3rd International HTC Symposium
May 10-13, 2023, Seul, South Korea

AGH University of Science and Technology

The upscaling of hydrothermal carbonization of sewage sludge: the comparative analysis of chemical and physical properties of solid and liquid products

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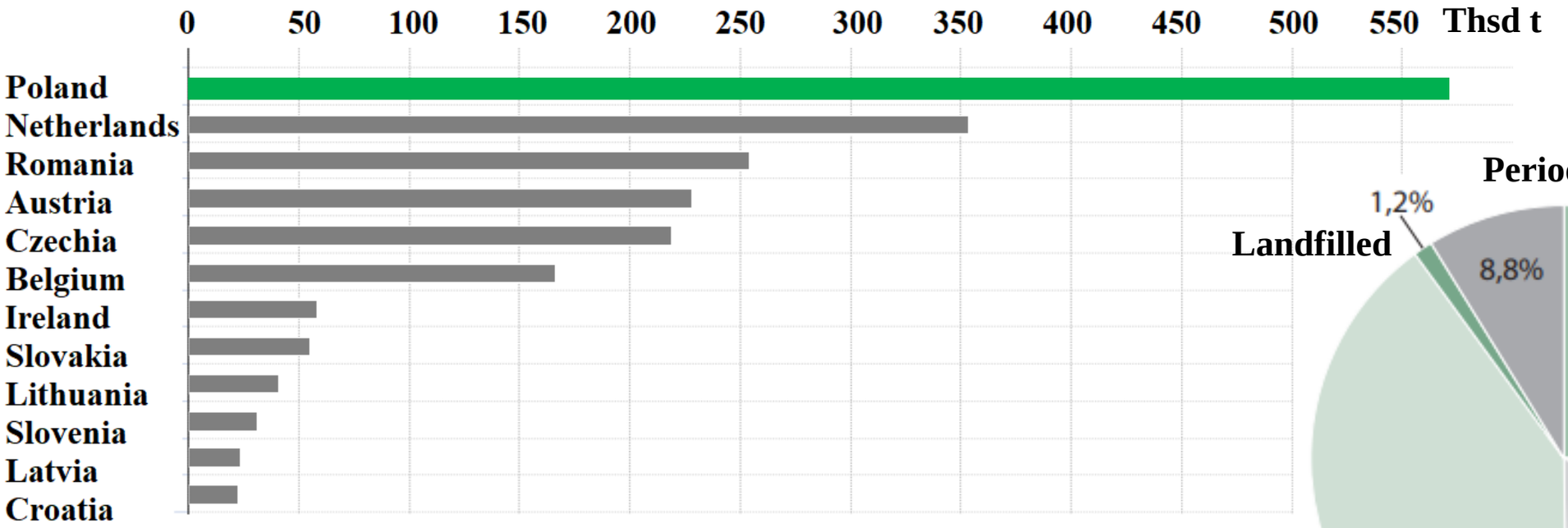
May 10, 2023

OUTLINE

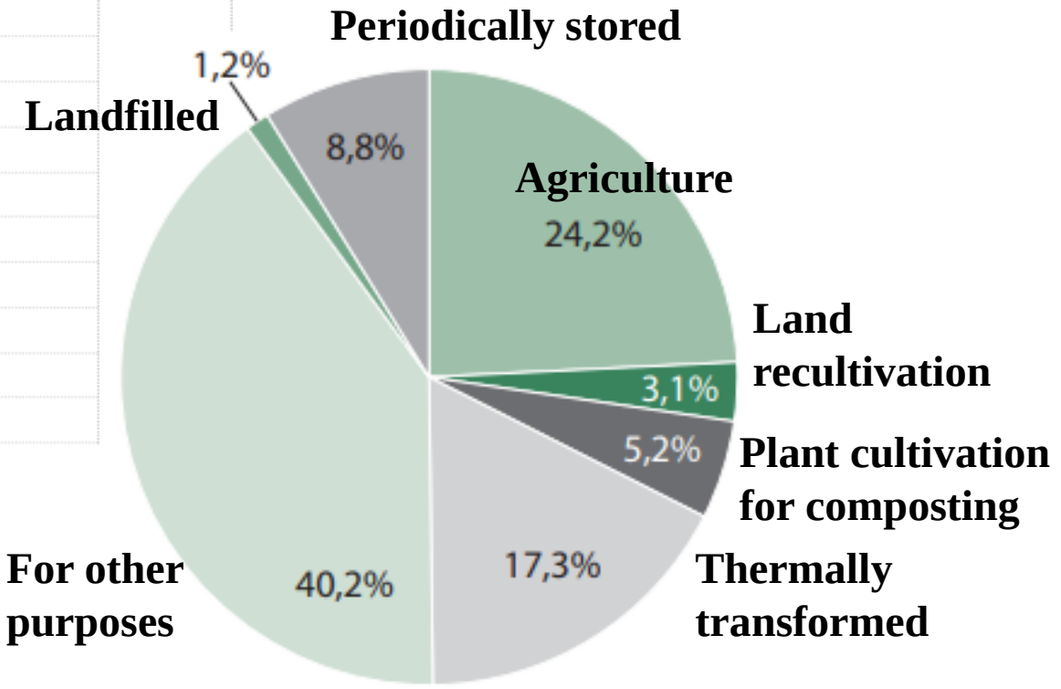
- Motivation
- Introduction
- Aim
- Material:
  - sewage sludge
- Methods:
  - HTC in 1, 4 and 200 L batch stirred reactors
  - hydrochar and post-processing liquid analyses
- Results
- Conclusions

MOTIVATION

Sewage sludge production and disposal from urban wastewater (db)*,**

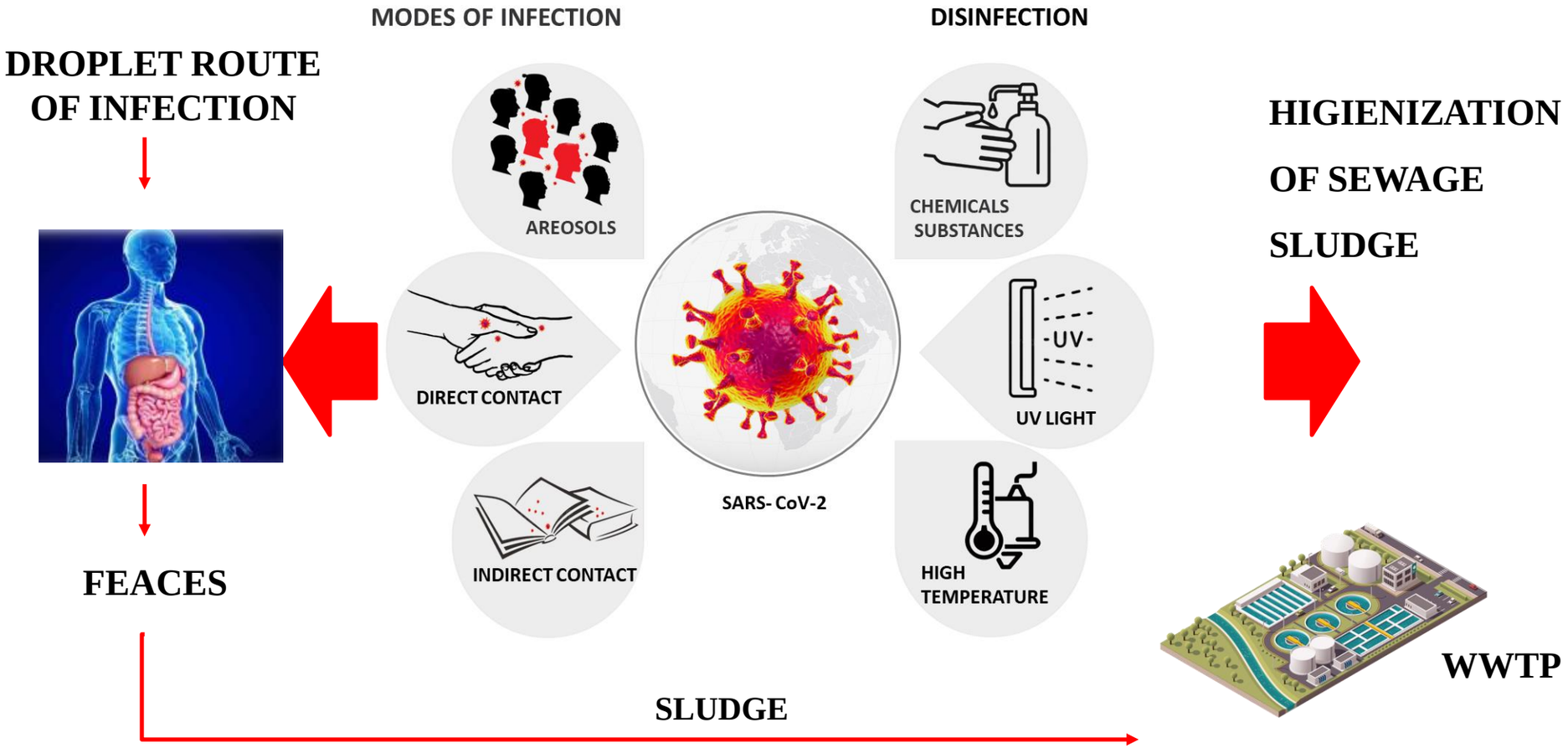


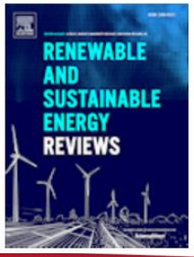
*EUROSTATE 2020



**STATISTICS POLAND 2020

SEWAGE SLUGE as POTENTIAL RISK of SARS-COV-2

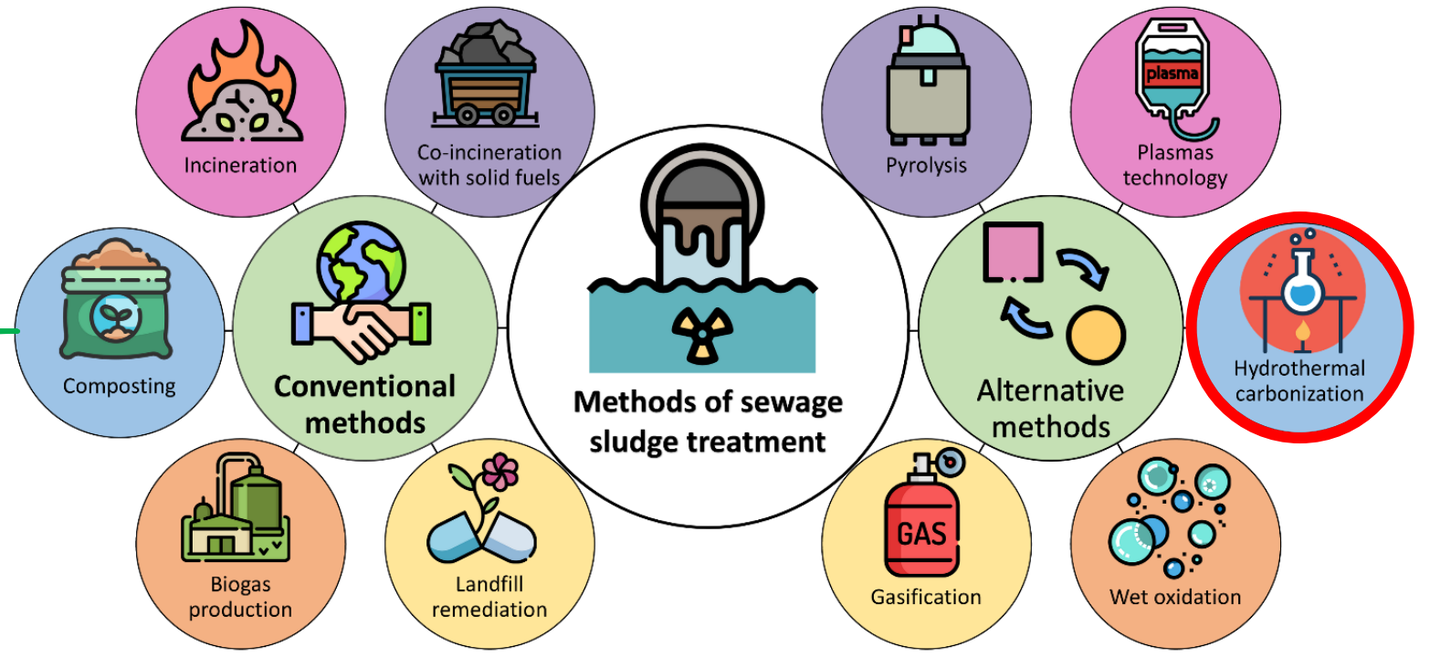




Czerwińska K.. Śliz M.. Wilk M. Hydrothermal carbonization process: Fundamentals. main parameter characteristics and possible applications including an effective method of SARS-CoV-2 mitigation in sewage sludge. A review. Renewable and Sustainable Energy Reviews 154 (2022) 111873

UNFAVOURABLE PROPERTIES of SEWAGE SLUDGE

- High content of moisture
- Insufficient dewaterability
- After mechanical dewatering dry mass c.a. 20%
- Organic content - biodegradable
- Bacteria. viruses. pathogens
- Pharmaceuticals
- Microplastics
- Heavy metals
- Odour
- High volume of waste
- Frequently disposed in landfill



THE AIM

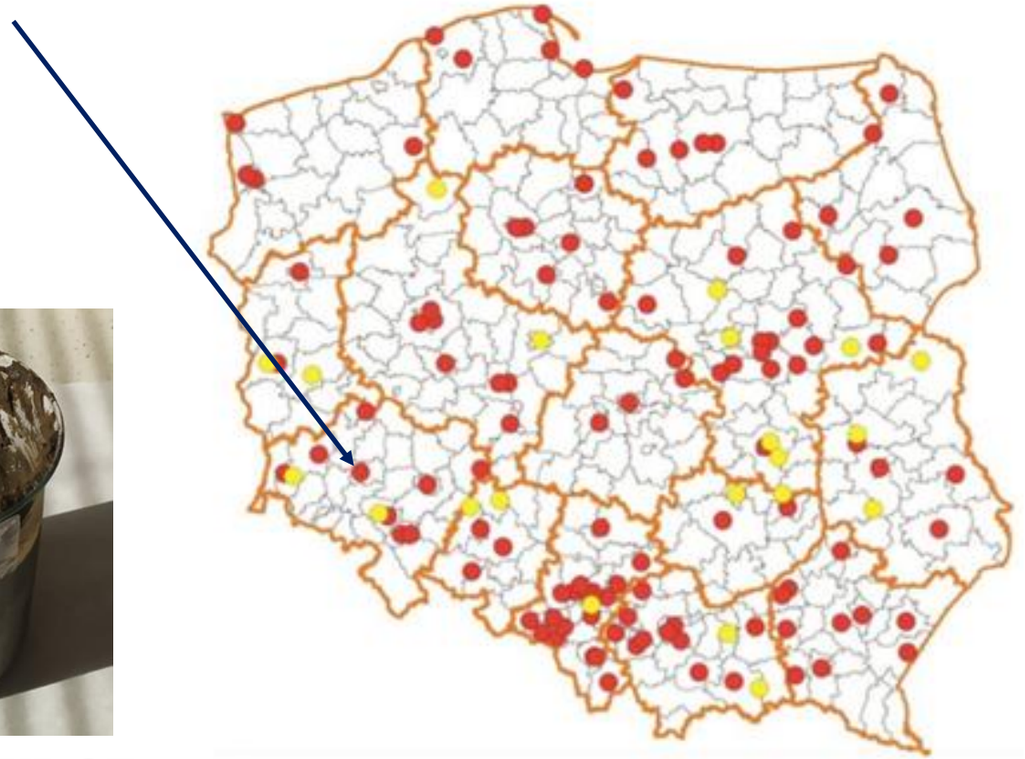
- **Upscale the reactor for hydrothermal carbonization proces of sewage sludge**
- **Compare the chemical and physical properties of HTC products derived from 1, 4 and 200 L volume of HTC reactors**
- **Confirm that chemical and physical properties of HTC products are similar**

MATERIAL (SEPTEMBER 2022)

Wastewater Treatment Plant in Lubin, Poland

OPEN DIGESTION CHAMBERS

SEWAGE SLUDGE



OPTIMAL CONDITIONS

Stabilization of sewage sludge	Organic matter content (o.m.c.) %
bad	> 65
poor	65 – 60
good	60-55
very good	55

Strategy for sewage sludge management for 2018-2022
Ministry of the Environment, Poland 2018

1 L Zipperclave Stirred Reactor
Parker Autoclave Engineers

Sample	Ash content** %	Organic matter content (o.m.c.) %
SS	35.56	64.44
HTC 200_2h_1 L*	36.58	63.42
HTC 220_2h_1 L*	39.96	60.04
HTC 210_2h_1 L	**51.38**	**48.62**
HTC 210_3h_1 L	55.33	44.67
HTC 220_2h_1 L	55.78	44.22

*December 2021
**EN ISO 18122:2016

PROCESS PARAMETERS

DEWATERED SEWAGE SLUDGE From OPEN DIGESTION CHAMBER

~ 85 % moisture

HYDROTHERMAL CARBONIZATION

210 °C, 2h, 150 prm

Water vapour pressure

Aqueous environment

HYDROCHAR

~2-15 %

POST-PROCESSING LIQUID

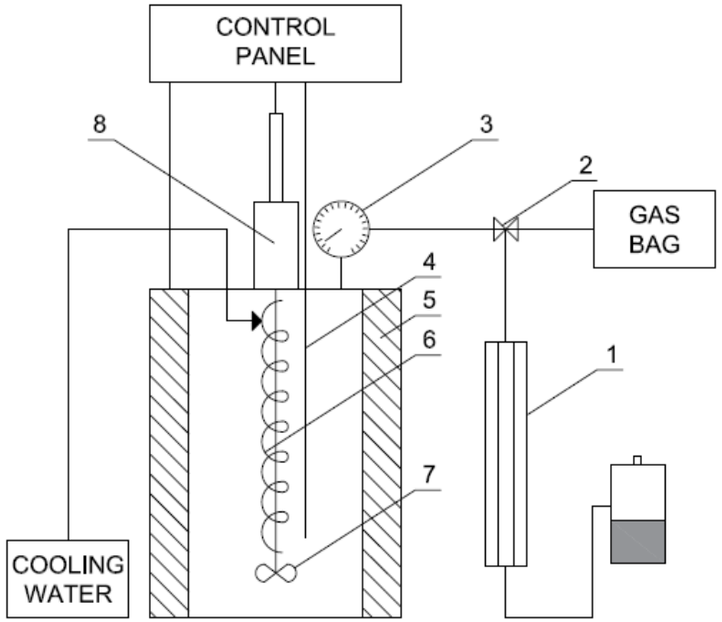
~90-85 %

GAS

~1 %

BATCH STIRRED REACTORS

1 and 4 L



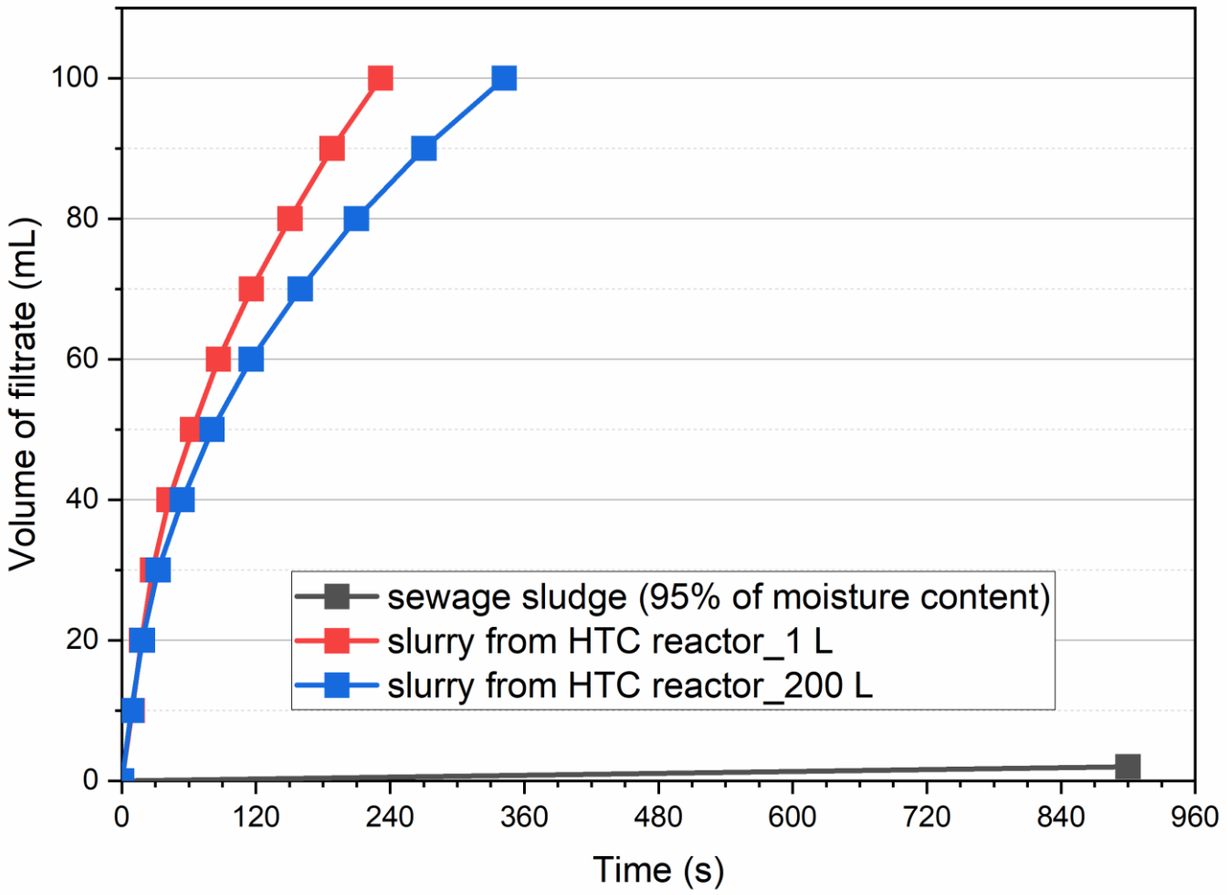
Parker Autoclave Engineers, USA

200 L

UiK Ltd. Żory, Poland

DEWATERING

sedimentation



Vaccum filtration process:

- Volume of slurry: 150 mL

I step:

- Fitration under pressure: 4 bar
- Registered time of collected filtrate: every 10 mL

II step:

- Filtration under pressure: 16 bar at 100 mL of collected filtrate

Total volume of filtrate: 130 mL
Total time: 6 min 25 s
Filtration cake: 35.4% d.m.

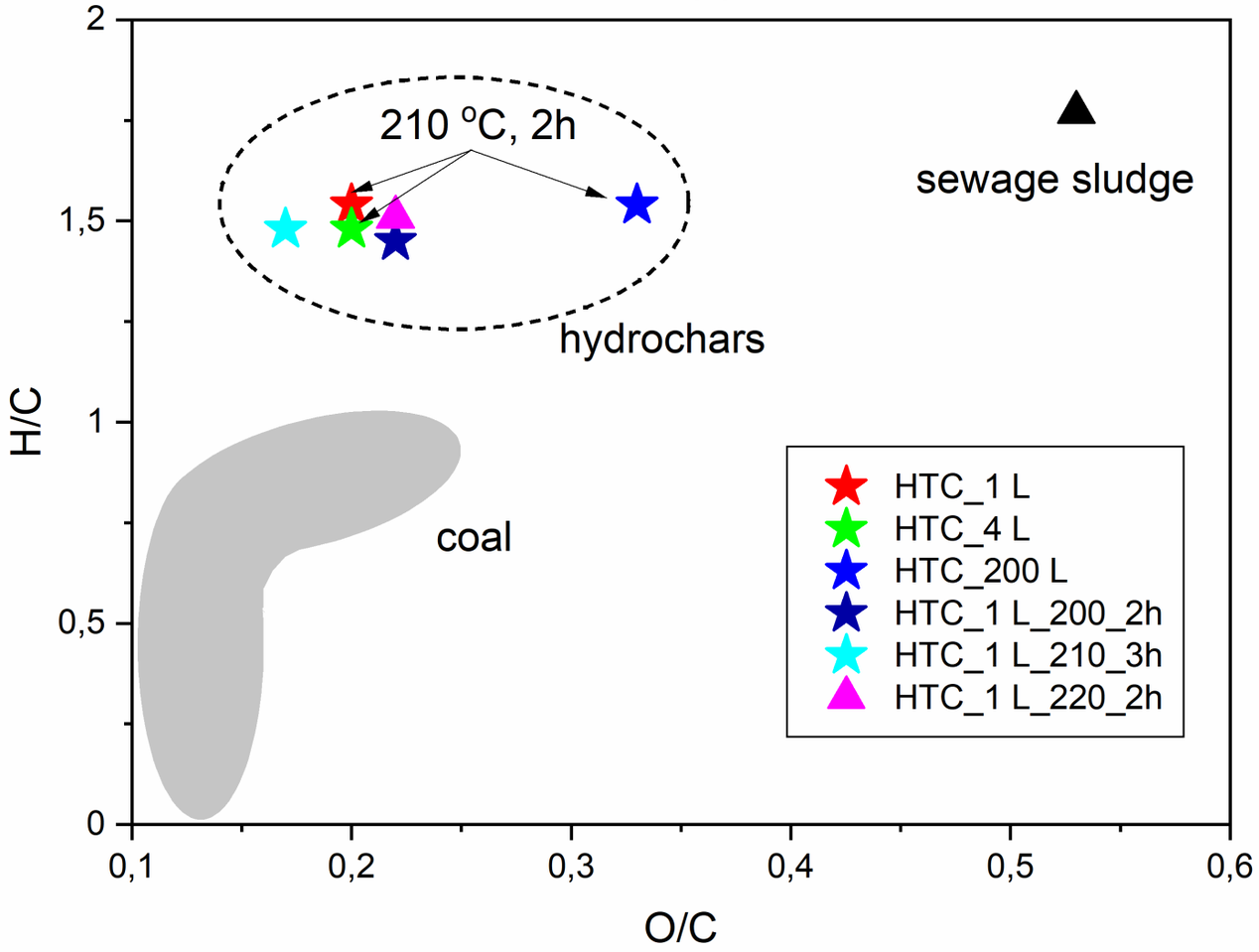
ANALYTICAL METHODS for SOLID SAMPLES

Type of analysis	Norm/method	Instrument
Ultimate analysis	PKN–ISO/TS 12902:2007	Elemental Analyser Truespec CHNS 628 Leco, USA
Moisture content	EN ISO 18134– 2:2017	Universal oven UN75plus, Memmert, Germany
Ash content	EN ISO 18122:2016	Muffle furnace FCF 22SHM CZYLOK Ltd., Poland
Volatile matter content	EN ISO 18123:2016	Muffle furnace FCF 22SHM CZYLOK Ltd., Poland
Higher heating value	PN-ISO 1928:2002	Leco AC500 isoperibolic calorimeter, USA
Thermal analysis (TGA)	Air environment, heating rate 10 K/min	Mettler Toledo Analyzer STAR W 16.10, Switzerland
Fourier Transformation Infrared Spectroscopy (FTIR)	range 400 – 4000 cm^{-1}	Bruker spectroscope, USA
Specific Surface Area (SSA)	BET (Brunauer-Emmett-Teller) multipoint adsorption	ASAP 2010 apparatus, Micromeritics Inst.

PHYSICAL and CHEMICAL PROPERTIES

Sample	Proximate analysis				Ultimate analysis					Energy parameters	
	FC %	Ash %	O.M.C. %	VM %	C %	H %	N %	S %	O %	HHV MJ/kg	LHV MJ/kg
SS	9.10	34.92	**65.08**	55.98	31.59	4.67	5.09	1.45	22.27	13.61	12.59
HTC_1 L	8.49	51.38	**48.62**	40.13	31.83	4.09	3.22	1.01	8.48	13.67	12.78
HTC_4 L	5.42	54.85	**45.15**	39.73	28.97	3.65	2.43	0.83	8.18	12.35	11.56
HTC_200 L	8.10	45.77	**54.23**	46.13	31.83	4.09	3.22	1.01	14.09	14.07	13.08

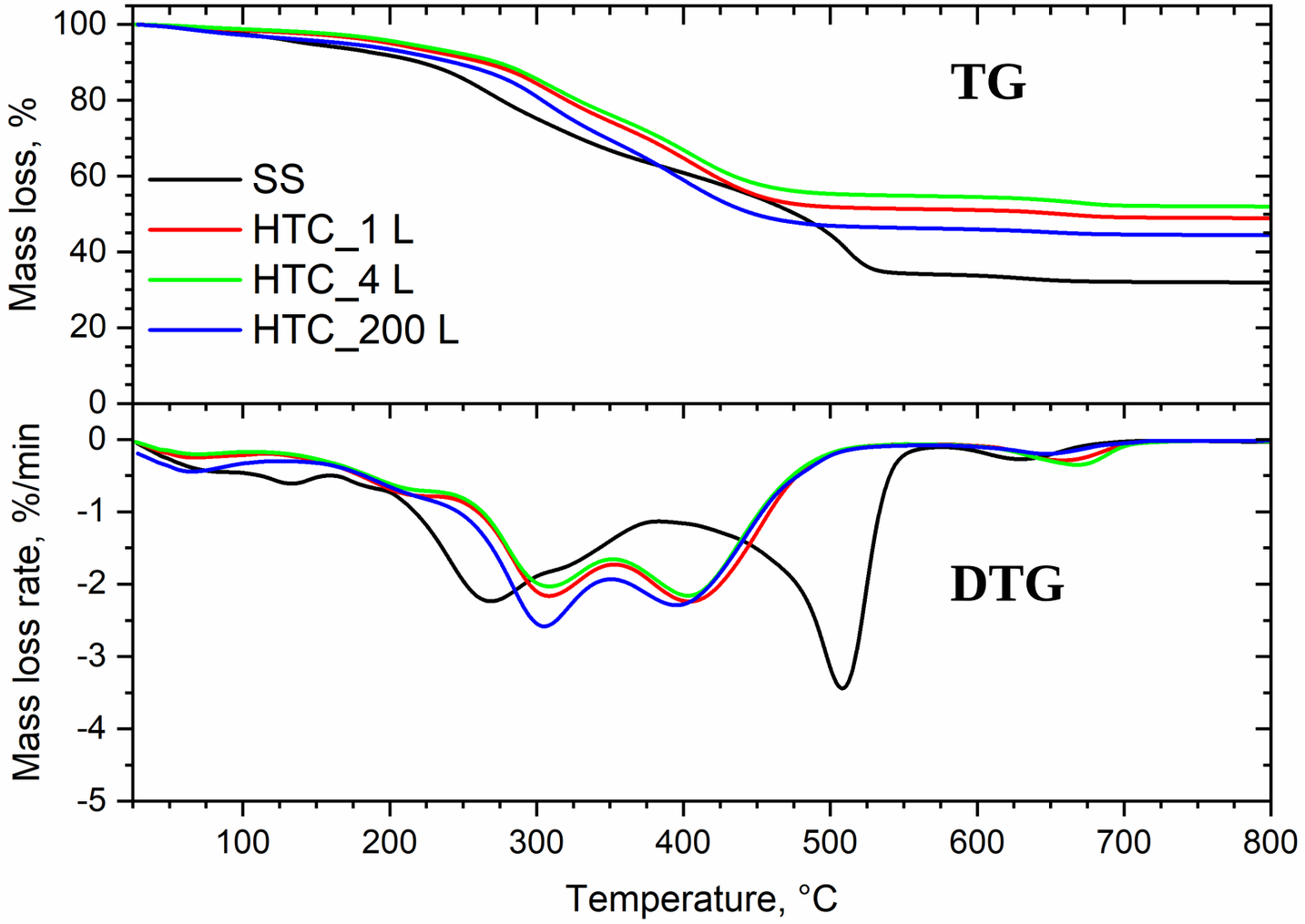
VAN KREVELEN DIAGRAM for SEWAGE SLUDGE and HYDROCHARS



energies

Wilk. M., Gajek. M., Śliz. M, Czerwińska. K., Lombardi L. Hydrothermal Carbonization Process of Digestate from Sewage Sludge: Chemical and Physical Properties of Hydrochar in Terms of Energy Application. Energies 15 ***(2022)*** *6499*

THERMAL ANALYSIS



XRF ANALYSIS

Compounds, %	SS	HTC_1 L	HTC_4 L	HTC_200 L
Na_2O	0.71	0.37	0.40	0.42
MgO	4.47	4.75	4.68	4.51
Al_2O_3	5.29	5.77	5.89	9.34
SiO_2	20.10	18.34	19.80	19.64
P_2O_5	**27.47**	**27.44**	**27.01**	**26.91**
SO_3	3.53	2.71	2.66	2.47
Cl	0.10	0.73	0.06	0.03
K_2O	1.86	1.02	1.03	1.12
CaO	20.60	22.06	21.36	18.67
Fe_2O_3	13.56	15.00	14.67	14.43
ZnO	0.30	0.35	0.34	0.39
PbO	0.04	0.04	0.04	0.03
Cr_2O_3	0.053	0.04	0.05	0.04
NiO	0.01	0.01	0.02	0.02
CuO	0.14	0.14	0.14	0.15

Slagging index

$$R_S = R_{B/A} \cdot S^d$$

Fouling index

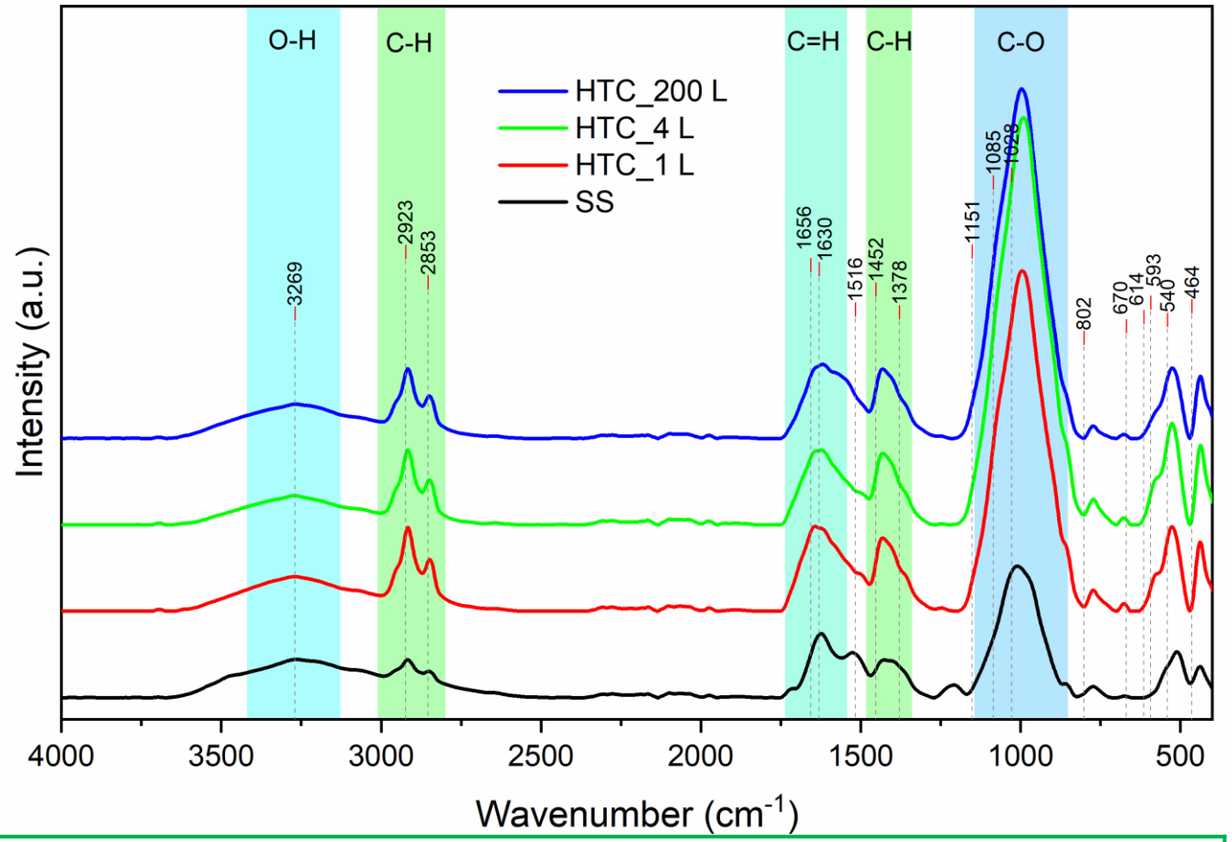
$$F_u = R_{B/A} \cdot (Na_2O + K_2O)$$

Indices	R_S slagging	Risk	F_u fouling	Risk
SS	3.92	Extremely high	6.95	High
HTC_1 L	2.29	High	4.07	High
HTC_4 L	2.23	High	3.85	High
HTC_200 L	2.51	High	3.51	High

R_s < 0.6 low slagging
R_s = 0.6–2.0 medium
R_s = 2.0 – 2.6 high
R_s > 2.6 extremely high

$F_u \leq 0.6$ low tendency
$0.6 < F_u \leq 40$ high
$F_u > 40$ extremely high

FTIR ANALYSIS



Sorptive analysis

	SS	HTC_1 L	HTC_4 L	HTC_200 L
Specific Surface Area m^2/g	1.06	10.48	13.04	25.00

METHODS for LIQUID SAMPLES

Type of analysis	Norm/method	Instrument
pH and conductivity	-	Multifunction Laboratory Meter CX-505 ELMETRON
Ultimate analysis	PKN-ISO/TS 12902:2007/ combustion in oxygen 950 ºC	Elemental Analyser Truespec Leco CHNS628
Heavy Metals (Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn) Alkali metals (Na) Alkali earth metals (Ca, Mg) Nonmetal (P)	Programmed methods of all Spectroquant® cell and reagent tests, additional user defined methods: 99 concentration mode, 20 kinetic mode, 20 wavelength scans	Prove 100 Spectrophotometer VI 1 UNIT VIS.BR wavelength range 320-1100 nm, Spectral bandwidth 4nm Spectroquant

CHARACTERISTICS of HTC POST-PROCESSING LIQUIDS

Parameters	Filtrate HTC_1 L	Filtrate HTC_4 L	Filtrate HTC_ 200 L
COD, mg/L	**30,340**	**28,010**	**29,000**
Phenol	101.00	95.75	
PO_4-P, mg/L	480	380	
PO_4^{3-}, mg/L	1,460	1,170	
P_2O_5, mg/L	1,090	880	
NH_4^+, mg/L	1150	1,500	
Mg, mg/L	315	----	
Ca [mg/l]	47.5	25	
TOC, mg/L	12,800	11,200	
Cl free, mg/L	31.5	30.8	
Cl total, mg/L	36.5	36.5	
N total, mg/L	2125	2625	
pH	7.01	7.82	
Conductivity, mS/cm	7.47	8.69	

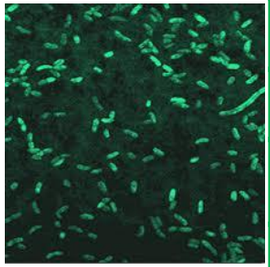
CHEMICAL and PHYSICAL PROPERTIES of POST-PROCESSING LIQUIDS

	pH	Conduc-tivity mS/cm	COD mg/L	Phenol mg/L	PO_4-P mg/L	PO_4^{3-} mg/L	P2O5 mg/L	NH_4^+ mg/L	Mg mg/L	Ca mg/L	TOC mg/L	Cl free mg/L	Cl total mg/L	N mg/L
Filtrate HTC_1 L	7.01	7.470	**30,340**	101.00	480.0	1460.0	1090.0	1150.0	315.0	47.5	**12,800**	31.50	35.50	2,125
Cycle	**Wash water properties from washed hydrochar**													
I	7.24	1.278	4,390	24.00	110.0	340.0	255.0	135.0	34.1	18.0	7,000	2.64	2.64	65
II	7.22	0.273	**1,075**	9.00	31.8	97.2	72.6	26.3	14.3	23.0	-	1.15	1.18	79
III	7.04	0.098	382	3.61	19.3	59.2	44.2	7.0	6.3	17.0	-	0.76	0.77	21
IV	6.97	0.059	228	2.38	11.6	35.6	26.6	2.4	8.8	17.0	-	0.64	0.69	11
V	6.88	0.047	146	1.58	7.5	22.9	17.1	<2.0	6.9	16.0	-	0.51	0.71	<10

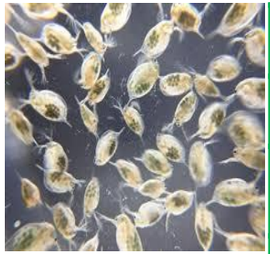
TOXICITY TEST of HYDROCHARS

Toxicity effect, %	Toxicity level
< 25.00	Non toxic
25.01 – 50.00	Low toxic
50.01 – 75.00	Toxic
> 75.00	High toxic

Lemna minor – aqueous plant; OECD Guideline 221			
HTC_1 L	washed	HTC_4 L	washed
exposition			
7 days			
58.33 toxic	50.00 low toxic	75.00 toxic	41.67 low toxic

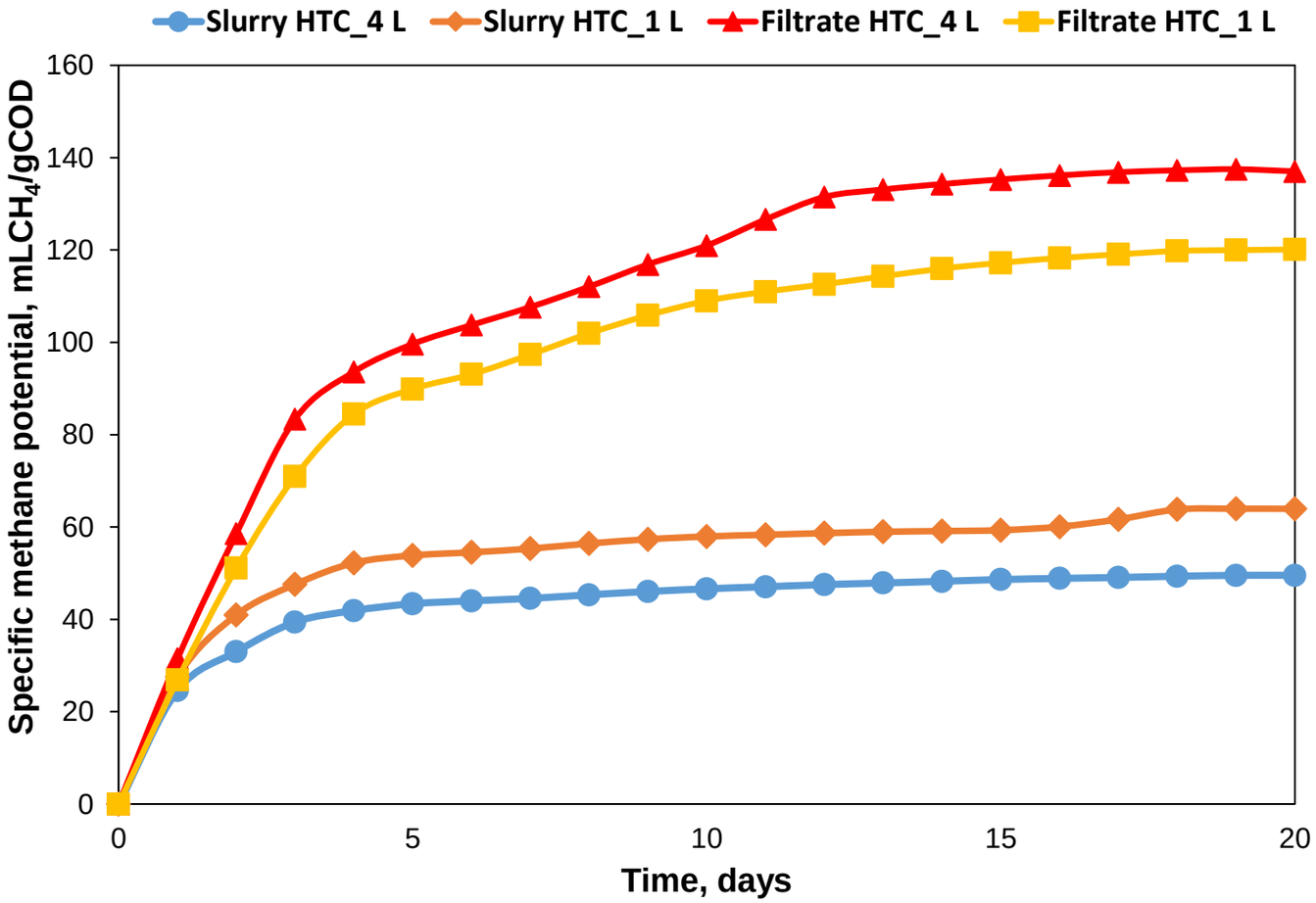


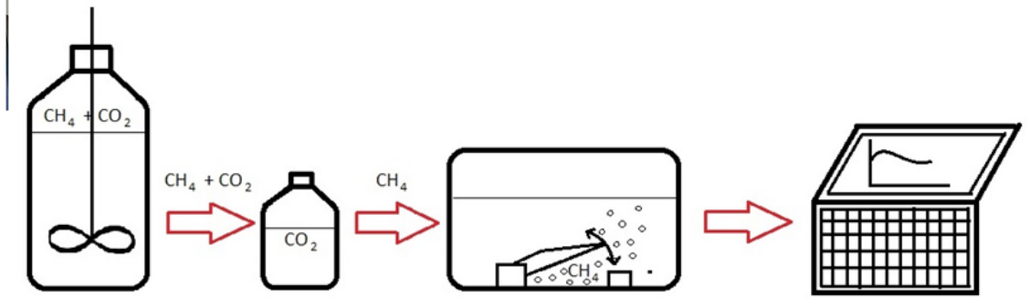
***Allivibrio fischeri – bacteria* (Micrtox®); ASTM D-5560**							
HTC_1 L		washed		HTC_4 L		washed	
exposition							
5 min	15 min	5 min	15 min	5 min	15 min	5 min	15 min
78.84 high toxic	75.98 high toxic	70.51 toxic	73.38 toxic	74.74 high toxic	75.10 high toxic	48.82 toxic	52.84 toxic



Daphnia magna – shellfish; OECD Guideline 202 i ISO 6341:2012							
HTC_1 L		washed		HTC_4 L		washed	
exposition							
5 min	15 min	5 min	15 min	5 min	15 min	5 min	15 min
75 high toxic	80 high toxic	70 toxic	75 toxic	75 high toxic	80 high toxic	50 toxic	50 toxic

METHANE POTENTIAL TEST





Automatic Methane Potential Test System Bioprocess Control

	Total COD mg/L	Methane potential $mLCH_4/g$ COD
Slurry HTC_4 L	26,900	49.6
Slurry HTC_1 L	86,000	64
Filtrate HTC_4 L	62,000	137
Filtrate HTC_1 L	32,700	120.1

CONCLUSIONS

- **Hydrochars derived at 200 °C and 2h in 1, 4 and 200 L volume of reactors have quite similar chemical and physical properties**

- Combustion properties are comparable
- Weak sorpitve properties
- The same ash composition indicating high slagging and fouling risks
- Low toxic level found for washed hydrochar for aqueous plant

- **Post-processing liquid**

- COD is at the similar level indicating high toxicity
- BMP for filtrate has shorter retention time

The upscaling was successful giving similar properties for HTC solid and liquid products.

THANK YOU FOR YOUR ATTENTION

Acknowledgements

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