15,969 frames/s) of one MW pulse



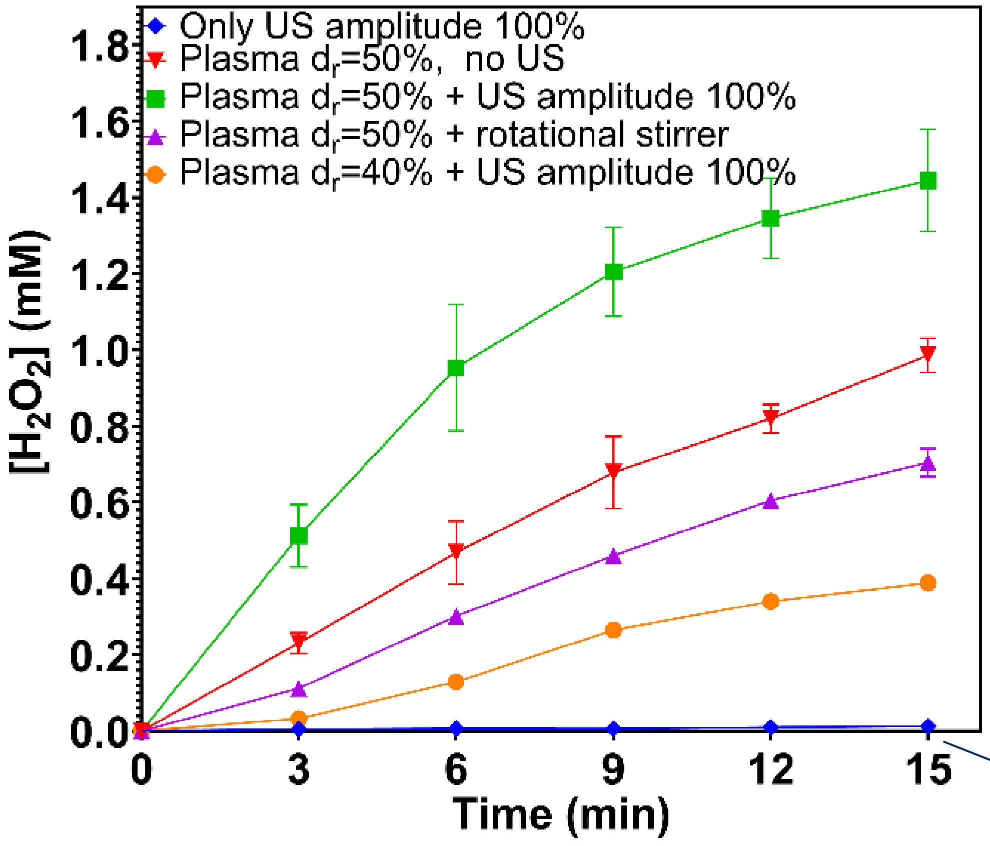
MW power during one pulse

Plasma in liquid and reactive species

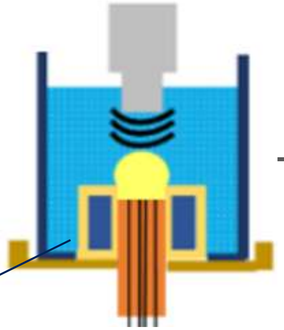
RONS produced in plasma directly in liquid [1]	**important for desintegration**
$^{\bullet}OH$	Main oxidants causing chain scission/ monomer release [2, 3]
$H^{\bullet}$	Abstract H, can initiate radical chains, less important than $^{\bullet}OH$ for oxidative scission
e^{-}_{aq}	Strong reductant, cause formation of hydroxide ion and increasing pH [4]
H_2O_2	mild oxidant but precursor for regenerate $^{\bullet}OH$
$O_2^{\bullet-}$ / $HO_2^{\bullet}$	Weaker oxidant, help in formation of H_2O_2 [2]
NO_2^- / NO_3^-	Only if air or N_2 dissolve in water, evidence of RNS formation, contribute in generation of peroxynitrite, decrease pH, faster hydrolysis [2]
O_3	Quenched in water[2]

1. Thirumdas, R., et al., *Plasma activated water (PAW): Chemistry, physico-chemical properties, applications in food and agriculture.* Trends in Food Science & Technology, 2018. 77.
2. Sewon Oh , E.E.S., *Recent advances in oxidative degradation of plastics.* Chem Soc Rev, 2024. 53.
3. Yinghui Lin , Y.Z., Yonghao Wang , Yuancai Lv , Linyan Yang , Zhijie Chen , Bing-Jie Ni , Xueming Chen, *Efficient degradation and mineralization of polyethylene terephthalate microplastics by the synergy of sulfate and hydroxyl radicals in a heterogeneous electro-Fenton-activated persulfate oxidation system.* Journal of Hazardous Materials 2024. 478.
4. Elg, D.T., et al., *Recent advances in understanding the role of solvated electrons at the plasma-liquid interface of solution-based gas discharges.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2021. 186.

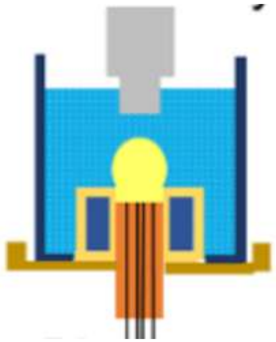
Plasma – Ultrasound: H_2O_2 evolution



Temporal evolution of H_2O_2 concentration for five different plasma and ultrasound treatment conditions



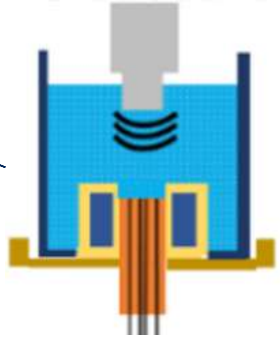
Plasma + US



Plasma

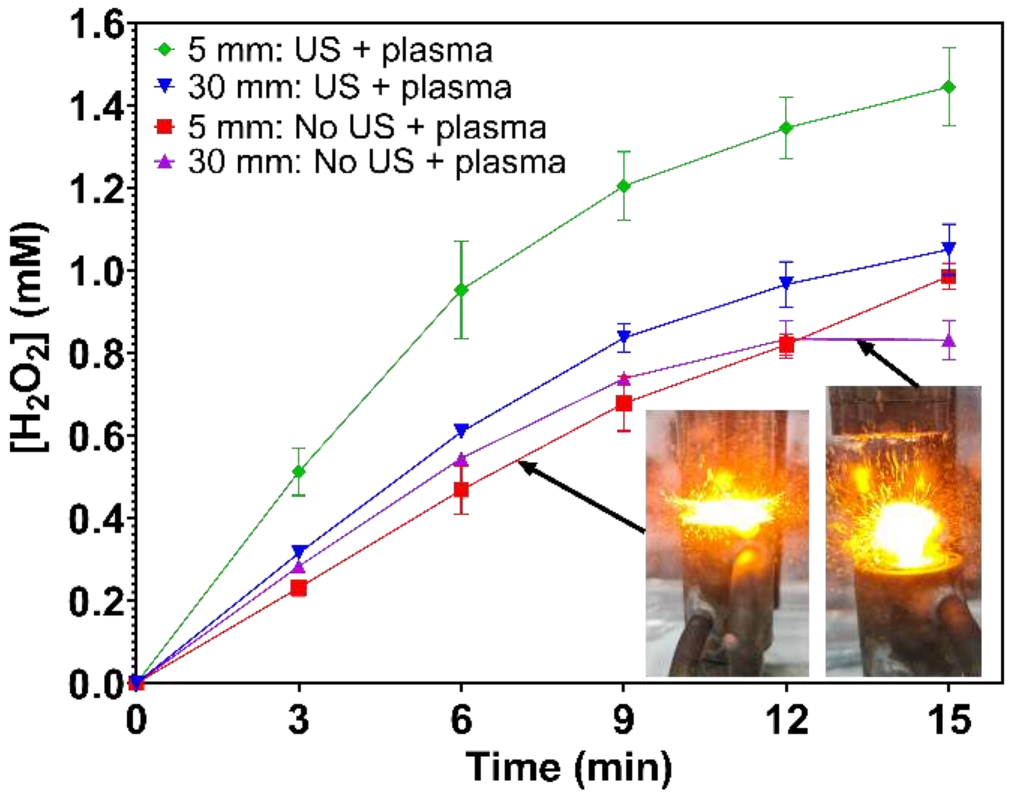
Frequency: 10 Hz
Duty cycle: 40 and 50 %
Microwave power: 1950 W
NaCl concentration: $10\,\frac{\mathrm{g}}{\mathrm{L}}$
Distance: 5 mm

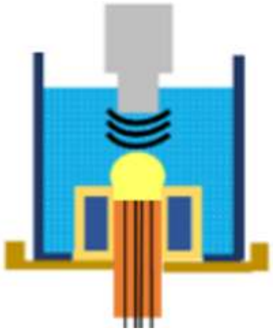
Plasma + Stirrer

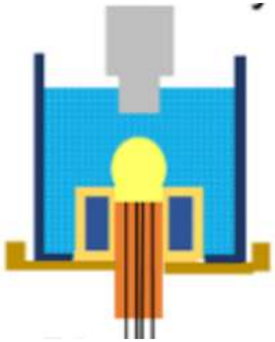


Plasma + US

Plasma – Ultrasound: H_2O_2 evolution





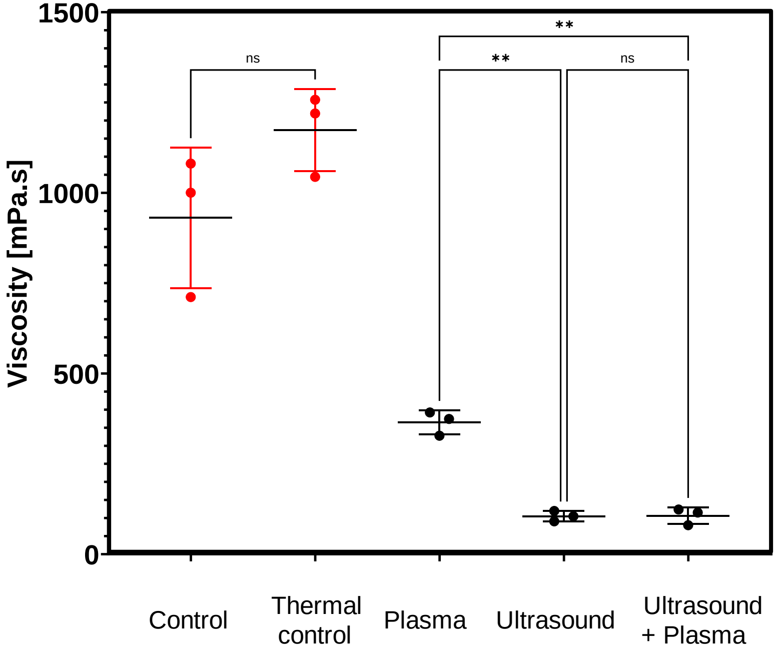


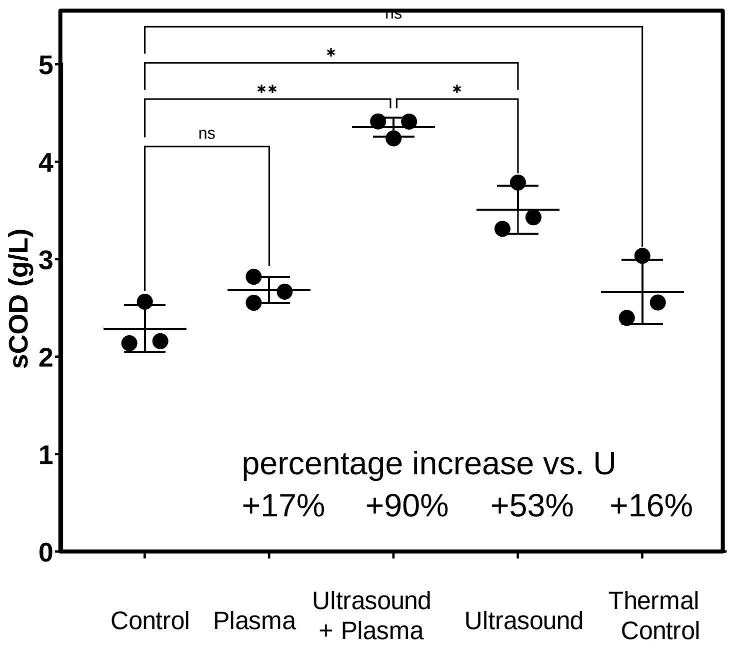
Temporal evolution of H_2O_2 concentration for two sonotrode positions (5 mm or 30 mm) with and without ultrasound

Frequency: $10\ \mathrm{Hz}$
Duty cycle: 50 %
Microwave power: $1950\ \mathrm{W}$
NaCl concentration: $10\,\frac{\mathrm{g}}{\mathrm{L}}$
Distance: 5 and 30 mm

Sugar beet pulp digestate; viscosity and COD

One sample: 4 kg digestate (circulating)
Ultrasound: nominal 1 kW, 20 kHz, amplitude 20 µm
Micro wave plasma: 6 kW puls power, 30 Hz, 30 % Dutycyle





Experiment

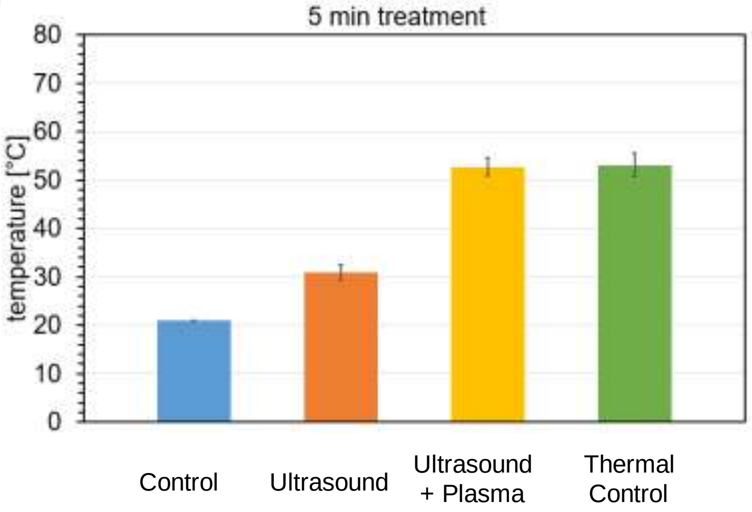
- Substrate: Digestate from cattle manure, Sandhagen
- Sample amount: 3.6 kg
- Treatments:
  1. Ultrasound only
  2. Ultrasound and MW plasma
  3. Ultrasound and MW heating (thermal control)

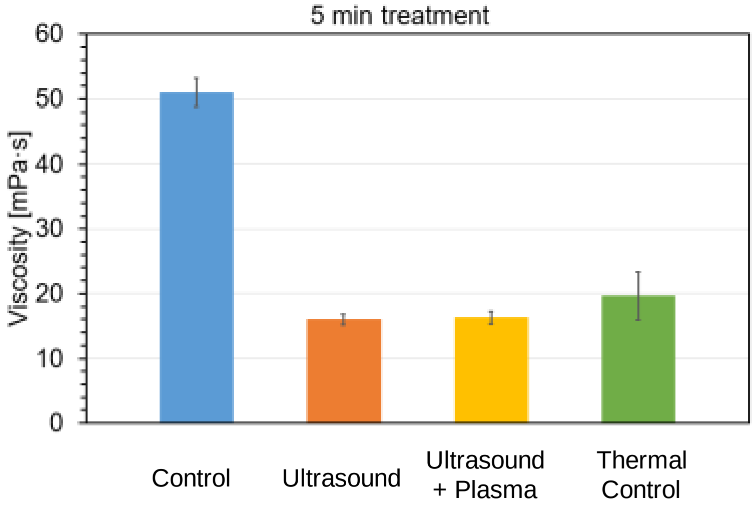
  - ➢ Each 10 min*

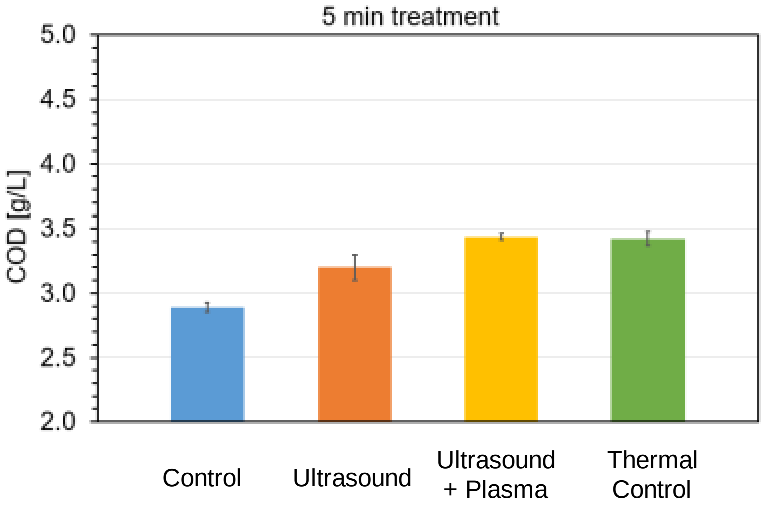
- Ultrasound settings: 1 kW, 20 µm amplitude
- Plasma settings: 6 kW pulses, 30 Hz, 40 % duty

*USP and UST were stopped after 9 min, as overheating needed to be avoided

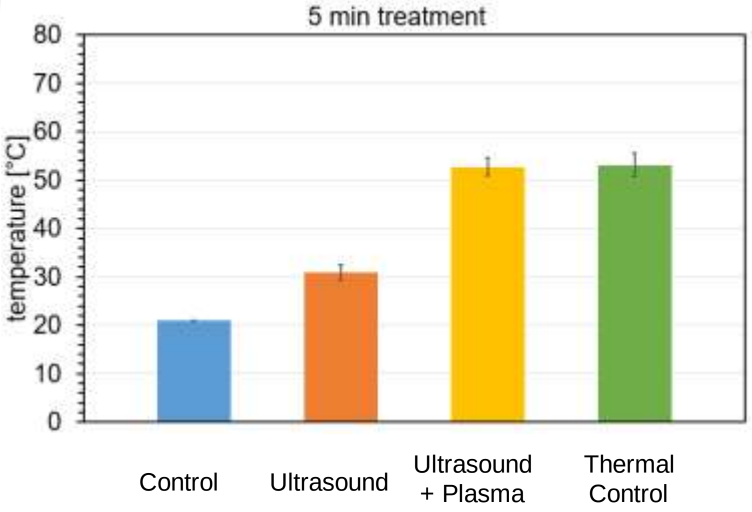
Results: 5 min treatment, digestate from cattle manure

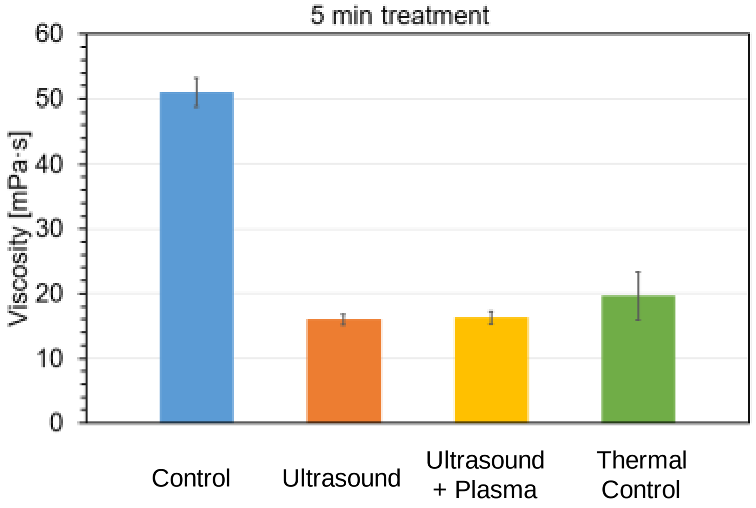


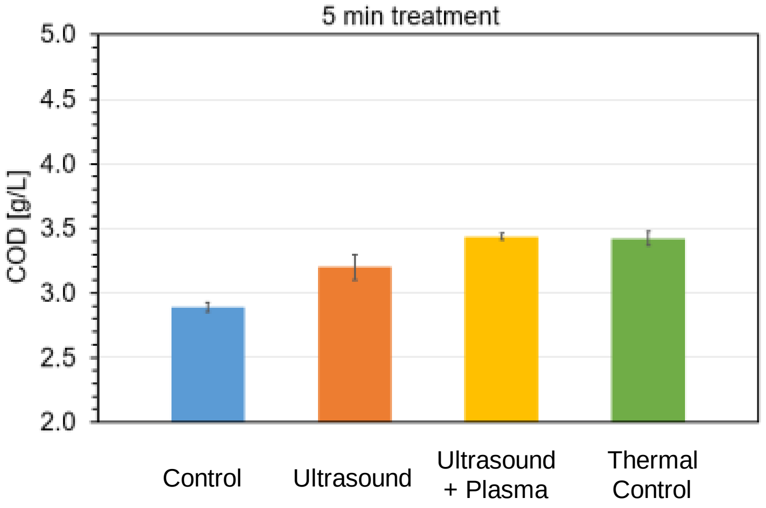


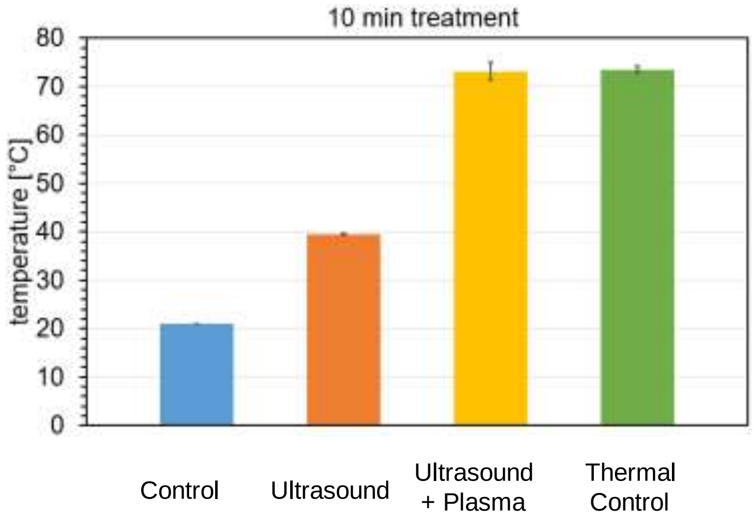


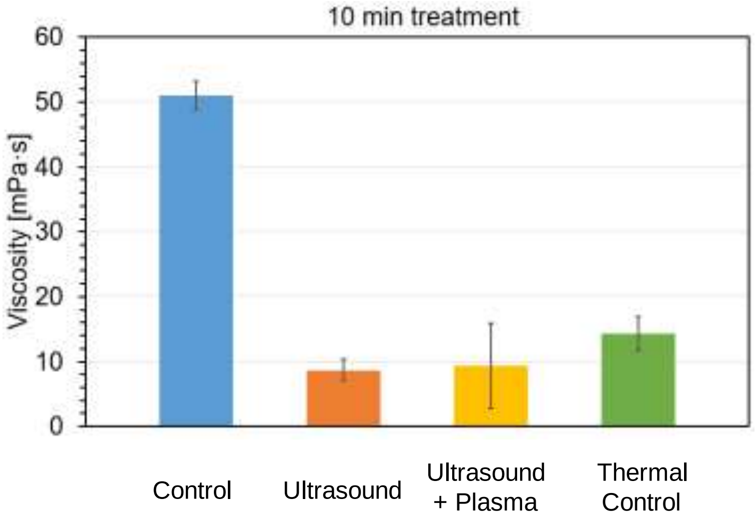
Results: 5 and 10 min treatment, digestate from cattle manure

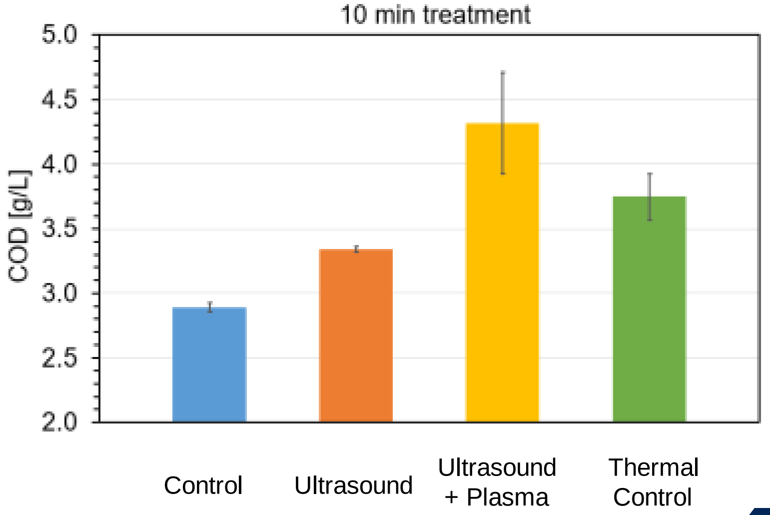




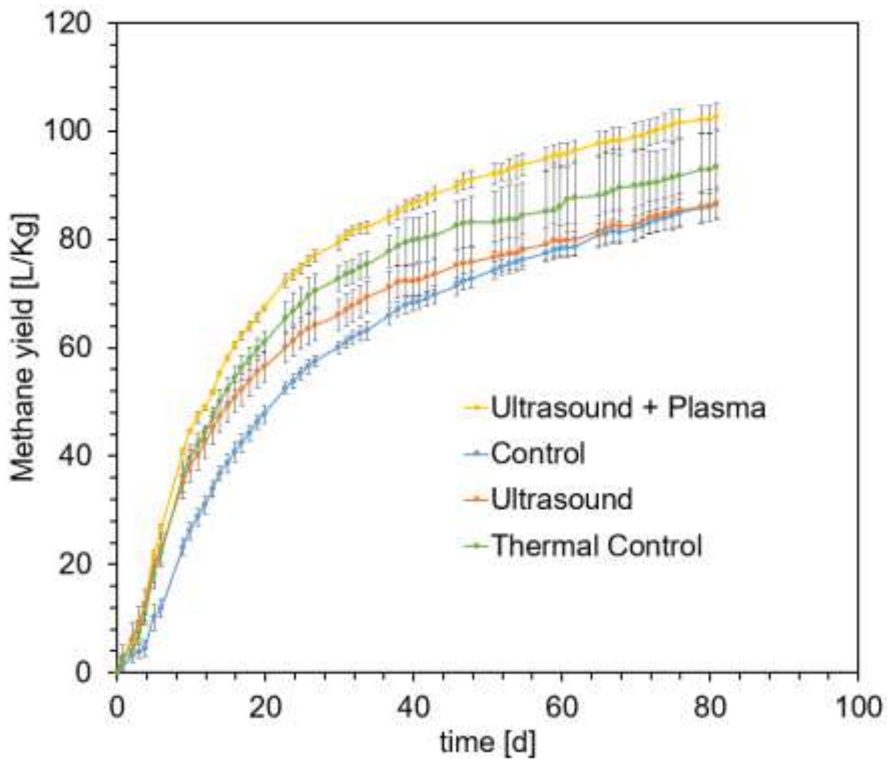


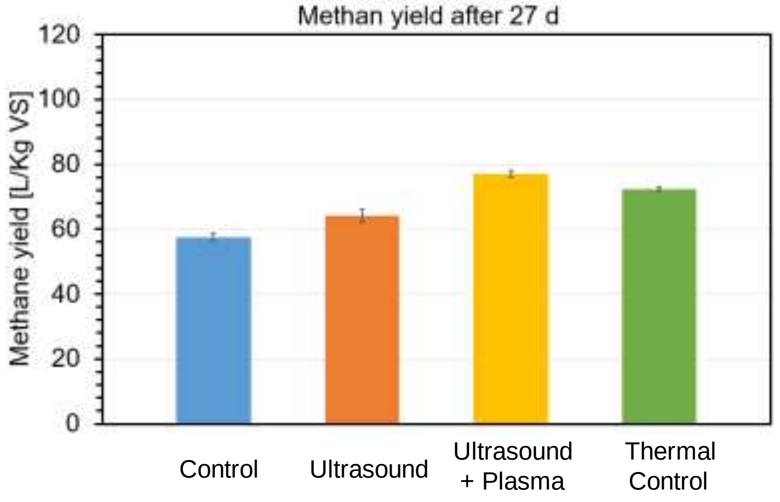


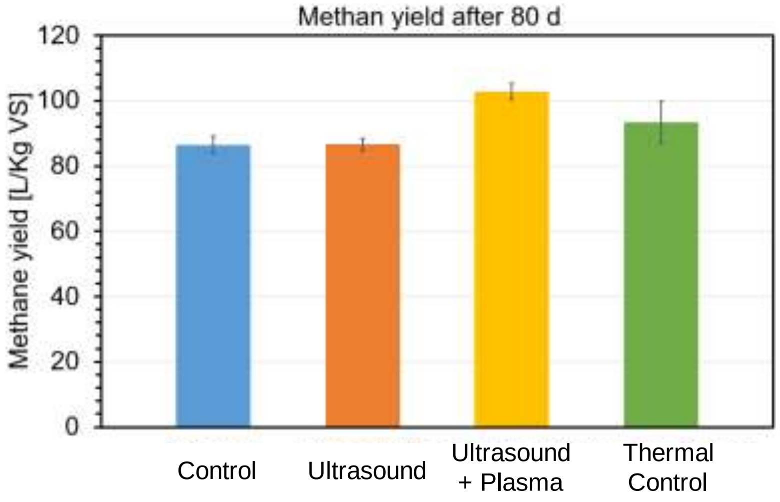




Methan evolution test, digestate from cattle manure







<u>After 27 days:</u>

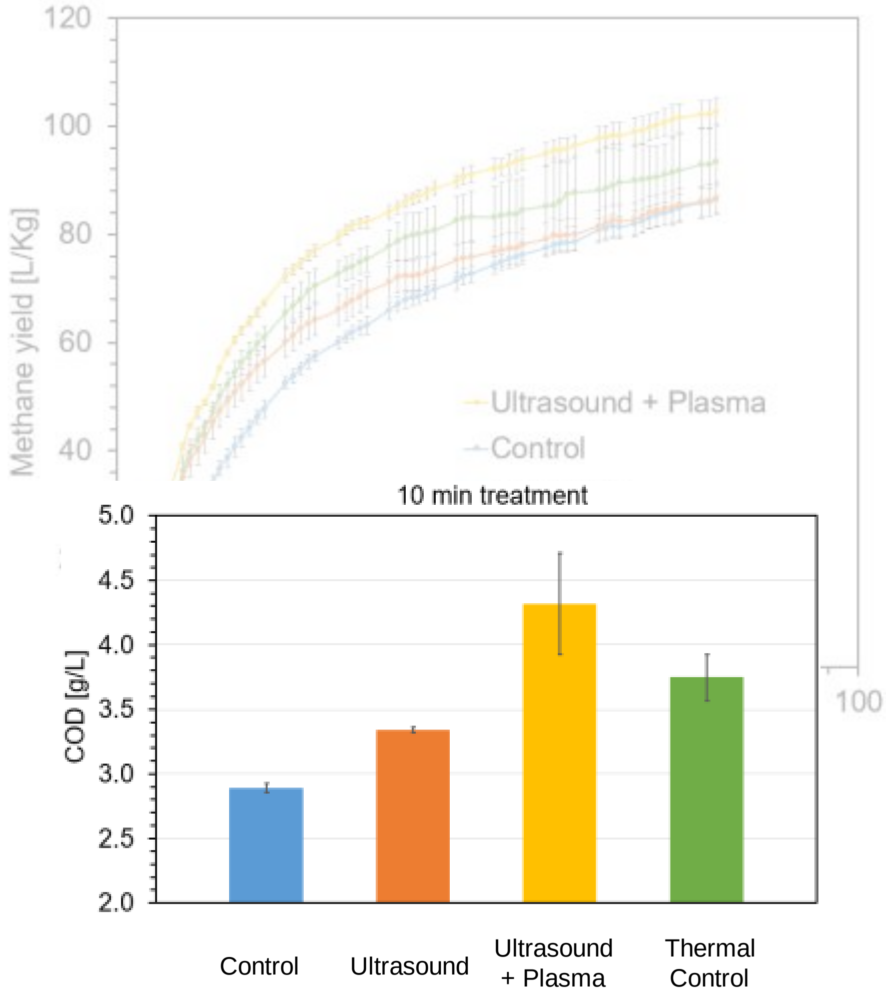
- All treatments enhance CH_4 yield
- USP HD > UST HD > US HD
- *Plasma HD more than Thermal HD*

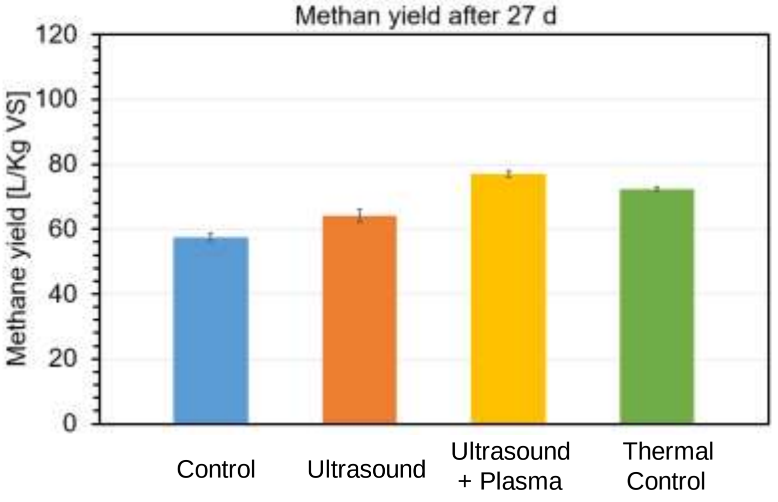
<u>After 80 days (abort criteria fulfilled):</u>

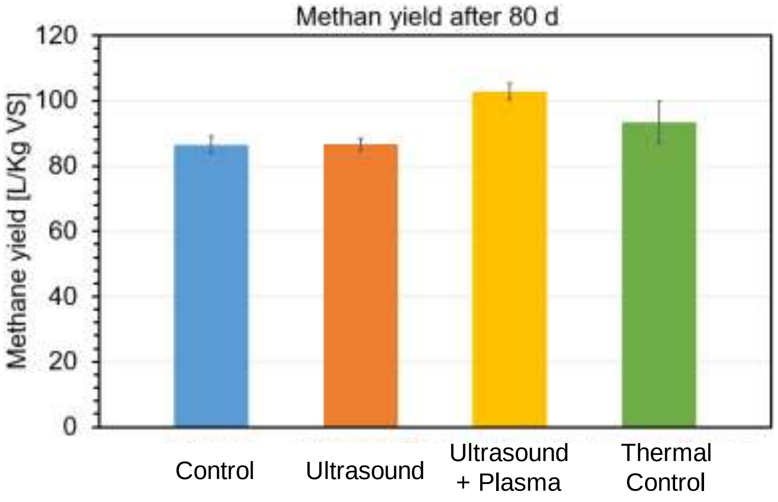
- US group falls behind control
- UST = USP > Control

➢ CH_4 yield scales similar to sCOD

Methan evolution test, digestate from cattle manure







<u>After 27 days:</u>

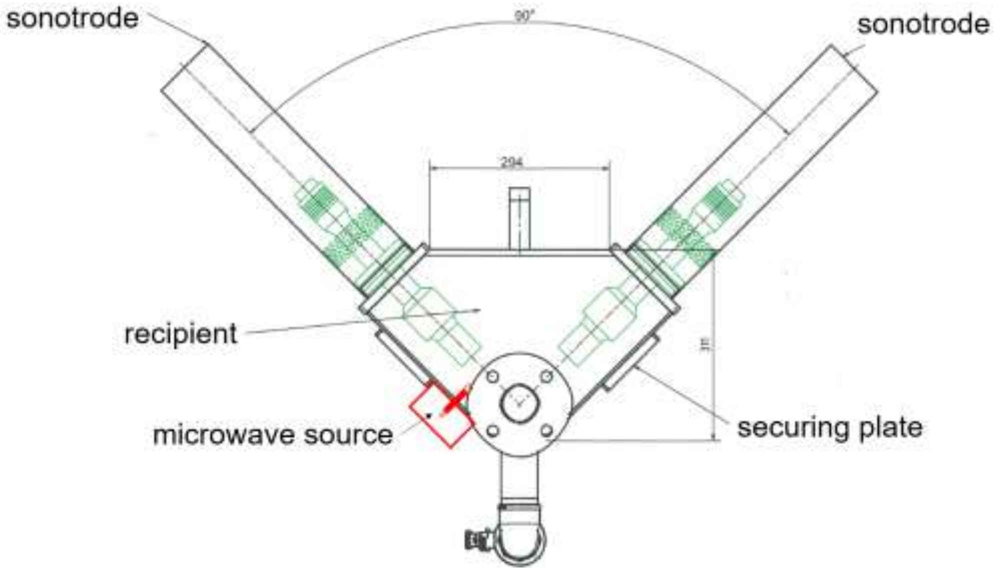
- All treatments enhance CH_4 yield
- UST LD = USP HD > US LD
- USP HD > UST HD > US HD
- *Plasma HD more than Thermal HD*

<u>After 80 days (abort criteria fulfilled):</u>

- US group falls behind control
- UST = USP > Control
- *Plasma = Thermal*

➢ CH_4 yield scales similar to sCOD

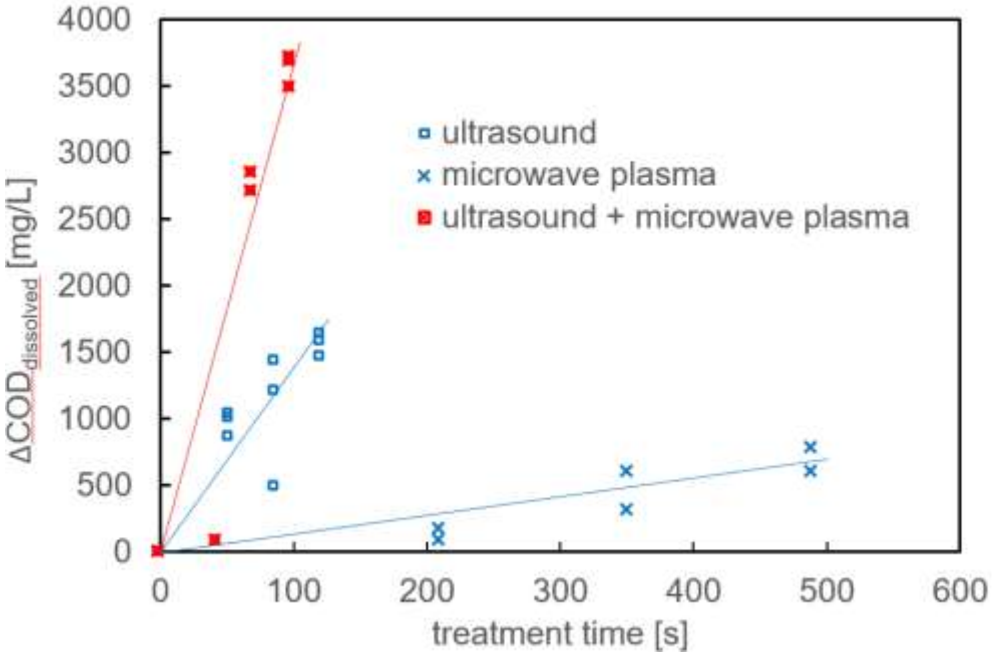
Comparison of Ultrasound & plasma treatments of manure



Schematic of plasma-ultrasound arrangement for cattle slurry treatment with 10 l recipient

View into the recipient on the microwave antenna

Comparison of Ultrasound & plasma treatments of manure



Change of dissolved chemical oxygen demand ($COD_{dissolved}$) of treated fermentation residues (cattle slurry); comparison of three different treatment procedures

Ultrasound:	disintegration of the biomass --> up to 20 % increase
Microwave:	digestion of biomass --> up to 12 % increase
Ultrasound + microwave:	biomass digestion --> up to 41 % increase

Nächste Schritte

- Test mit 300 L Fermentern beim IBZ in Hohen Luckow
  1) ohne Gärrestbehandlung
  2) nur Ultraschall
  3) Ultraschall + Plasma

- Aufbau eine Anlage für 4000 L Fermenter

- Industriepartner haben Interesse an einer Kommerzialisierung

Weitere Anwendungen

- Aufschluss von Lignozellulose für die Gewinnung von Lignin (BMFTR Förderung, LiBiPlUs, FKZ: 031B1585)

- Aufschluss von Biopoymeren (Leibniz Förderung, SUSTAIN)

- Aufschluss von Lignin (beantragt)

- P-Gewinnung aus Klärschlamm (in Vorbereitung)

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ATB Leibniz-Institut für Agrartechnik und Bioökonomie

BioBG Mehr Erfolg mit effizienter Energie

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