WET OXIDATION TO TREAT HTL WASTEWATER

Patrick Biller, Guido Ceragioli , Lars Thomsen, Leendert Vergeynst, Williane Vieira Macêdo ,
Alastair James Ward, Konstantinos Anastasakis , Giulia Zoppi, Carolin Schuck

WET WASTES

Manure

1.4 b t EU

Wastewater sludge

12 m t EU

Food waste

60 m t EU

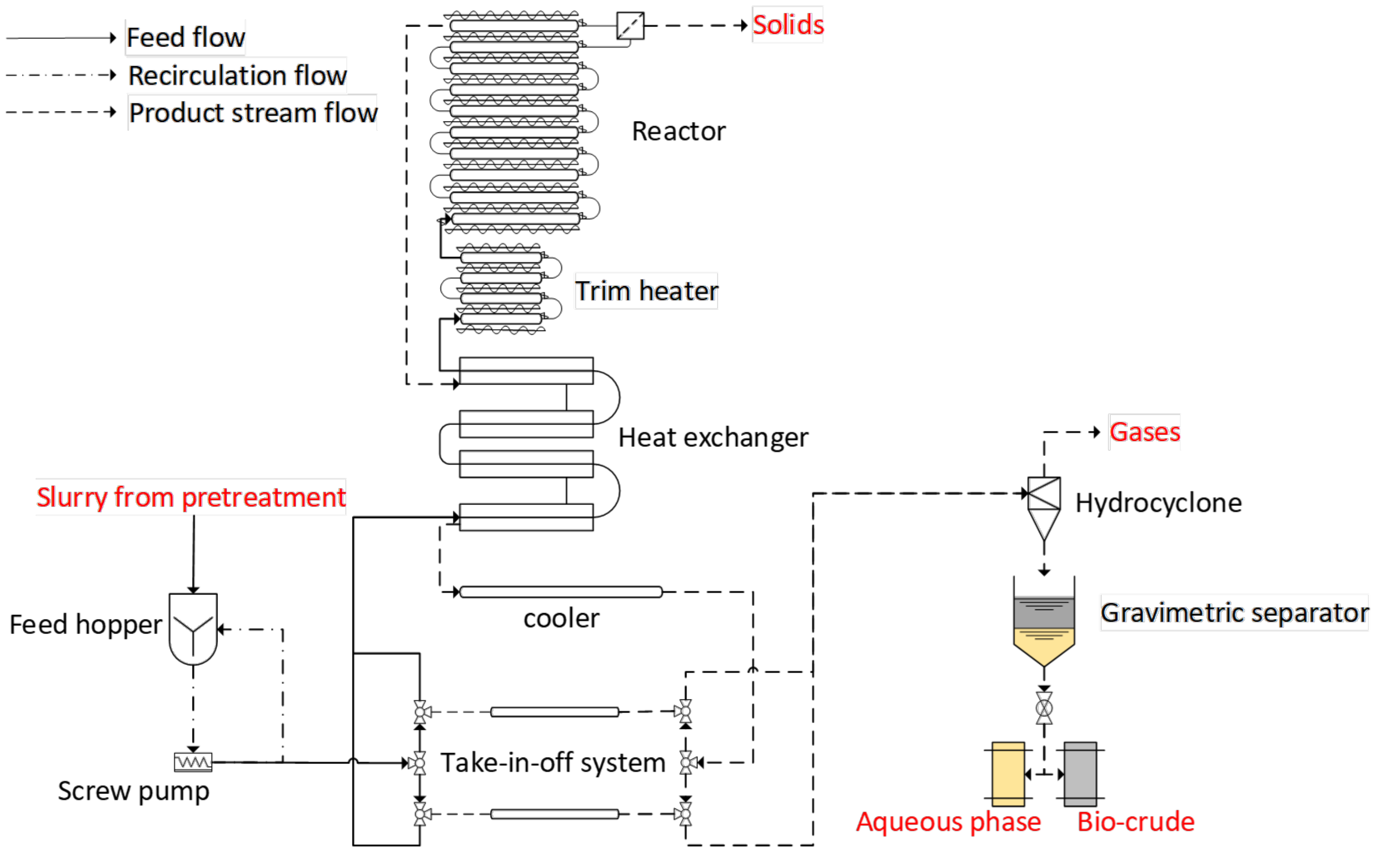
Digestate from AD

190m t EU

Commonality:

- High availability
- Less feedstock competition
- High water content
- High inorganic content
- High P content
- High N content
- Presence of micropollutants etc
- Presence of heavy metals

HTL PILOT PLANT



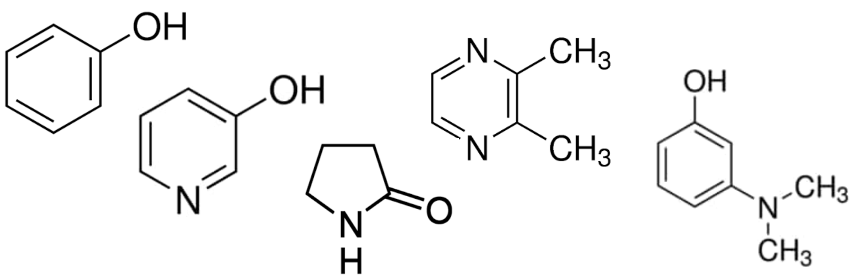
- 65 L/h slurry flow rate
- 3 kg/h bio-crude production
- Subcritical region (300-350°C)
- Heat exchange >75%
- EROI ~3

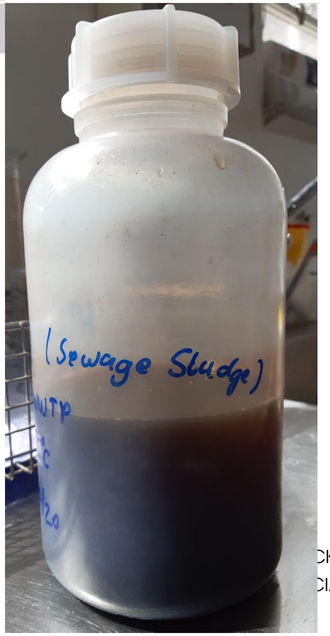
HTL WASTEWATER

What to do with the water?

Temperature	PO4	NH4+	TOC	COD
300°C	4.3	372.5	20,000	50,833
325°C	2.3	635	15,700	42,250
350°C	7.6	720	20,200	51,850

Units mg/L





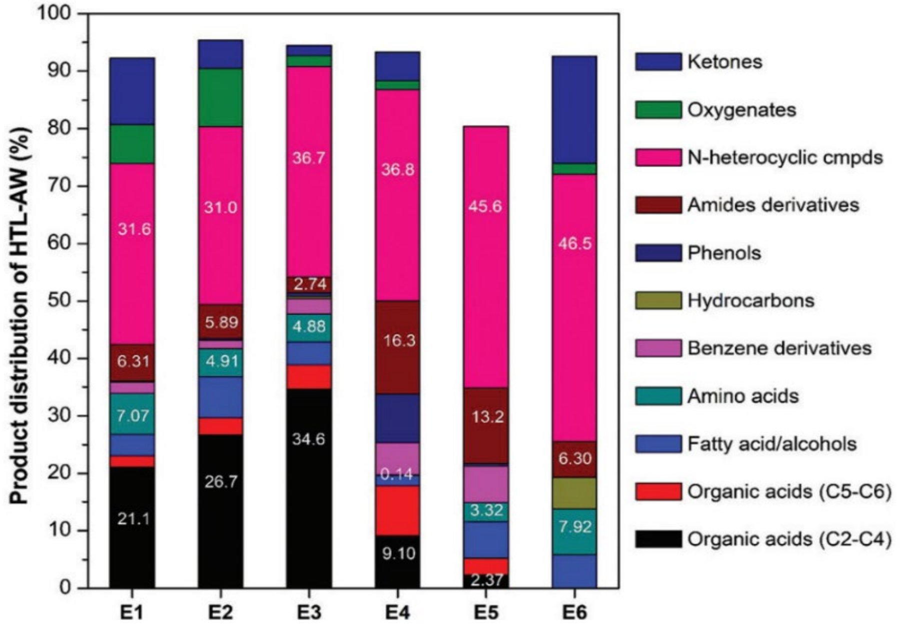


Figure 2 - Shows composition of organic compounds in the HTL wastewater, based on functional groups. E1-E4 shows composition of processed mixed wastewater algae. E5 and E6 are based on Spirulina as feedstock to the HTL under different process conditions (Gu et al., 2019)

Green Chem., 2019, 21, 2518–2543

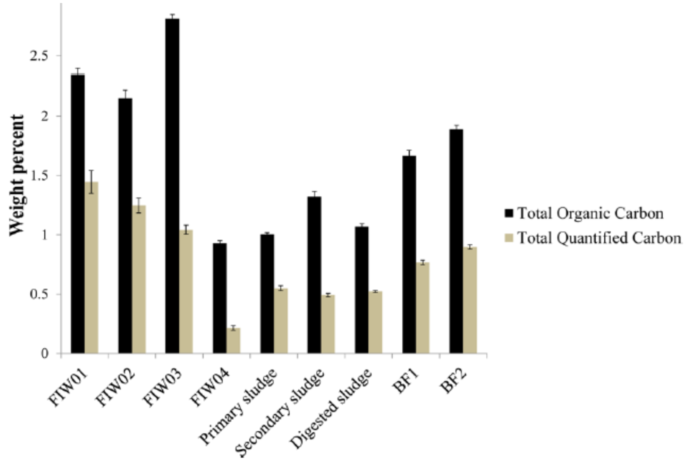


Figure 6. Total organic carbon and quantified carbon of the aqueous byproducts generated from HTL of food industry waste, municipal waste, and biomass grown on wastes: BF1 biomass feedstock grown on corn stover lignin residue; BF2 biomass feedstock grown on municipal waste.

DOI:10.1021/acssuschemeng.6b02367
ACS Sustainable Chem. Eng.2017, 5, 2205−22142208

CK BILLER
CIATE PROFESSOR

BIOLOGICAL TREATMENT

Results Anaerobic digestion:

- Straw+manure derived water showed no inhibition at 65% COD load
- Sludge derived water inhibition at 15% COD load
- Nitrogen aromatics in sludge water are higher and cause inhibition

Results WWTP:

No impact of heterotrophic bacteria

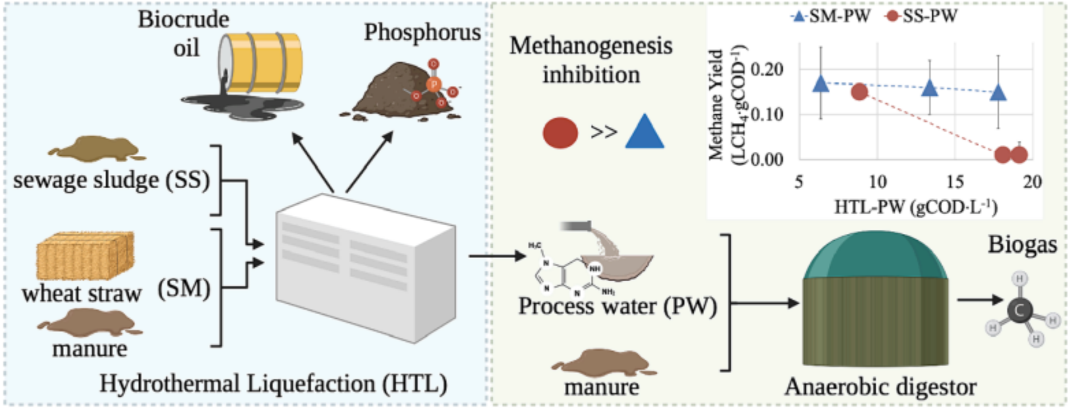
- >92% biodegradability of COD and organic N
- 45% higher denitrification rates with HTL-PW than with influent

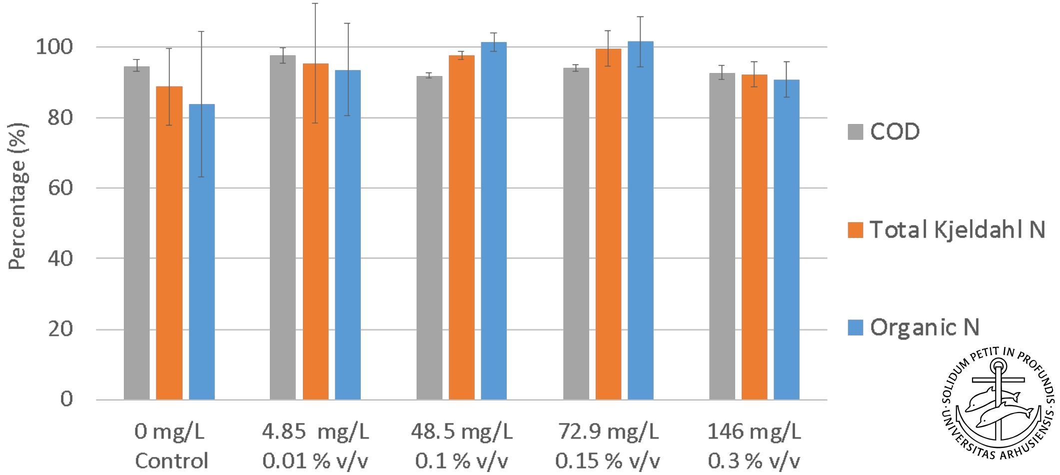
Nitrifying bacteria can deal with it

- 8% nitrification inhibition in worst case (shock-load)
- No nitrification inhibition in continuous reactors

BUT: Huge load on total inlet COD (~20%)

https://doi.org/10.1016/j.biortech.2024.130559





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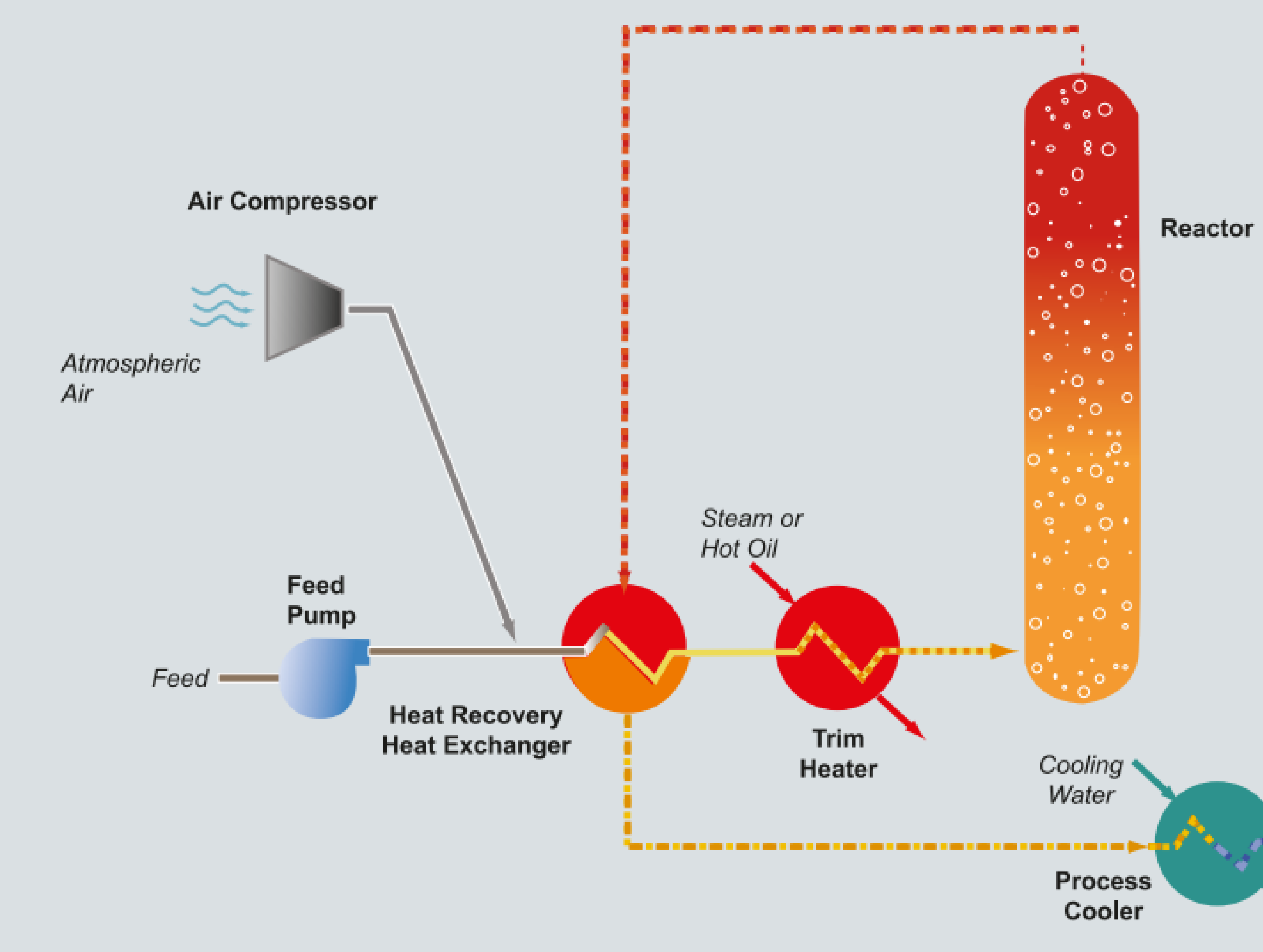
Investigations by Leendert Vergeynst (AU)

https://doi.org/10.1016/j.jenvman.2023.119046

WET AIR OXIDATION PROCESS

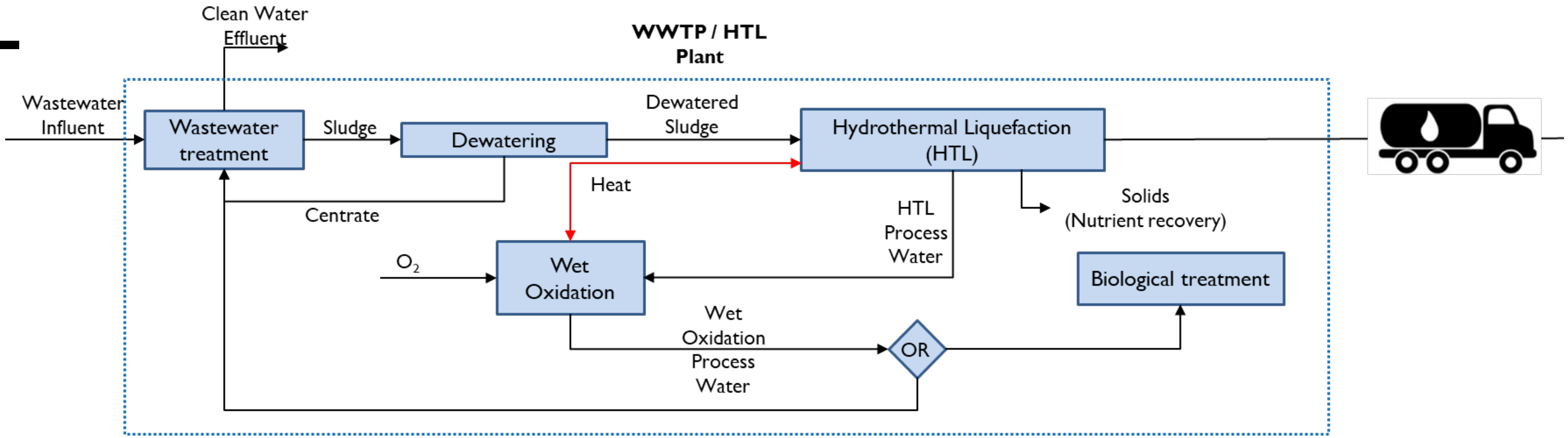


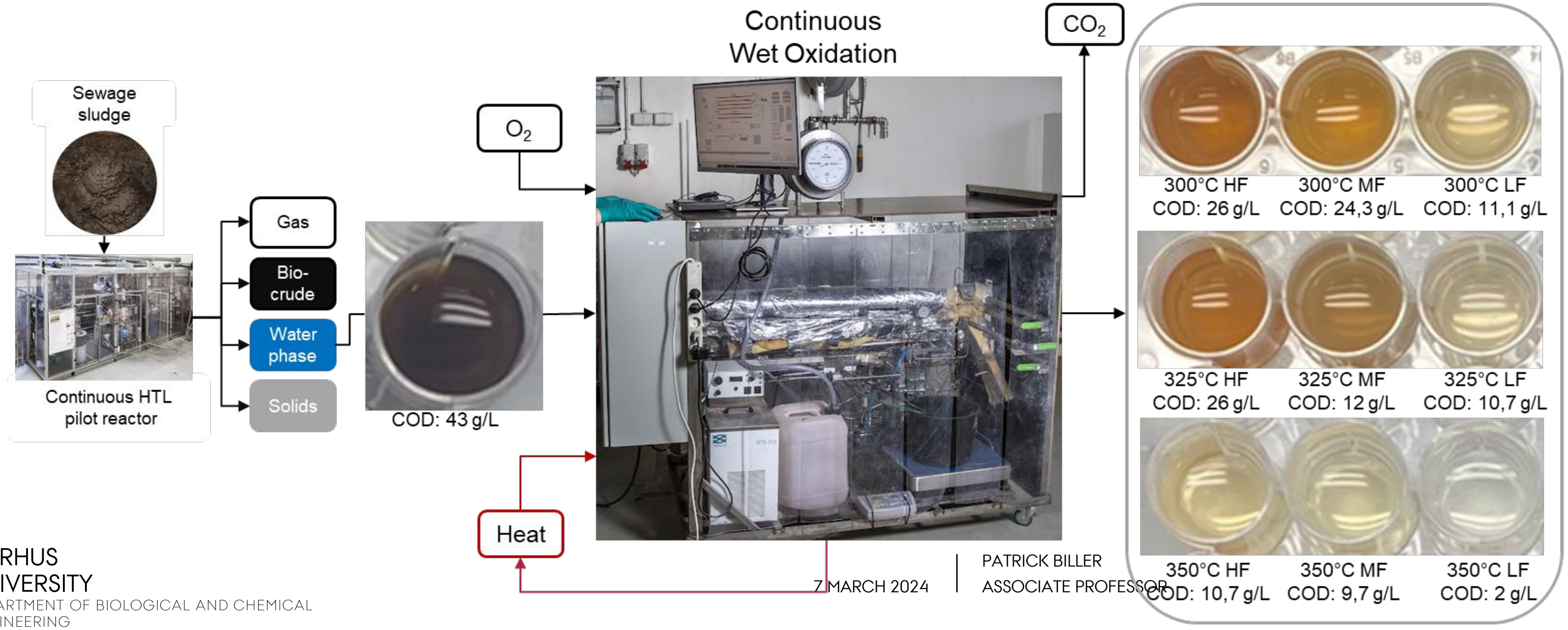
$$\text{Organics} + O_2 \rightarrow CO_2 + H_2O$$

$$\text{Organics} + O_2 \rightarrow \text{Acetic Acid} + O_2 \rightarrow CO_2 + H_2O$$

DOI: 10.5772/60935

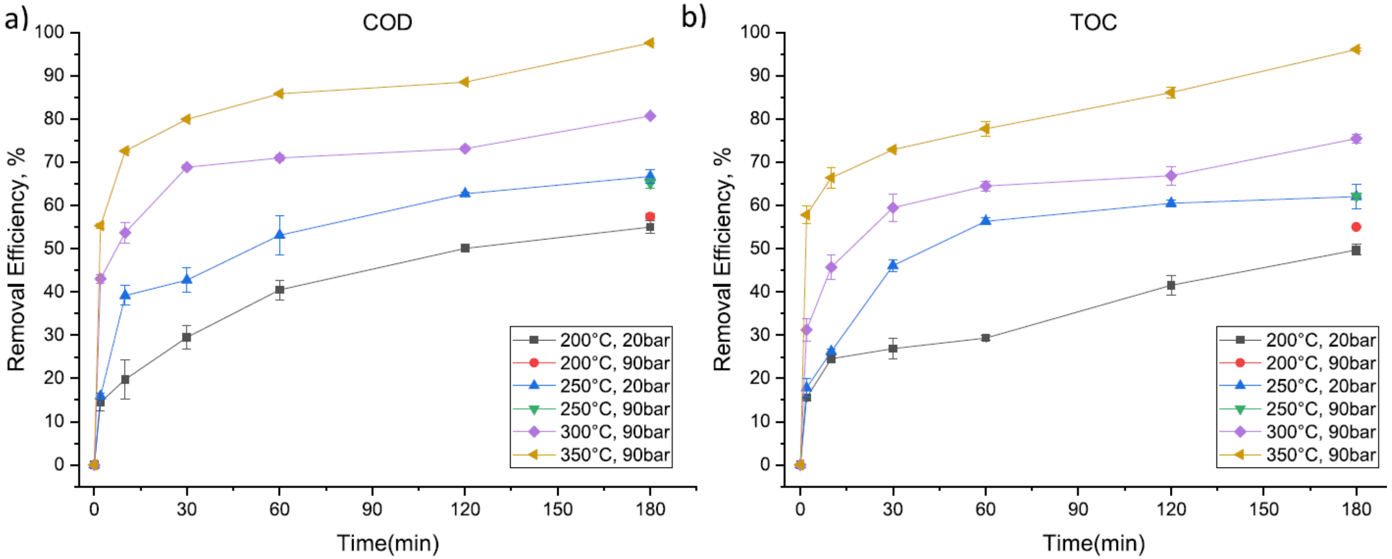
WET OXIDATION

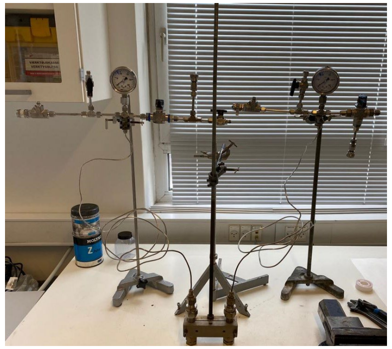




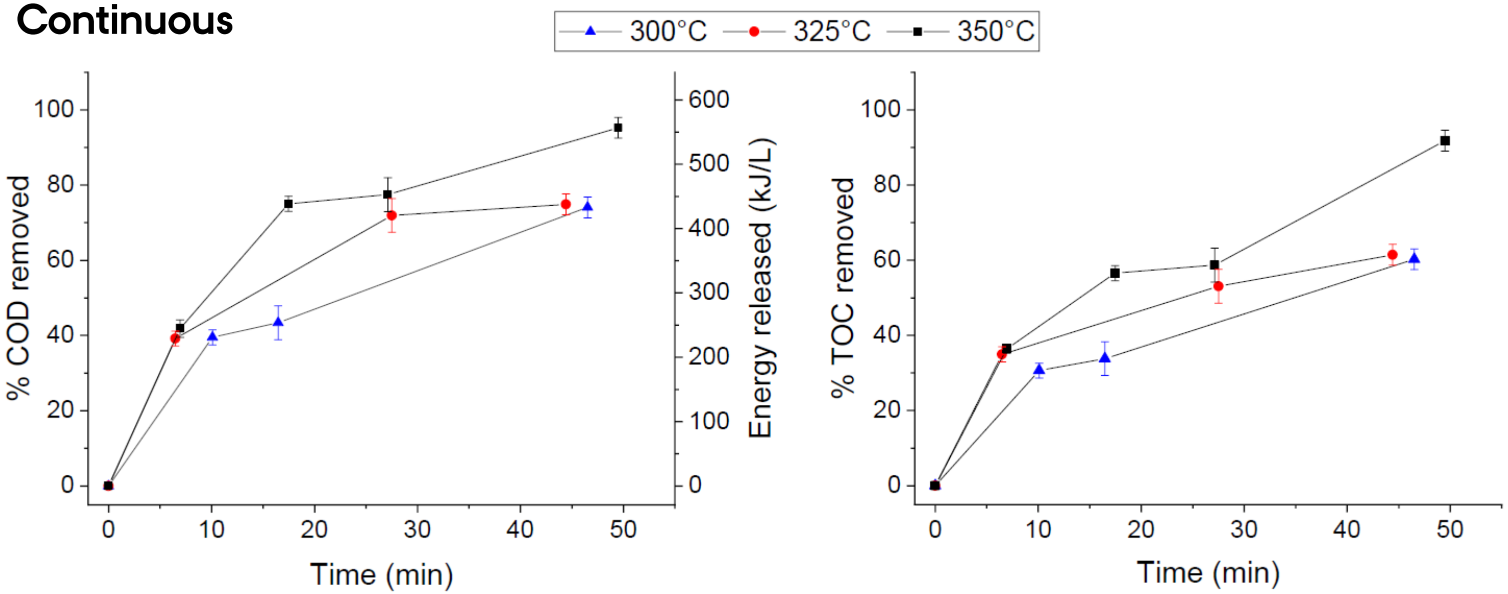
WO RESULTS

Batch





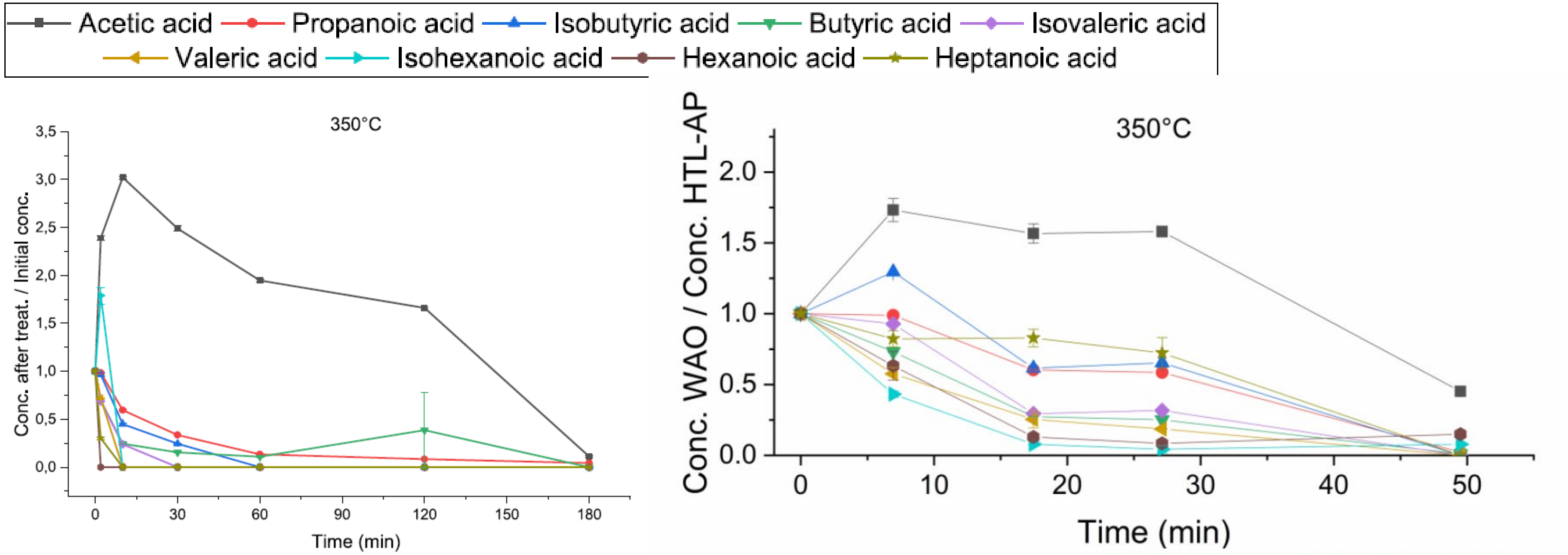
Continuous

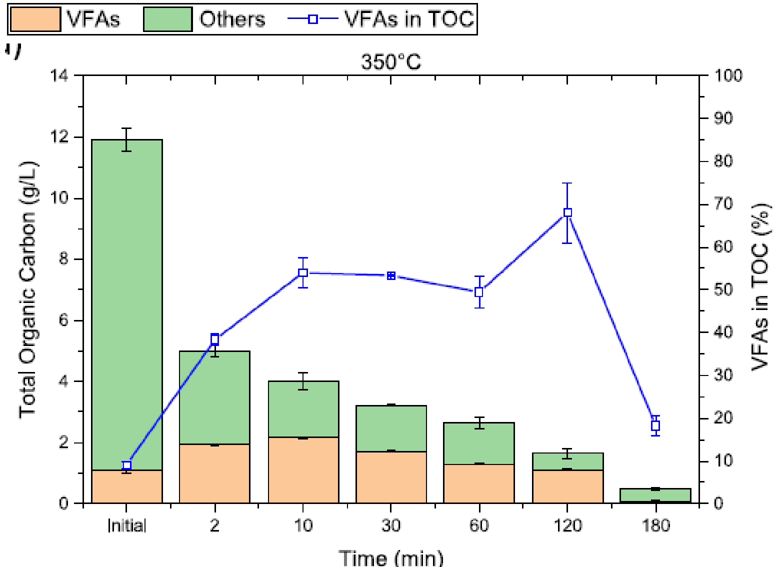


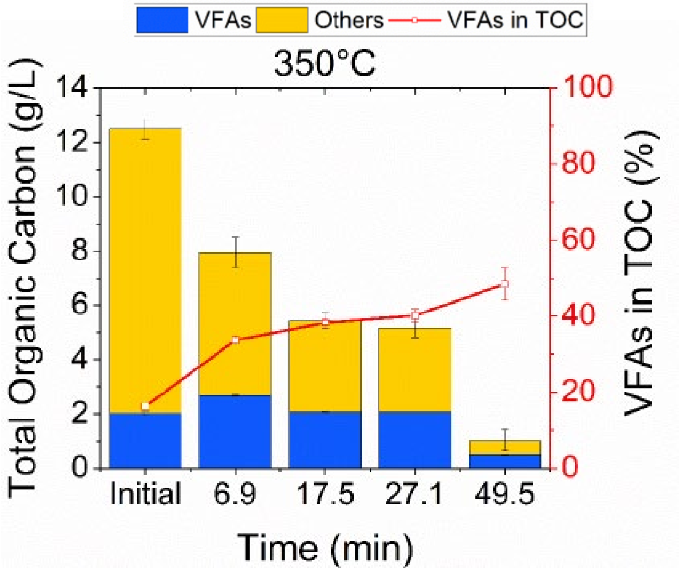
https://doi.org/10.1016/j.watres.2021.117863

VFA PRODUCTION

- Stopping the WO process at reasonable residence times is an option
- VFA share is highest
- Opens up possibilities of acetic acid recovery







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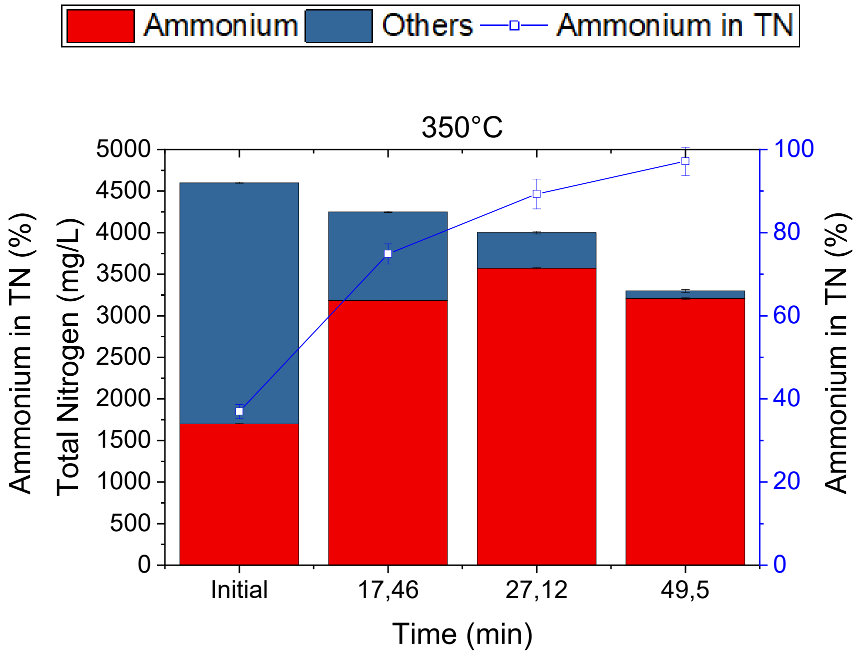
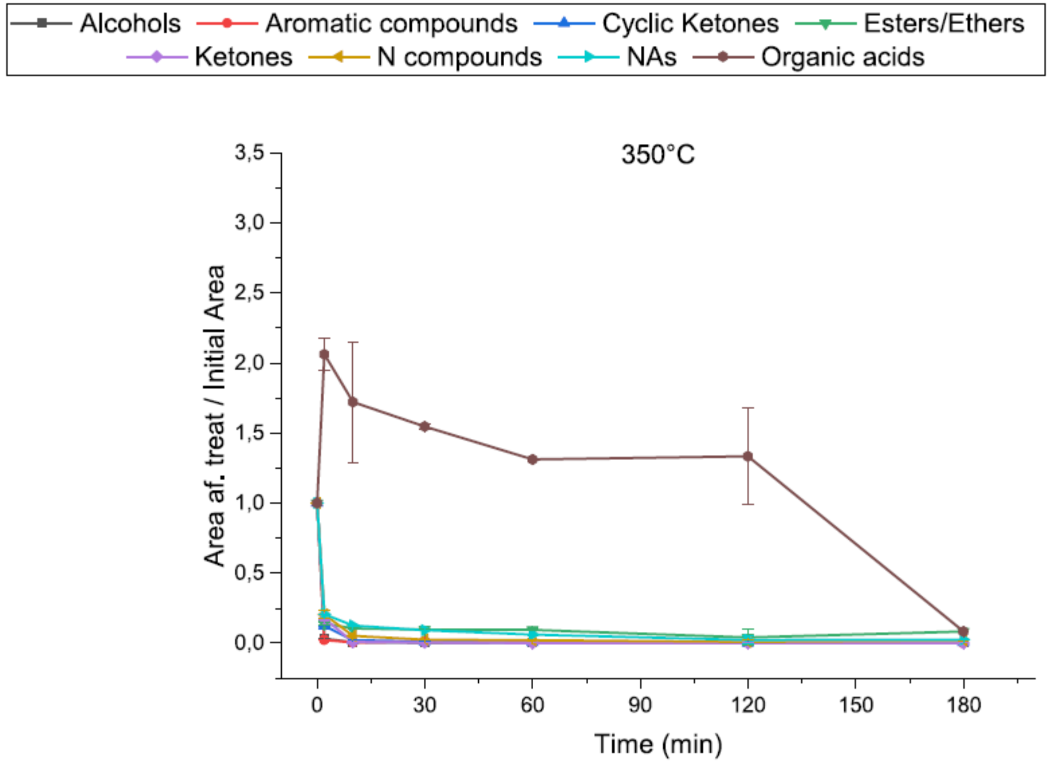
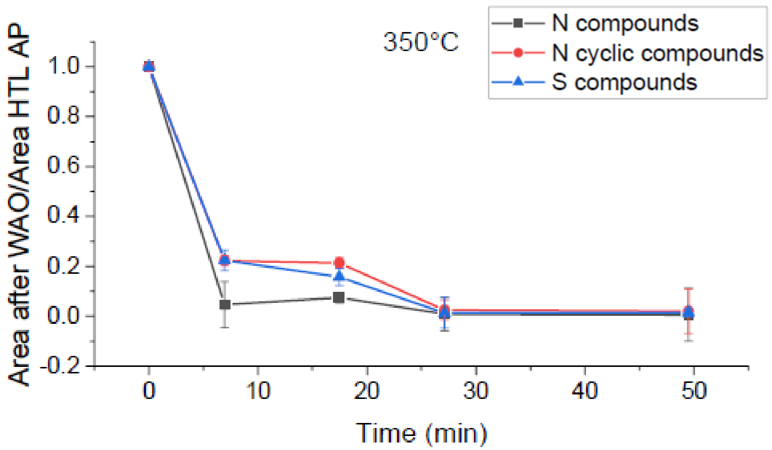
N IN WO

- GC-MS analysis shows fast and almost full degradation of most compound classes
- Organic-N compounds are efficiently converted to NH4
- Recovery of NH4 is attractive



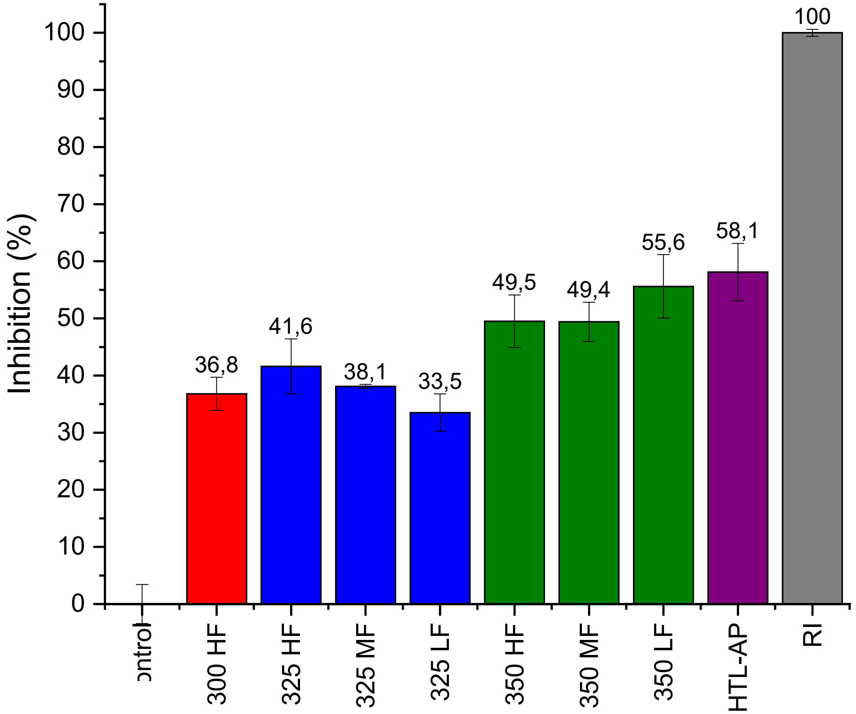




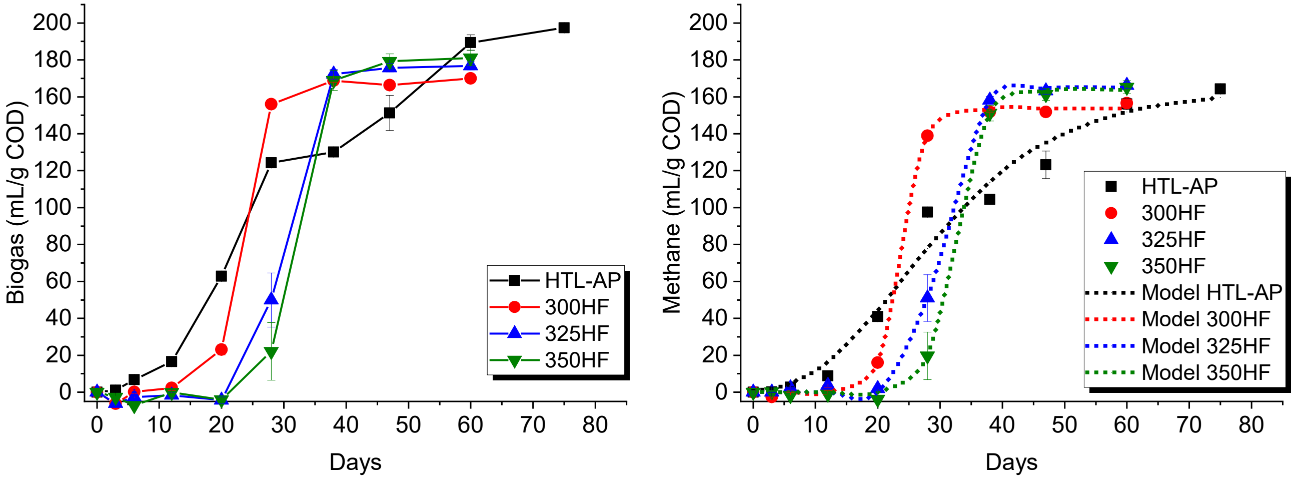
https://doi.org/10.1016/j.watres.2021.117863

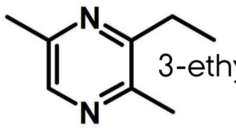
BIOLOGICAL TREATMENT OF WO WATER

- conversion of ammonia to N-NOx inhibition
- constant v/v dilution



Biomethane potential tests





3-ethyl-2,5-dimethyl-Pyrazine

Sample	B (mL CH_4/g COD)	Rmax (mL CH_4/g COD/day)	λ (day)	R^2
HTL	164	4.2724	9.7128	0.982121
300HF	154	21.9947	19.5267	0.999512
325HF	165	20.1613	25.4737	0.999693
350HF	164	19.6198	27.2293	0.999648

HR MS ANALYSIS

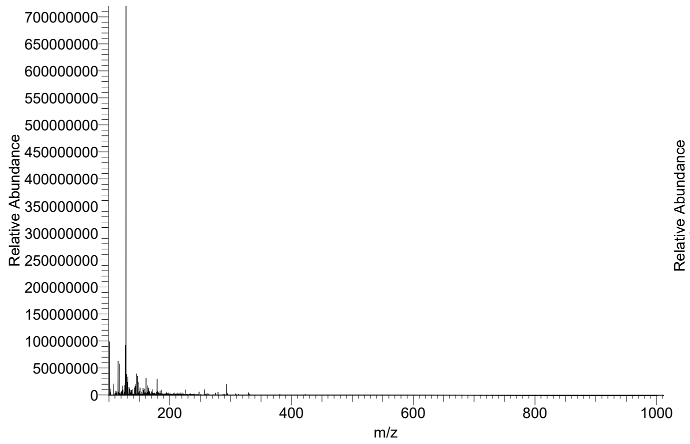
Analysis by:
Jhonattas de Carvalho Carregosa & Alberto Wisniewski Jr
(PEB), Department of Chemistry, Federal University of Sergipe, Brazil

	(–)-HESI		(+)-HESI	
Samples	Number of ions S/N>=3	% of ions reduction	Number of ions S/N>=3	% of ions reduction
HTL-AP	2254	-	2833	-
300-HF	1927	15	1517	46
300-MF	1553	31	1399	51
300-LF	1303	42	1174	59
325-HF	1827	19	1743	38
325-MF	1488	34	1575	44
325-LF	1420	37	1179	58
350-HF	1823	19	1849	35
350-MF1	1259	44	1288	55
350-MF2	1389	38	1656	42
350-LF	837	63	973	66

- Up 65 % reduction in number of ions
- Average Mw reduced from ~180 to ~170 but increase at high severities
- Appearance of new high Mw compounds

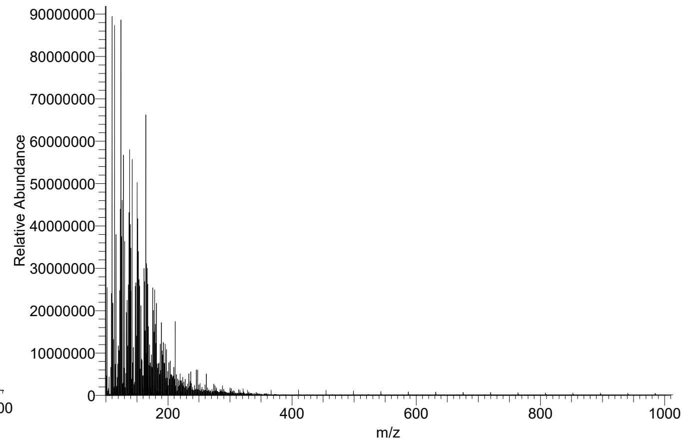
HTL process water (-)

HTL-AP- HESI (-) #140-271 RT: 4.72-5.86 AV: 132 SB: 120 0.03-1.07 NL: 7.20E8
T: FTMS - p ESI Full lock ms [100.0000-1000.0000]



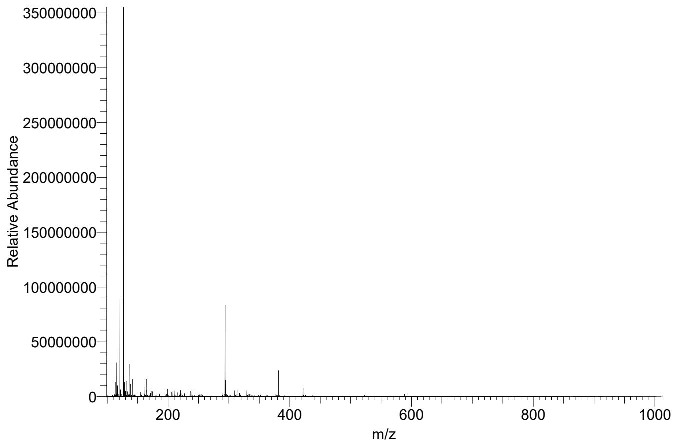
HTL process water (+)

HTL-AP (HESI) + #146-228 RT: 3.63-4.40 AV: 83 SB: 90 0.06-0.91 NL: 9.18E7
T: FTMS + p ESI Full lock ms [100.0000-1000.0000]



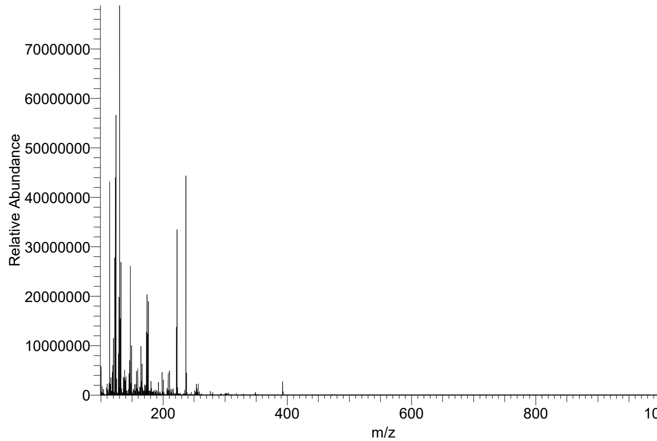
WO-350-50 - HESI (-) #116-206 RT: 4.26-5.04 AV: 91 SB: 94 0.07-0.88 NL: 3.55E8
T: FTMS - p ESI Full lock ms [100.0000-1000.0000]

WO water 350°C (-)



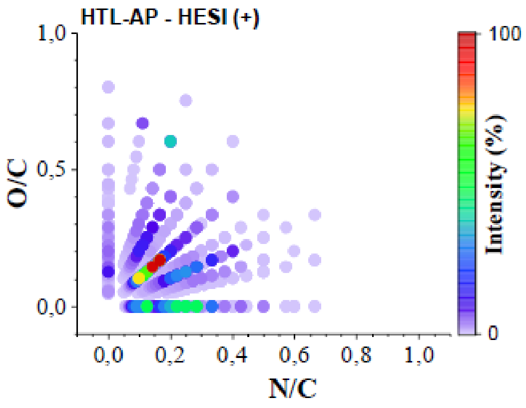
WO-350-50 - HESI(+) #223-355 RT: 9.92-11.07 AV: 133 SB: 86 0.14-0.96 NL: 7.87E7
T: FTMS + p ESI Full lock ms [100.0000-1000.0000]

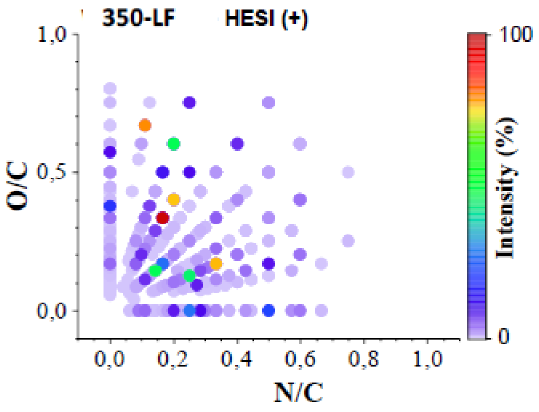
WO water 350°C (+)

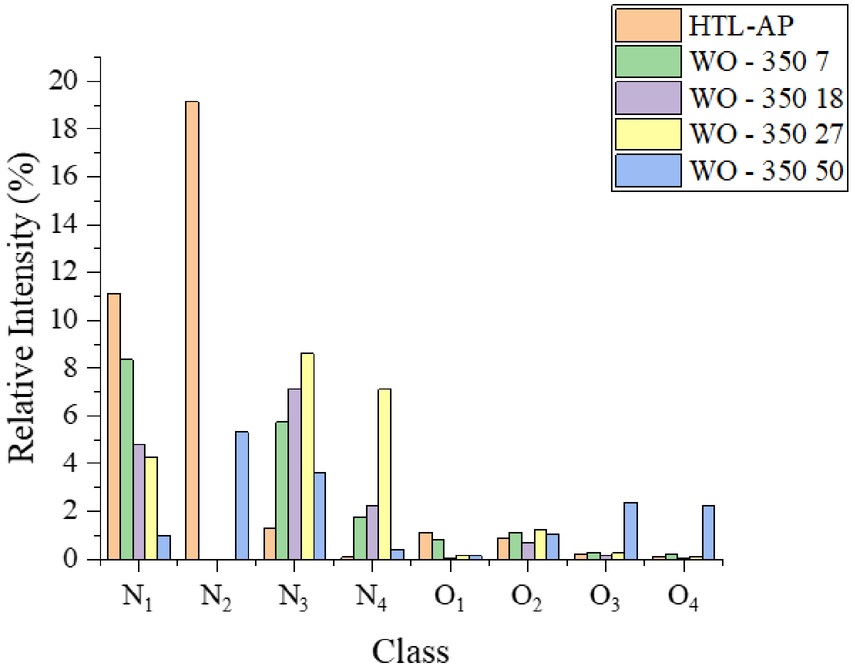


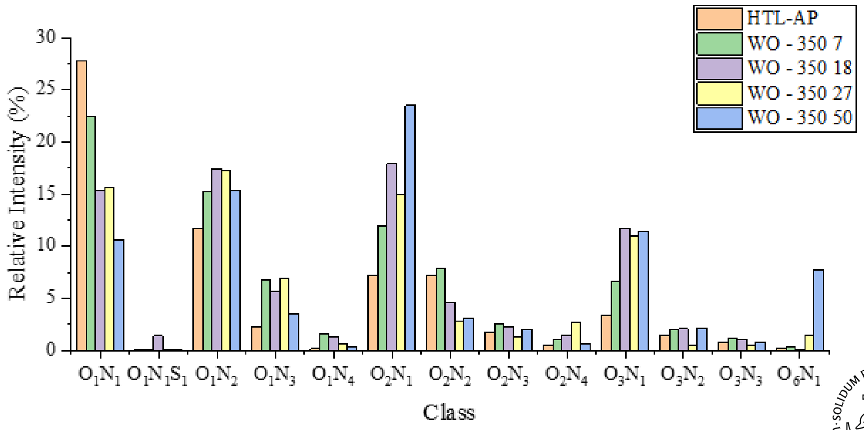
HR MS ANALYSIS

- N1 and N2 degraded
- O1N1, O1N2, O2N1 etc are more recalcitrant





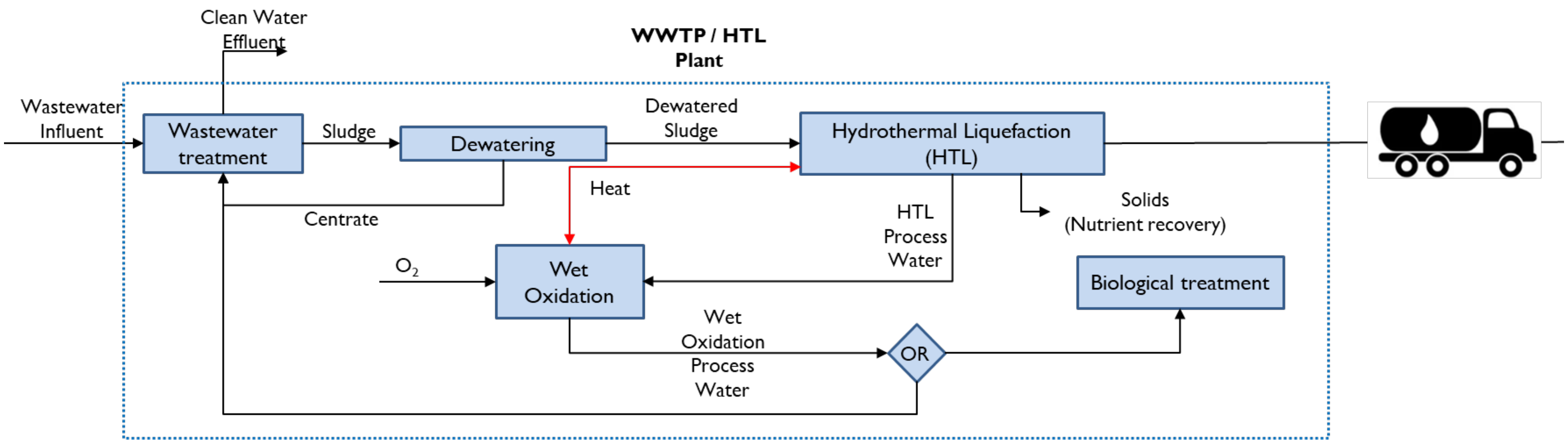




<u>Analysis by</u>:
Jhonattas de Carvalho Carregosa & Alberto Wisniewski Jr *(PEB), Department of Chemistry, Federal University of Sergipe, Brazil*

SSOR

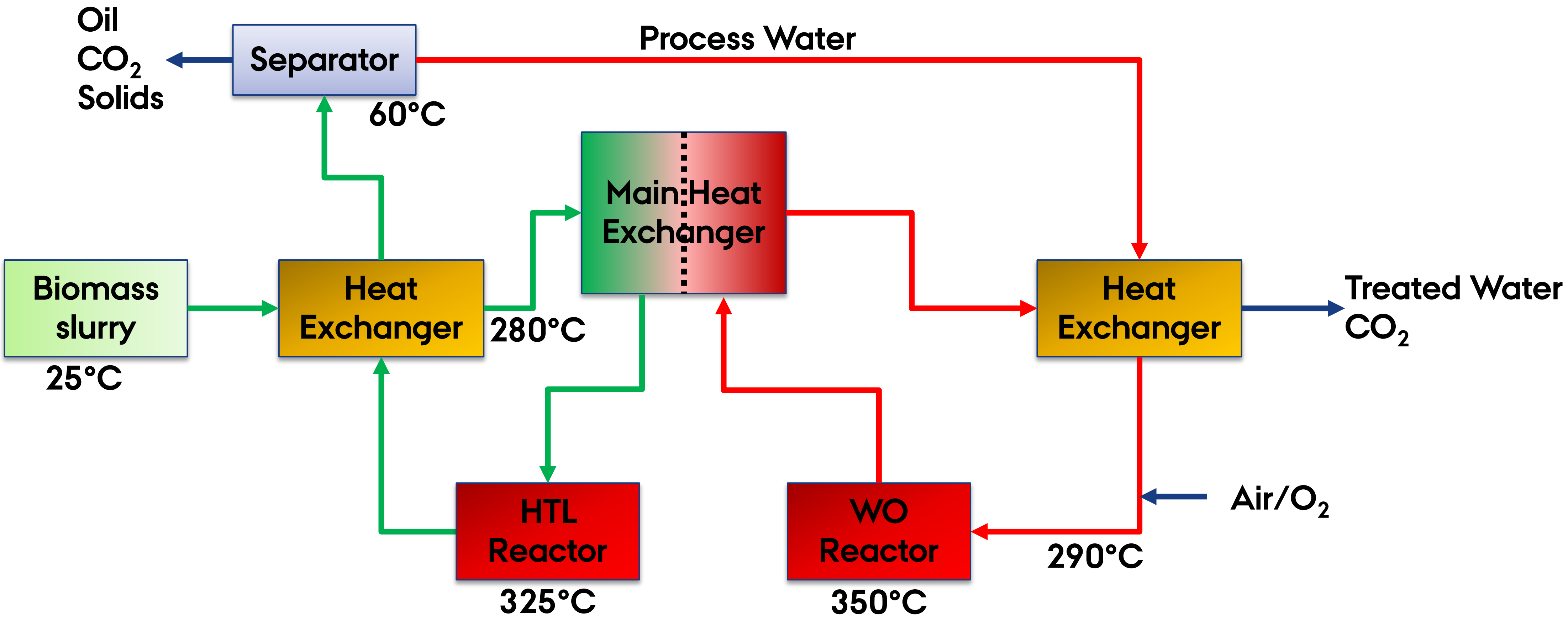
WET OXIDATION



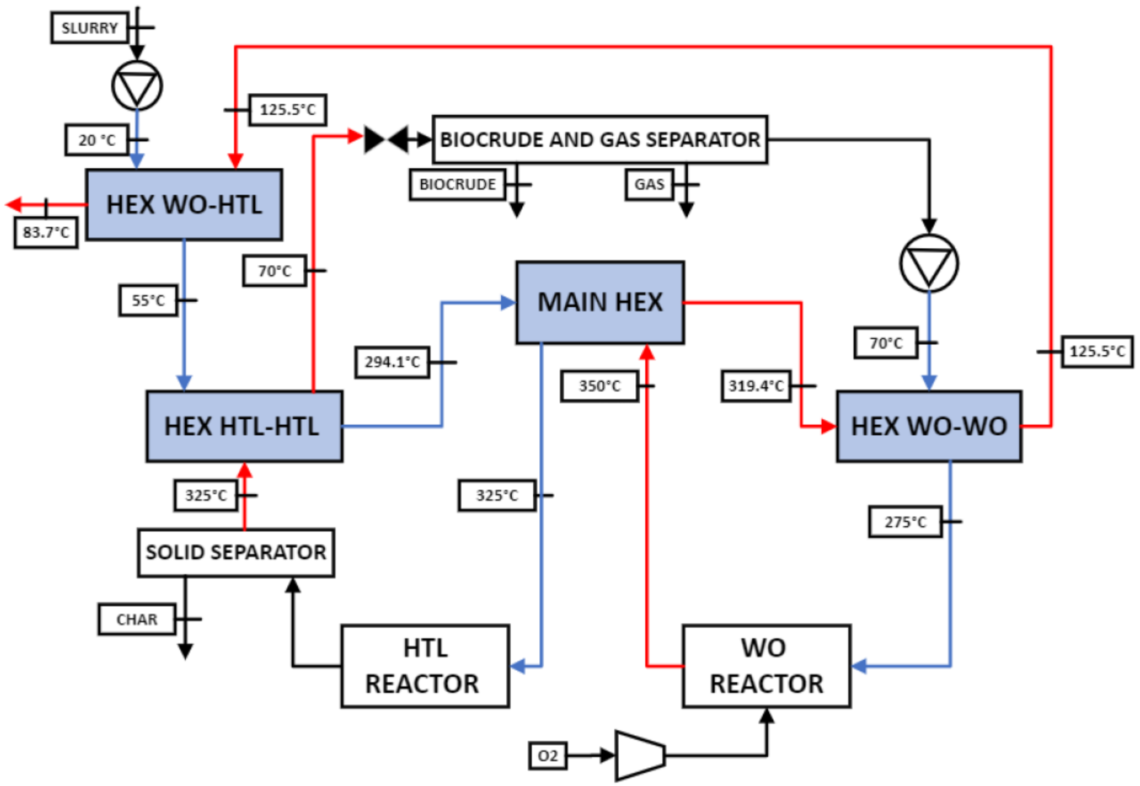
$$ER = COD_{removed}(mol) * 435(\frac{kJ}{mol}O_2)$$

H. Debellefontaine, J.N. Foussard / Waste Management 20 (2000) 15–25

HTL-WO INTEGRATION



HTL-WO INTEGRATION



3.6 Network setup

The considered fluxes, based on the results of the batch experimental test 325°C/20min, for the exchanger network are reported in the following Table 3.7:

Table 3.7 - Initial flux subdivision based on the 325°C/20min HTL batch experiments and literature data for WO.

Flux name	T_{in} [°C]	T_{out} [°C]	$\dot{m}$ $\left[\frac{kg}{s}\right]$	Cp* $\left[\frac{kj}{kg*K}\right]$	$\dot{m}Cp$* $\left[\frac{kW}{K}\right]$
Slurry Heating	20	200	1	4.26	4.26
	200	250	1	4.54	4.54
	250	300	1	5	5.00
	300	315	1	5.5	5.50
	315	325	1	5.86	5.86
Aqueous Phase Heating	70	200	0.835	4.27	3.57
	200	250	0.835	4.54	3.79
	250	275	0.835	4.87	4.07
Slurry cooling	325	315	0.91	5.86	5.32
	315	300	0.91	5.5	4.99
	300	250	0.91	5	4.54
	250	200	0.91	4.54	4.12
	200	70	0.91	4.27	3.88
Aqueous phase cooling	350	345	0.885	7.76	6.48
	345	330	0.885	6.84	5.71
	330	315	0.885	5.98	4.99
	315	300	0.885	5.50	4.59
	300	250	0.885	5.00	4.18
	250	200	0.885	4.54	3.79
	200	20	0.885	4.27	3.57

From Table 3.7 is evaluated the total heating and cooling demand:

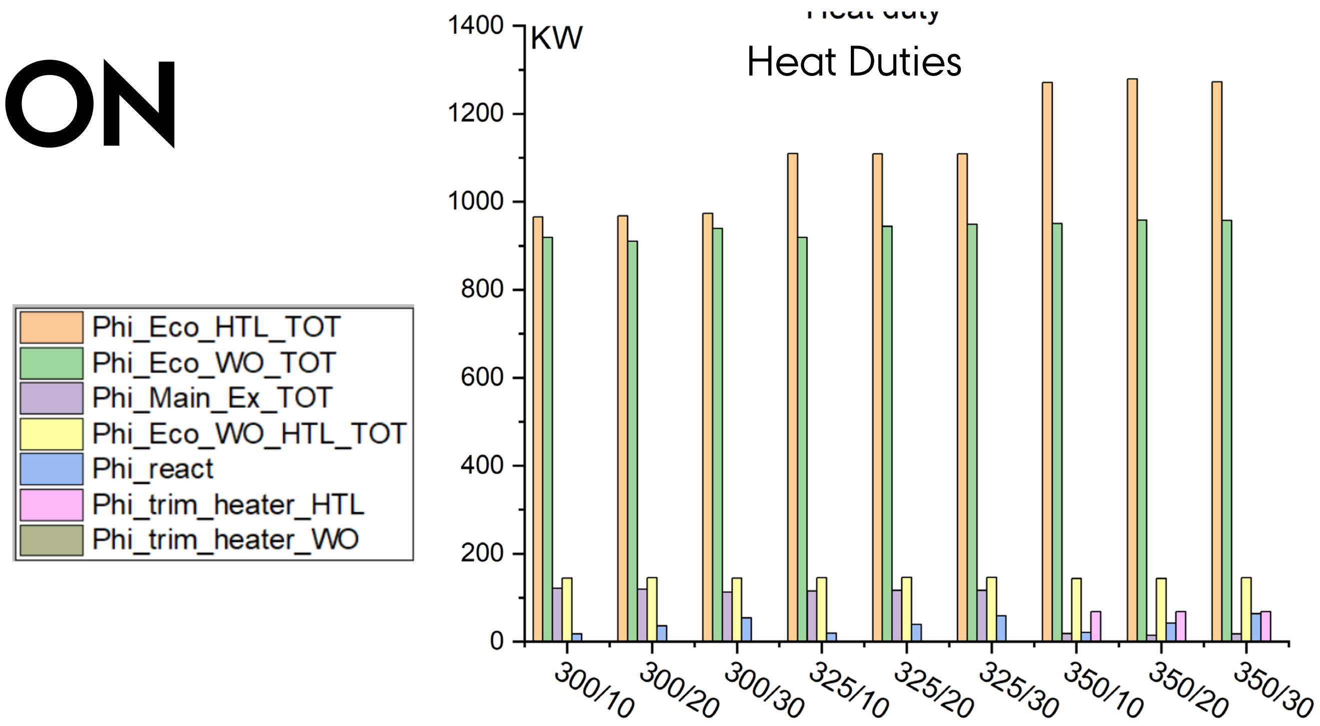
$$\phi_{max,heat dem.} = 2141\ kW$$

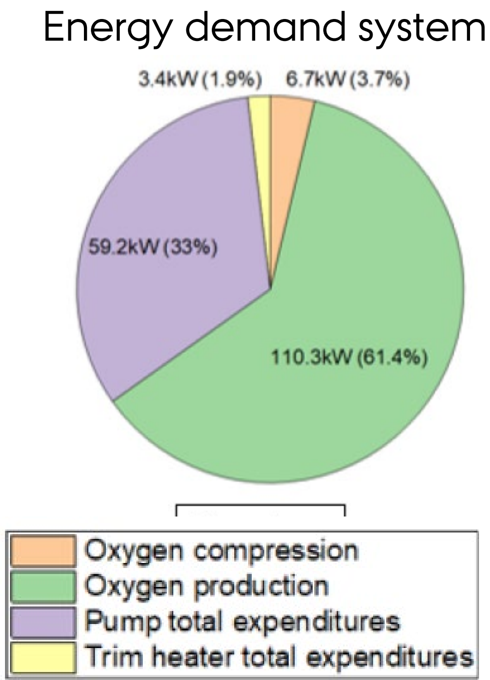
$$\phi_{max,cooling dem.} = 2368\ kW$$

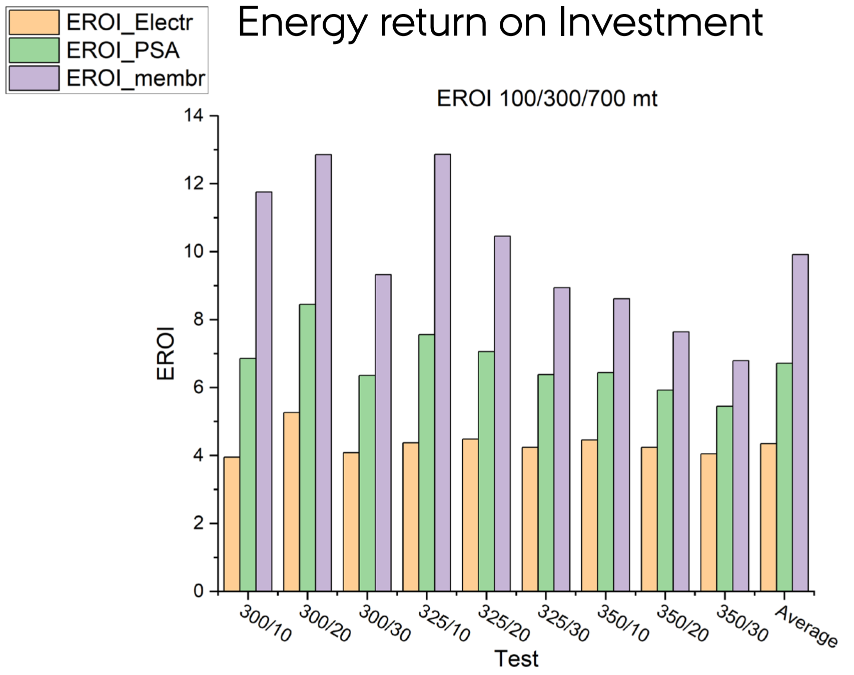
- Modelling only found 160 KJ/mol vs theoretical 435 KJ/mol O2
- Only 55% COD removal achieved in ASPEN model vs~80% experimental
- Autothermicity confirmed in ASPEN Energy analyser

HTL-WO INTEGRATION

- As long as HTL is not run at 350C and WO at 350C there is no heat demand for HTL
- Pumping and oxygen production are highest energy input
- Source of Oxygen very important for overall energy balance
-







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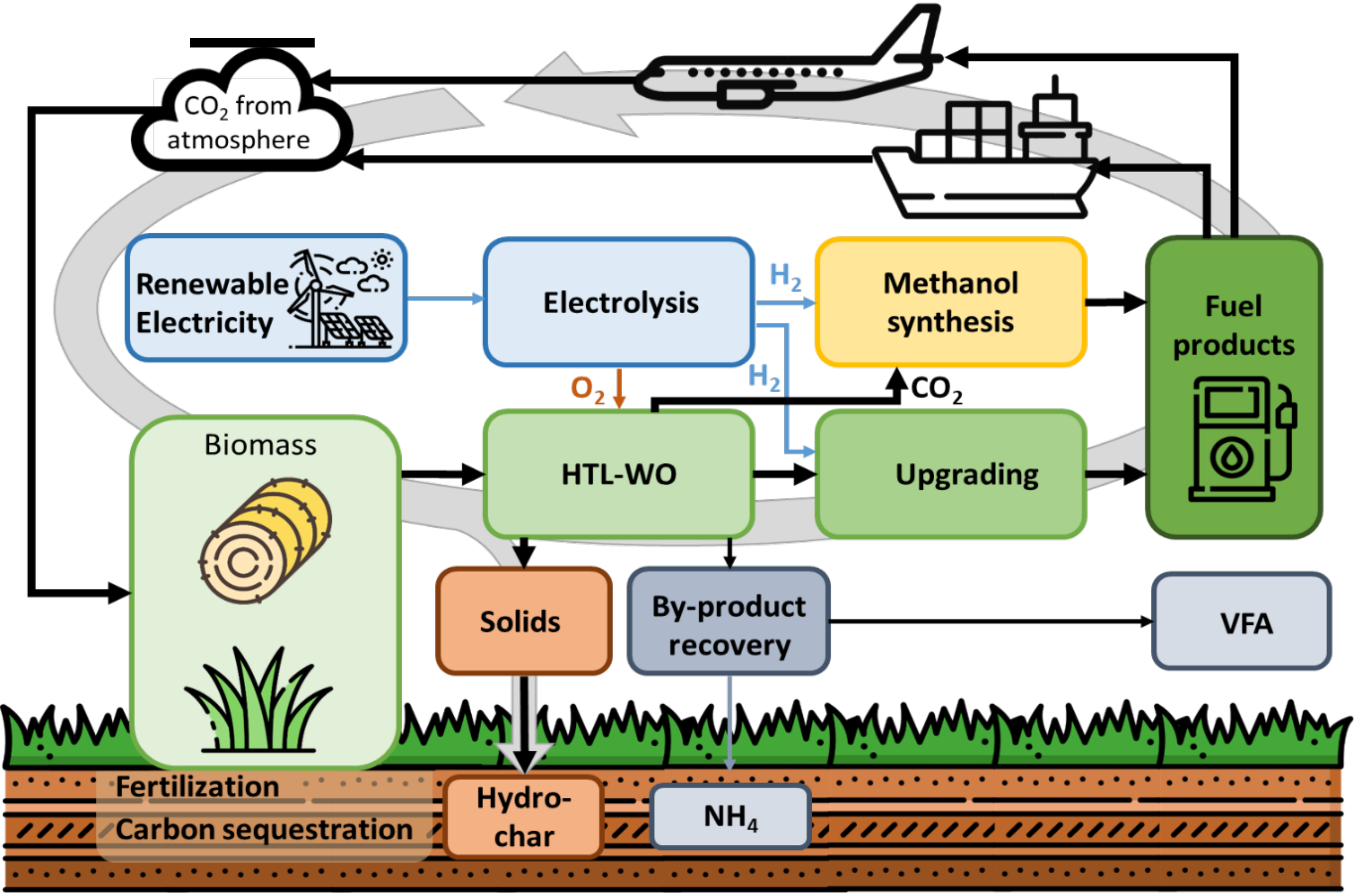
CIRCULAIR



https://project-circulair.eu/

New follow-on HORIZON EU Project

Objectives:

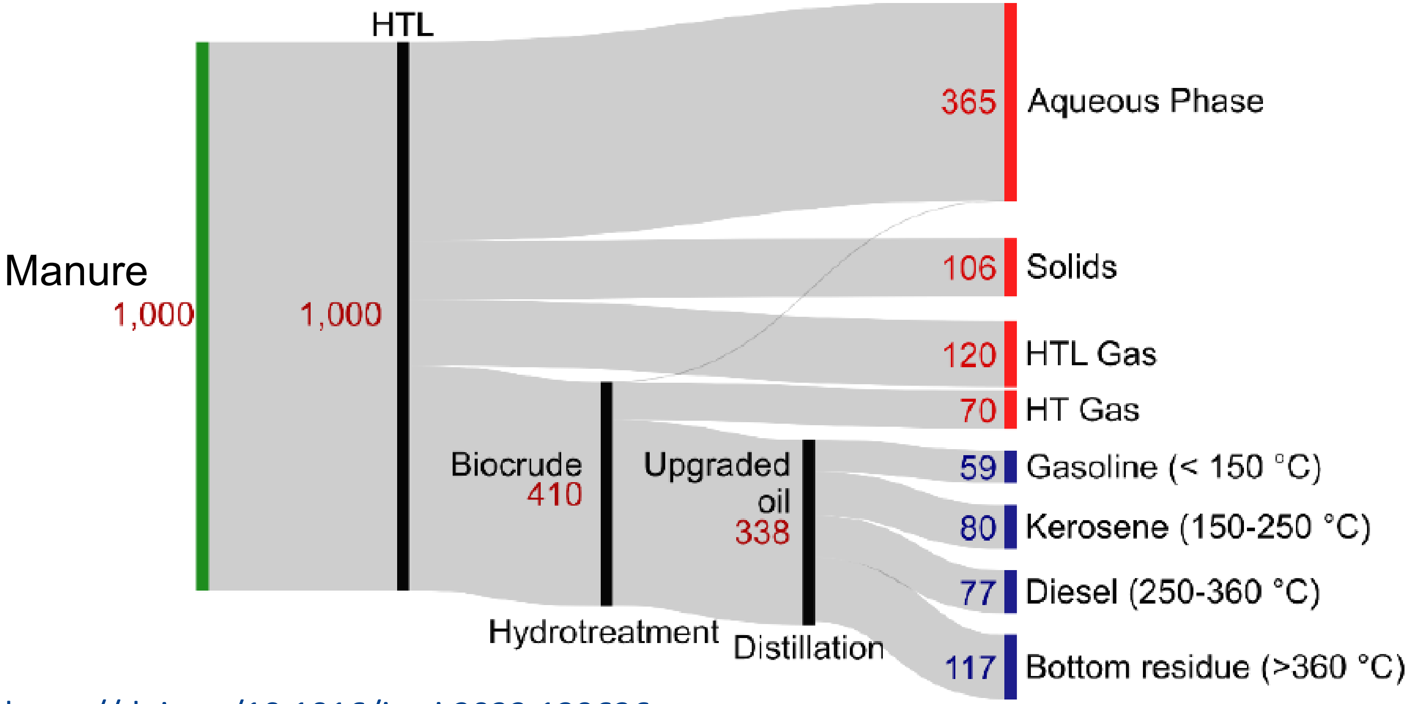
- *Integrate process water valorization (wetOx)*
- *Producing on spec jet fuel*
- *Carbon negative fuel production*
  - *valorizing all C streams*
  - *Sequestering C in biochar*
- *Autothermal HTL process*
- *Methanol synthesis at Foulum Power-2-X facilities*

CARBON BALANCE

CIRCULAIR

State of the art:

50% carbon lost to gas and process water

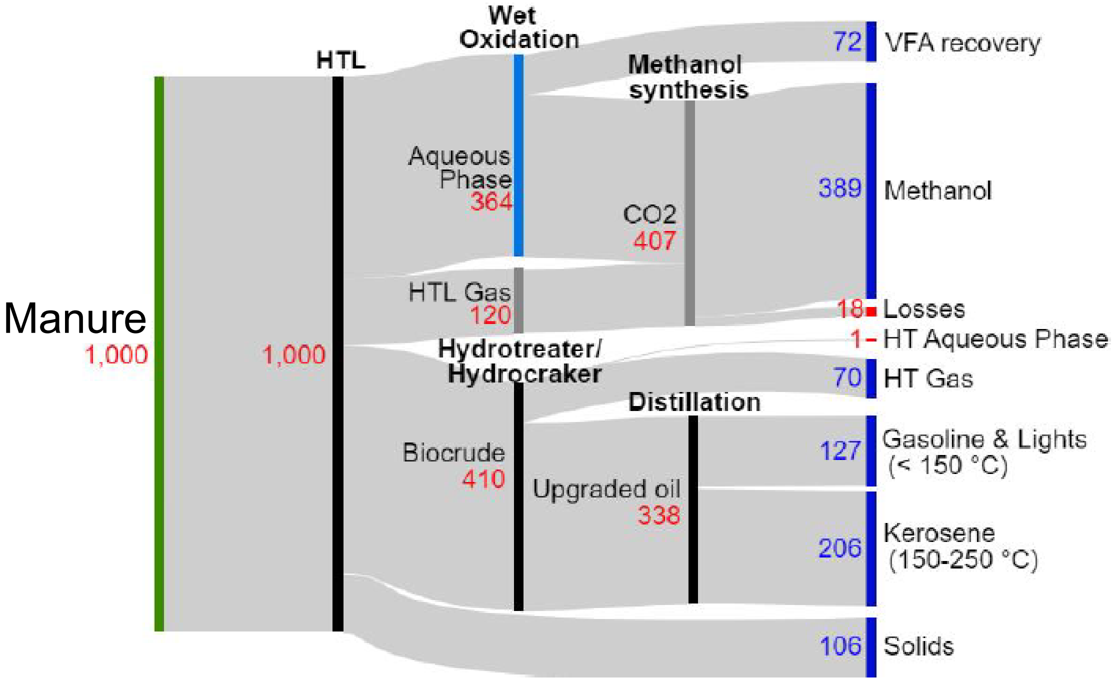


https://doi.org/10.1016/j.cej.2022.139636

Ambition:

>90 % carbon utilisation

~20% jet fuel yield



SUMMARY

- WO is efficient in converting HTL water phase organics
- Autothermal integrated HTL-WO is an attractive concept
- Use of CO2 for Power-2x and O2 from electrolysers looks promising
- Recovery of acetic acid and NH4 sould be investigated
- Final use of post-WO water and toxicity needs to be investigated

THANK YOU

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EUDP

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