Evaluation of On-site Biological Treatment Options for Hydrothermal Liquefaction Aqueous Phase Derived from Municipal Sludge

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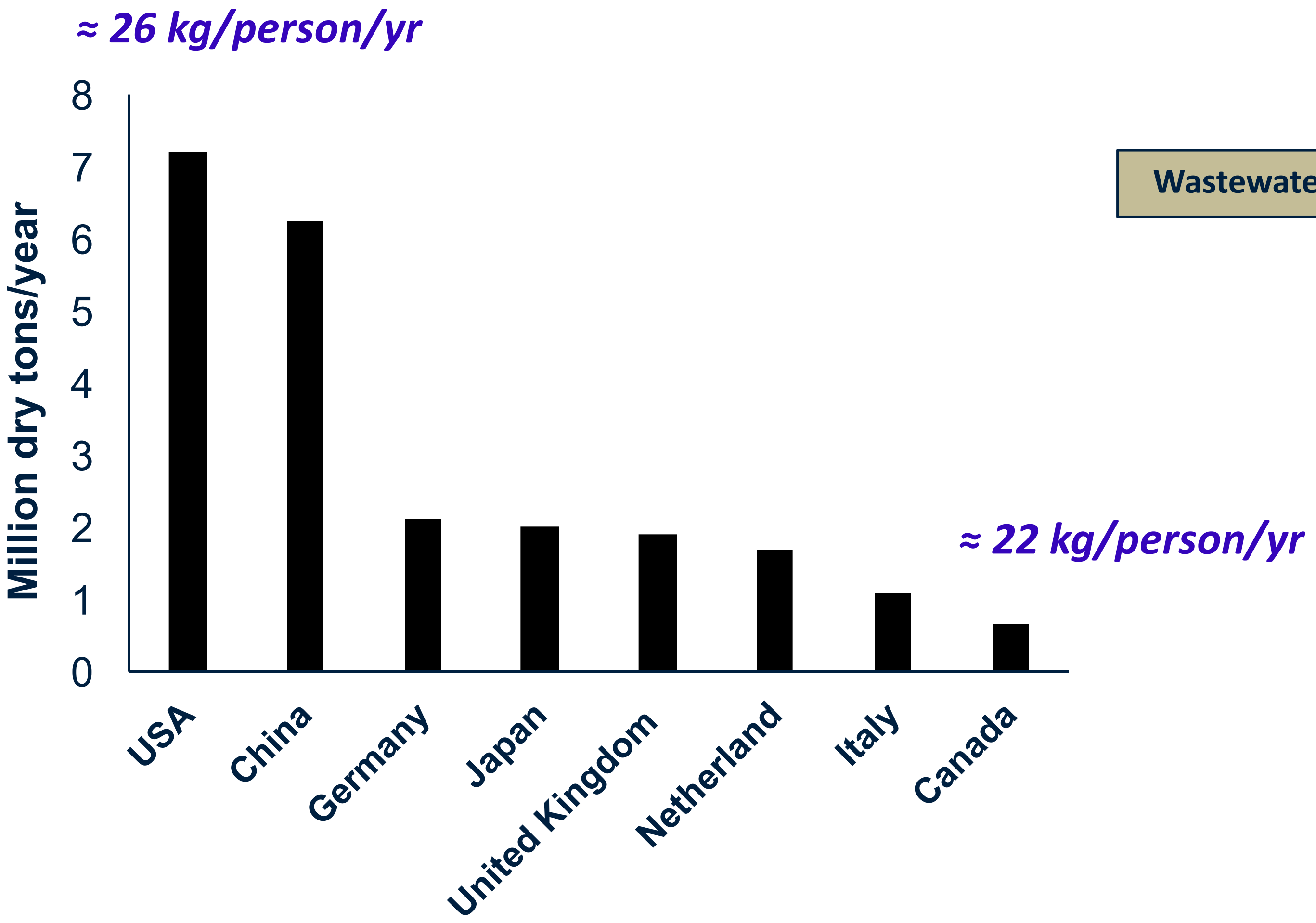
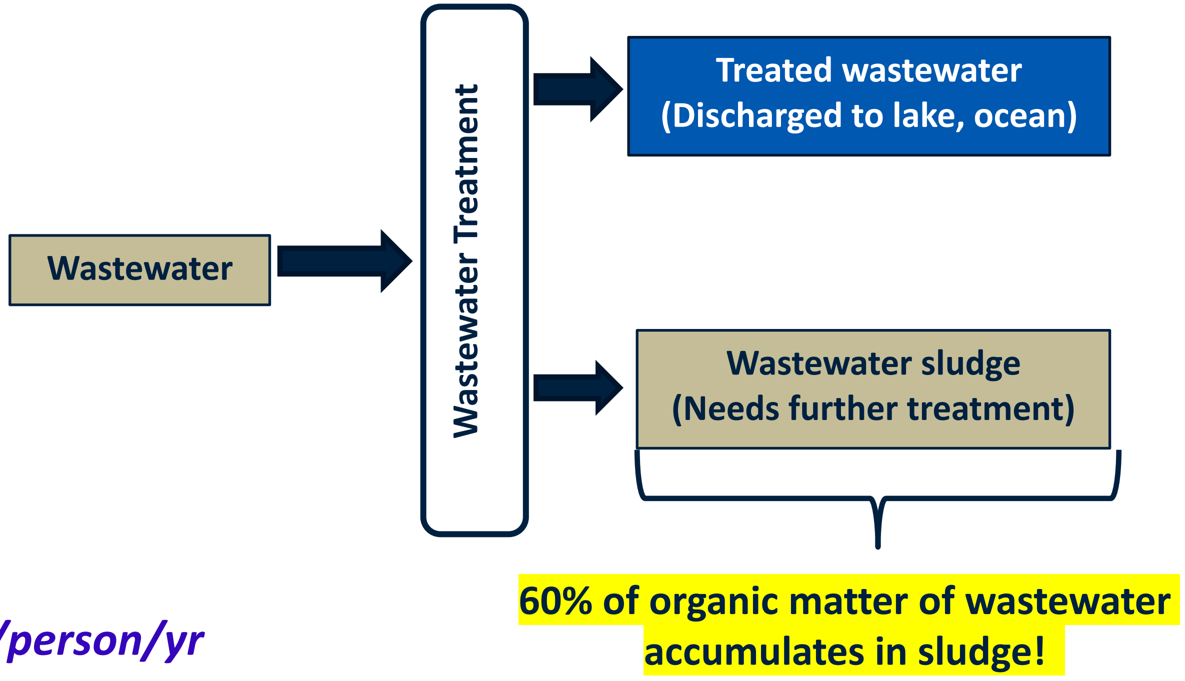
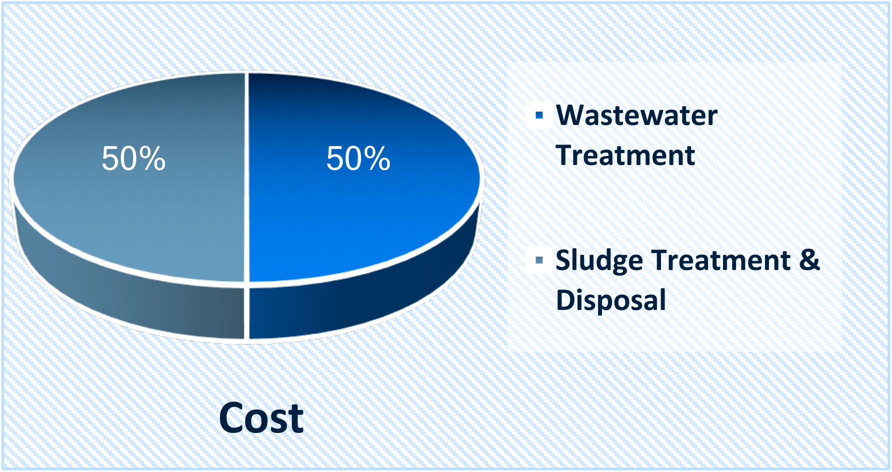
IEA Bioenergy Technology Collaboration Program, March 19, 2024, ***Webinar***

Global Challenge: Wastewater Sludge Production

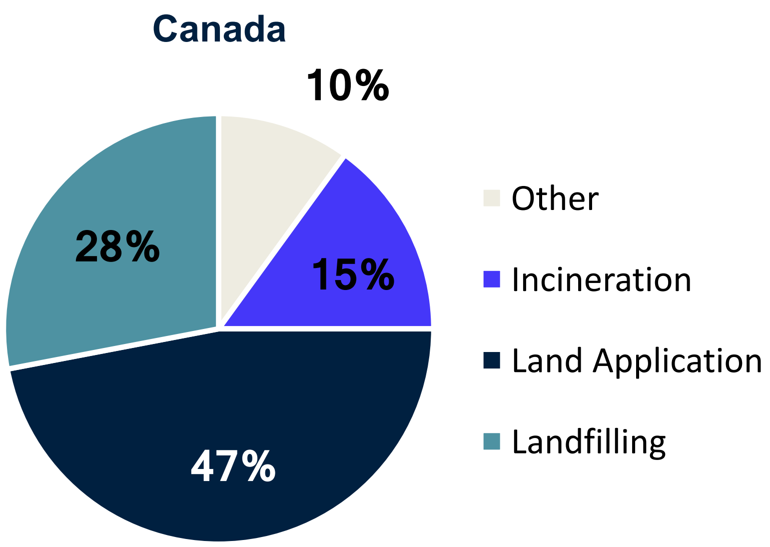


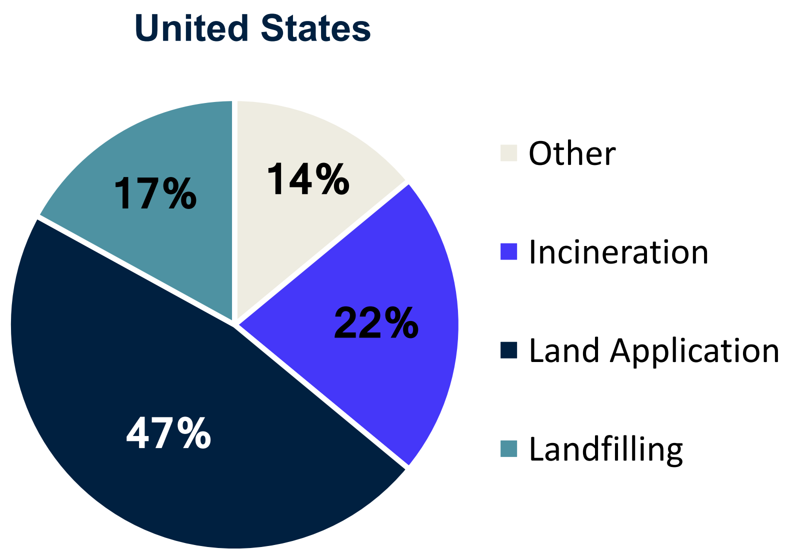




- USEPA (1999)
- Peres-Elvira et al., Rev Env Sci BioTech (2006)
- Zhen et al., Renew Sust Energ Rev (2017)

Wastewater Sludge Disposal Methods





Zhen et al., Renew Sust Energ Rev (2017)

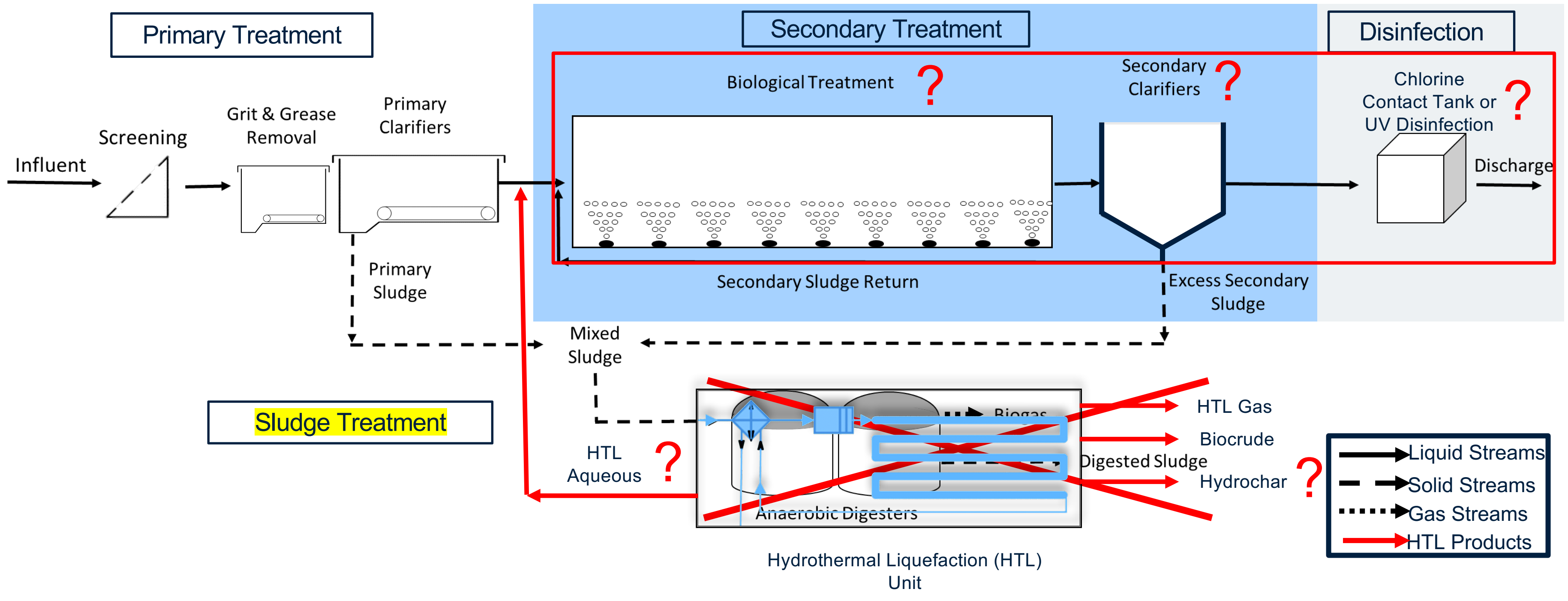
- Landfilling (no longer permitted for organic waste in many Provinces of Canada)
- Incineration (more popular in Europe due to land restriction)
- Land application as fertilizer most common (regulated by Organic Matter Recycling Regulations)
- **Land application** is the cheapest but is getting more **challenging** due to **public opposition to heavy metals, pathogens, emerging contaminants of concern such as hormones, pesticides, pharmaceuticals.**

Thermochemical vs. Biochemical Processes for Wastewater Sludge Treatment

	Hydrothermal Liquefaction (HTL) + Aqueous Valorization	Anaerobic Digestion (AD)
Carbon conversion yield	> 90%	50-60%
Sludge volume reduction	High	Low
Retention time requirement	10-45 min	15-30 days
Foot print requirement	Low	High
Sterilization efficiency of sludge (i.e. pathogens)	High	Low
Removal of trace contaminants (i.e. hormones, antimicrobials, pharmaceuticals)	High	Low
Limitations of scale for energy recovery	Low	High
Value-added product recovery potential (i.e. bioenergy, nutrients, liquid fuel)	High	Medium
Technology readiness level (TRL) (1-9, 9 most mature)	Low (5-6)	High (9)
Capital/operational cost	High	Low/Medium
Advanced technology/expertise requirement	High	Medium
Adaptability to existing wastewater treatment plants	**Unknown**	High

Key question to answer in the ongoing Industrial Research Chair Program!

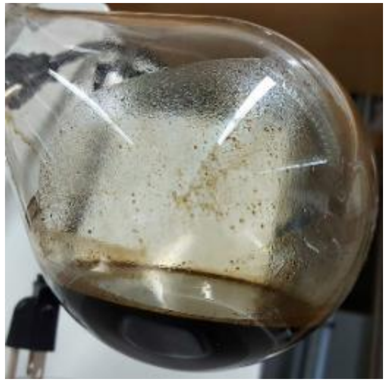
Main Challenge: Incorporating HTL Process into a Wastewater Treatment Plant



Natural Research Council of Canada (NSERC)/Metro Vancouver Industrial Research Program in Wastewater (2020-2025):

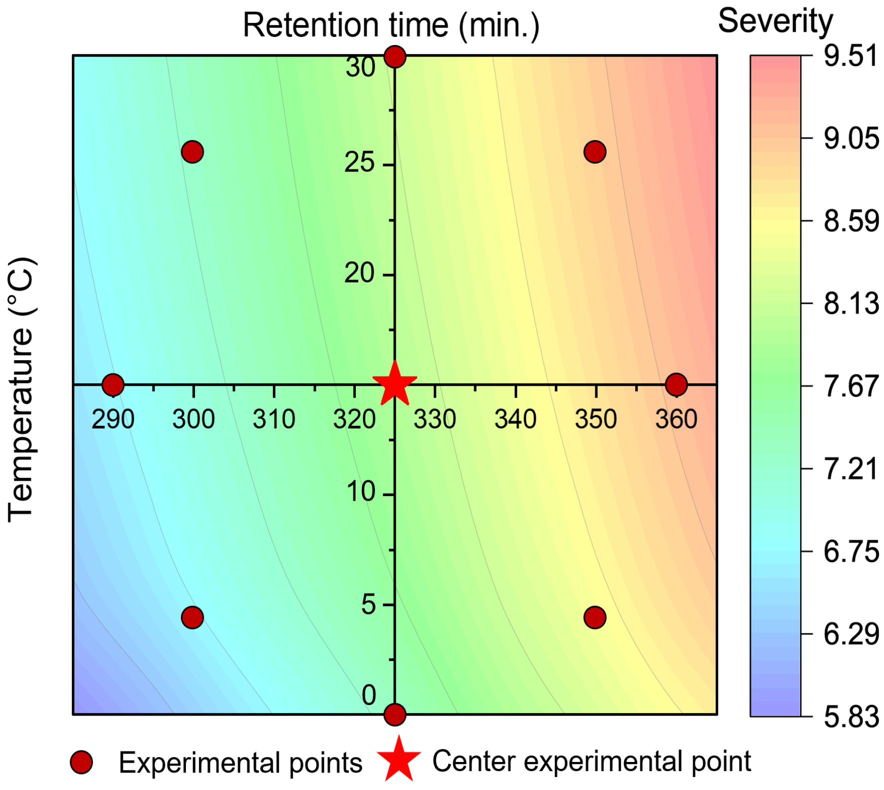
- What are the optimum HTL conditions (temperature/pressure/time) for municipal sludge processing?
- Can HTL aqueous be used for biological H_2/CH_4 production for downstream biocrude upgrading? Any inhibitors?
- Can we recover N, P from HTL aqueous and hydrochar streams, respectively, as commercial fertilizer?
- What is the fate of trace contaminants of emerging concern (hormones, pharmaceuticals, antimicrobials) during HTL?

OPTIMUM HTL CONDITIONS FOR MAXIMUM *BIOCRUDE YIELD* FROM MUNICIPAL SLUDGE?



HTL Optimization Experimental Design for Municipal Sludge

- **Experimental Design**: Central composite design
- **Data Analysis**: Response surface method
- **Total experimental runs**: ***19 runs*** (duplicate of **8** non-center points and triplicate of **center point**).



$$\text{Severity} = \log\left[\int_0^t e^{\left(\frac{T(t)-T_b}{\omega}\right)} dt\right]$$

- t is the time (minutes),
- $T(t)$ is temperature at given time (t) (°C),
- T_b is the base temperature (100°C),
- ω is fitted parameter assigned the value of 14.75

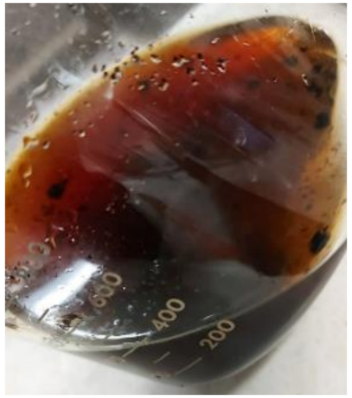
Run	Reaction temperature (°C)	Residence time (min)
1	**325**	**15**
2	350	25.6
3	300	25.6
4	300	25.6
5	350	4.4
6	300	4.4
7	**325**	**15**
8	350	25.6
9	300	4.4
10	350	4.4
11	360	15
12	290	15
13	325	0
14	**325**	**15**
15	360	15
16	290	15
17	325	0
18	325	30
19	325	30

Basar, I.A., Liu, H., Eskicioglu, C., 2023. Chem. Eng. Journal, *467, 143422*.

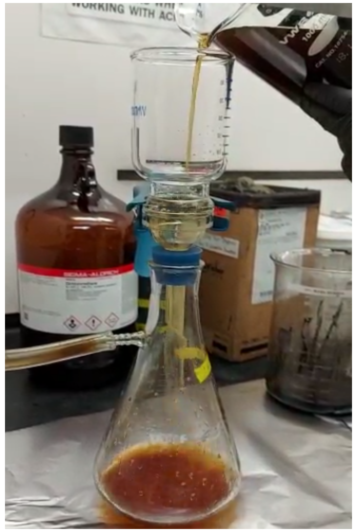
HTL Bench-scale Operation and Product Separation

Dewatered mixed sludge
(20 wt% total solids)[a]

Parr reactor (1-L, CSTR, maximum 500°C, 345 bar)



HTL product mixture

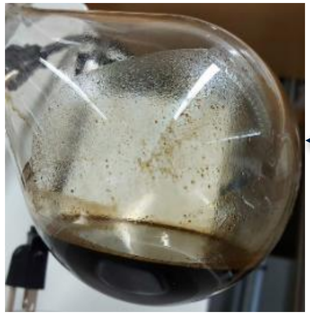


Filtration (20 µm)

HTL aqueous

Hydrochar+biocrude retained on filter

Hydrochar



Biocrude dissolved in DCM[b]

DCM evaporation

Biocrude

[a]Centrifugation dewatering conditions: 4,400 ×*g* for 15 min followed by 10,000 ×*g* for 5 min.
Mixed sludge: mixture of primary and secondary sludge (50:50% by vl.) from Annacis Island WWTP, BC, Canada.
[b]DCM – dichloromethane

Parameters in HTL Optimization for Biocrude Recovery

Factors	Range	Responses
HTL reaction temperature	290–360 °C	**Biocrude:** CHNSO, ash, higher heating value (HHV), yield, energy recovery.
HTL residence time	0–30 min	**Hydrochar:** CHNSO, ash, HHV, yield, heavy metals, P recovery, combustion potential.
Sludge type	Mixed primary and secondary sludge 50/50 by volume to represent annual average flow in Annacis Island WWTP	**Aqueous:** CN, yield, organic and inorganic compounds analysis, aerobic/anaerobic degradability, NH_3/H_2 recovery.
Sludge solids content	Fixed at 20 wt% for process efficiency	**Gas:** Composition, yield.

Biocrude Findings:

- **H. Liu**, I.A. Basar, N. Lyczko, A. Nzihou, C. Eskicioglu, *Chemical Engineering Journal* 449 (2022) 137838.

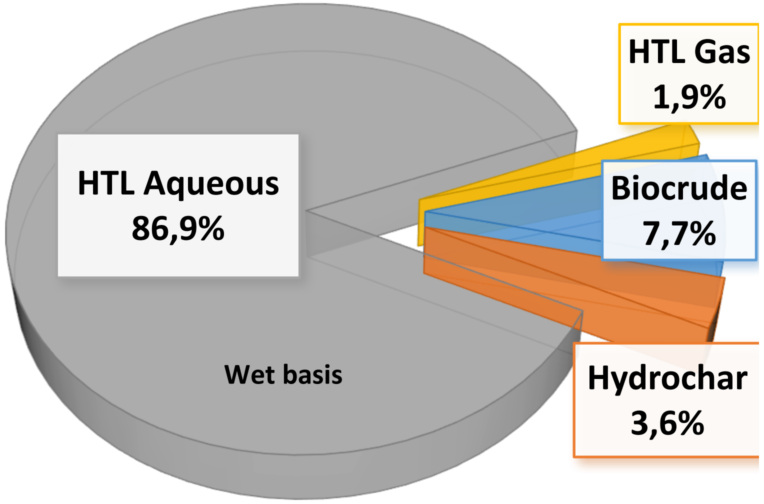
Hydrochar Findings:

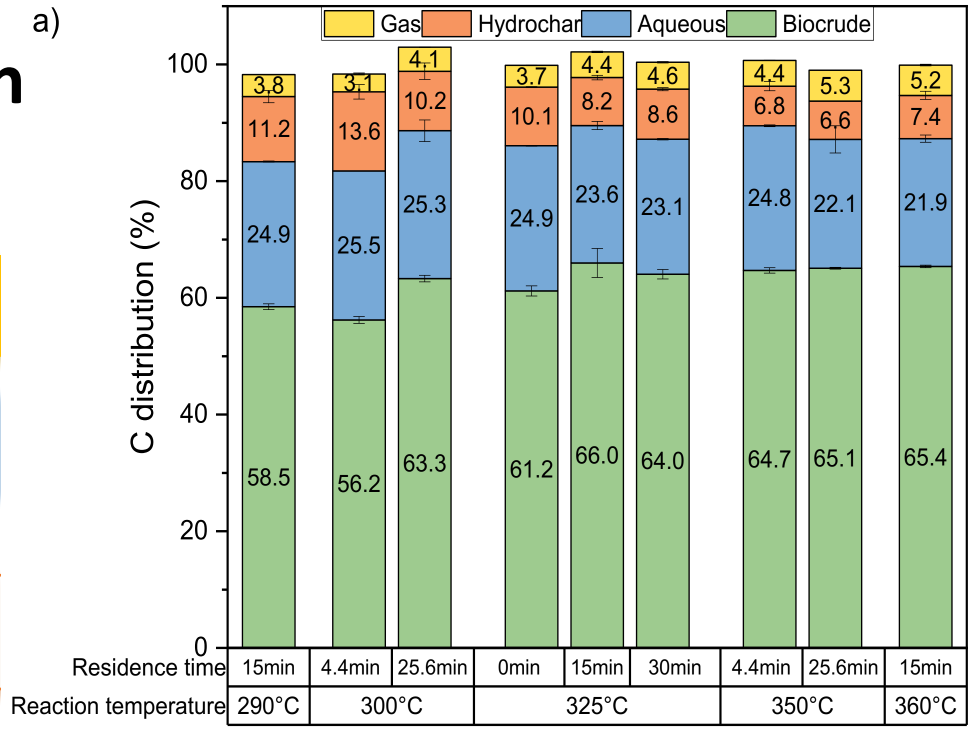
- **H. Liu**, I.A. Basar, A. Nzihou, C. Eskicioglu, *Water Research* 199 (2021) 117186.
- **H. Liu**, G. Hu, I.A. Basar, J. Li, N. Lyczko, A. Nzihou, C. Eskicioglu, *Chemical Engineering Journal* 417 (2021) 129300.
- **H. Liu**, N. Lyczko, A. Nzihou, C. Eskicioglu, *Journal of Cleaner Production* 383 (2023) 135398.
- **H. Liu**, N. Lyczko, A. Nzihou, C. Eskicioglu, *Water Research* 241 (2023) 120138.
- **H. Liu**, N. Lyczko, A. Nzihou, C. Eskicioglu, *Chemical Engineering Journal* 473 (2023) 145191.

Today's topic: HTL aqueous!

A continuous-flow HTL pilot-plant is under construction with 10,000 L feedstock (dewatered sludge) capacity at Annacis Island WWTP (BC, Canada)

HTL Product Distribution





C/N Distribution

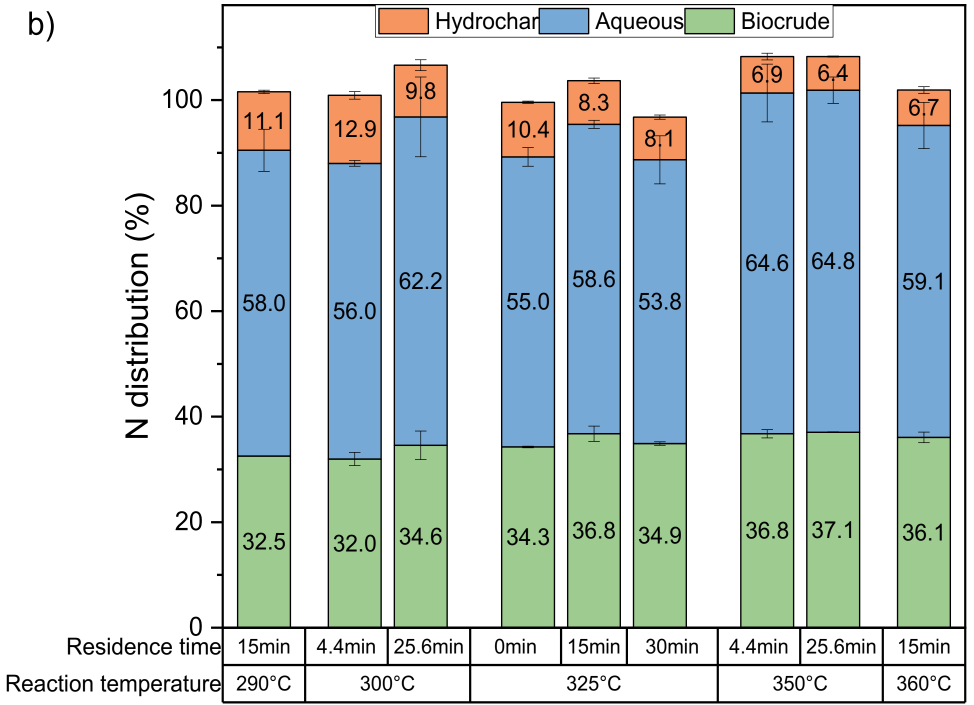
The majority of N present in **HTL aqueous (54-65%)** creates significant **challenges** (potential toxicity) for it's biological **treatment** but also **opportunities** for **NH_3 recovery** as a commercial product within WWTP.

Significant volume (87%) of **HTL aqueous** is generated with **<u>no safe treatment/disposal.</u>**

Small volume (3.6%) of **HTL hydrochar** is generated, which indicates **<u>cost savings</u>** for biosolids transport/disposal, compared to anaerobic digestion.

The majority of **C** (56-66%) is present in **biocrude oil**.

Aqueous also contains significant **C** (22-26%), **opportunity for valorization**.



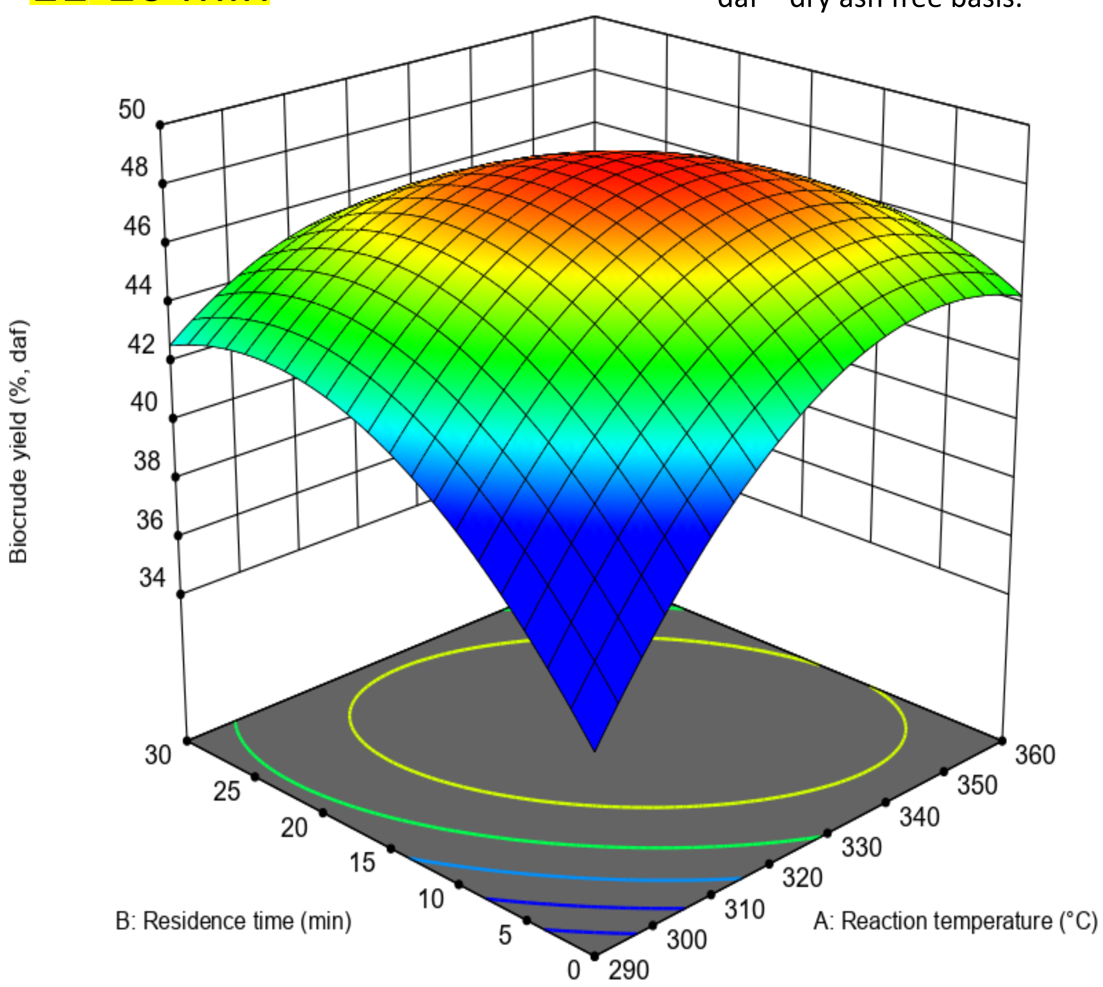
Liu, H., Basar, I.A., Lyczko, N., Nzihou, A., Eskicioglu, C., 2022. Chem. Eng. Journal, 449, 137838.

Biocrude Yield (in Dry Ash Free Feedstock)

Optimum range for maximum biocrude yield (>48%, daf):

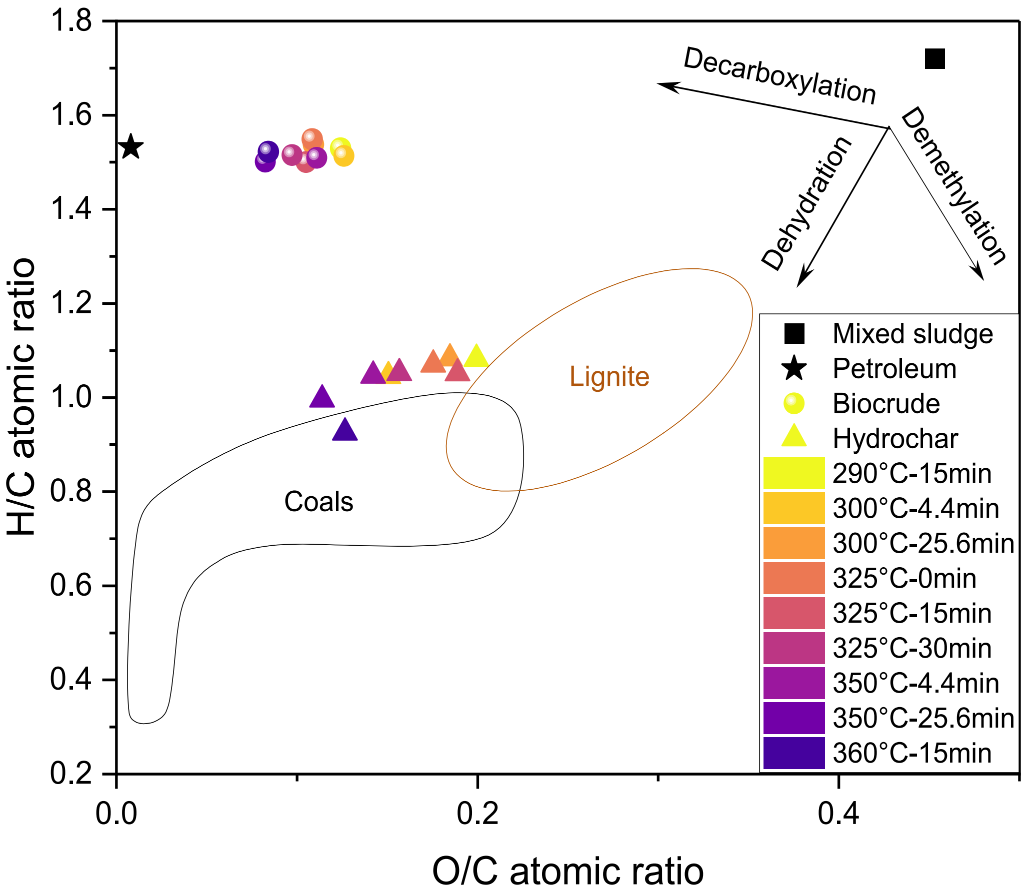
- 325-342ºC
- 11-20 min

daf – dry ash free basis.



After 350ºC, biocrude oil cracking & conversion to gaseous compounds start.

van Krevelen Diagram for HTL Products



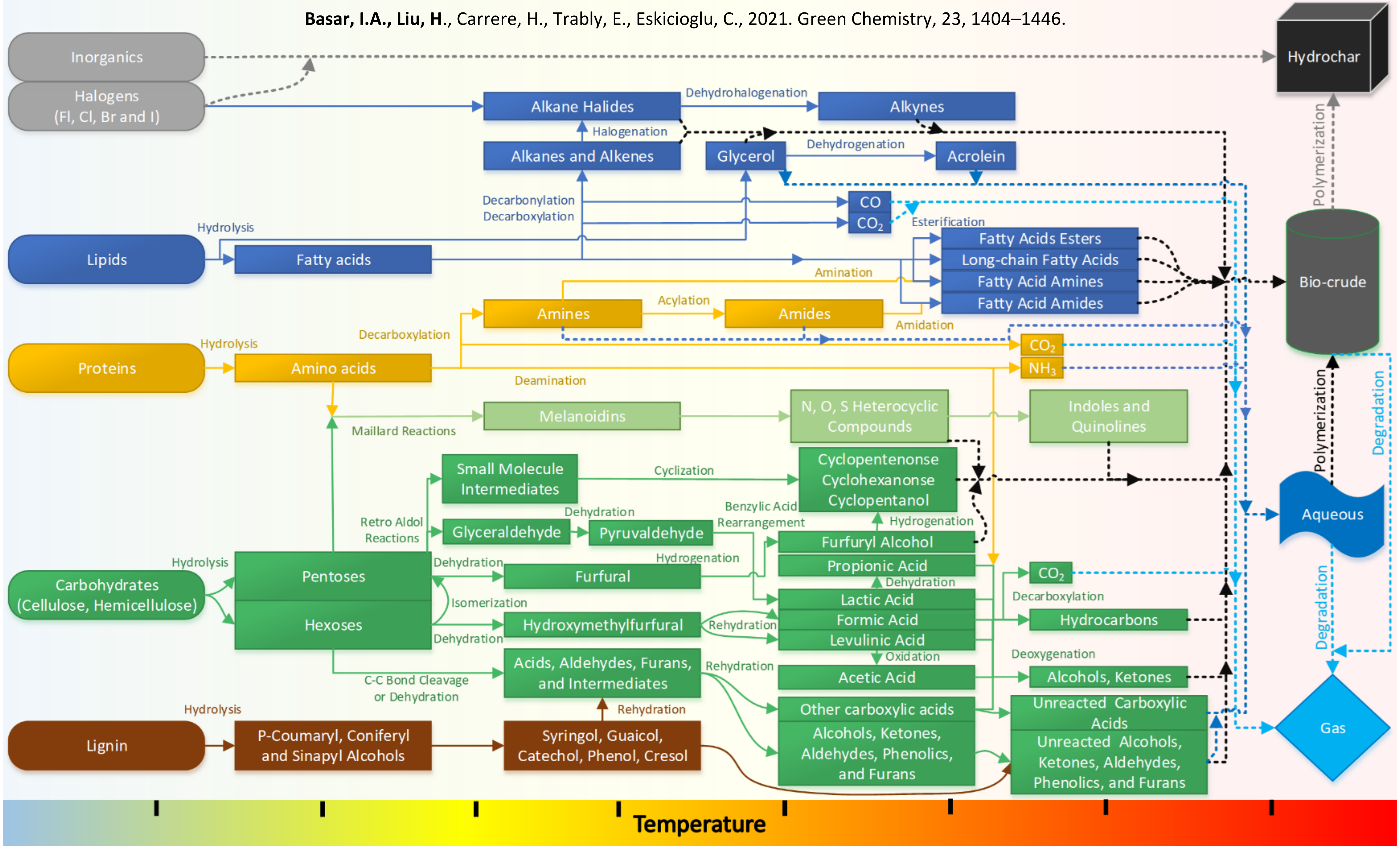
Biocrude oil and *hydrochar* have similar properties to petroleum and *coal*, respectively.

Liu, H., Basar, I.A., Lyczko, N., Nzihou, A., Eskicioglu, C., 2022. Chem. Eng. Journal, 449, 137838.

HTL AQUEOUS CHARACTERIZATION, TREATMENT AND RESOURCE RECOVERY OPTIONS?

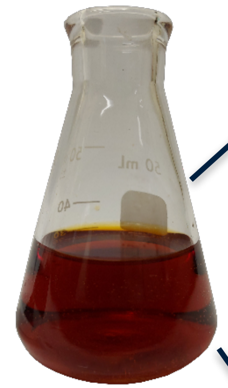
For WWTPs, there may be a trade of between maximizing biocrude yield and minimizing toxicity of HTL aqueous to downstream processes

HTL Pathways for Municipal Sludge to Product Conversion



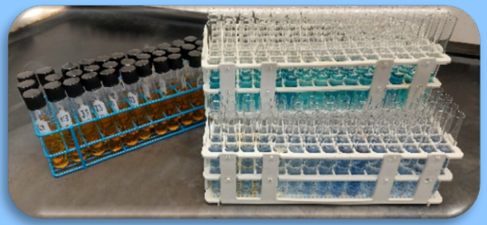
HTL aqueous characterization is not a trivial task !! Very complex pathways and byproducts.

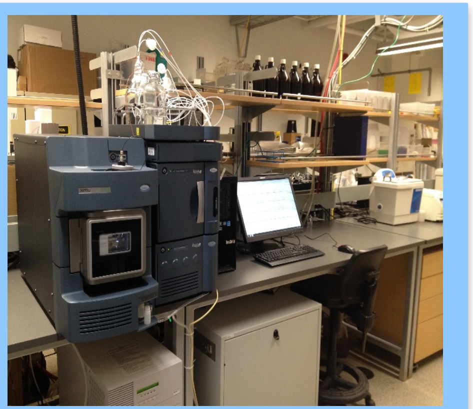
HTL Aqueous Characterization and Biodegradability Assessment



Chemical characterization:

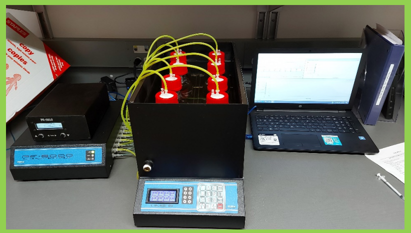
- Chemical oxygen demand (COD)
- Proteins (Lowry method), total sugars
- Total ammonium nitrogen (TAN), phosphorus (PO_4^{-3})
- Short chain and medium chain fatty acids (GC/FID)
- Total alkalinity, pH
- Total phenolic compounds
- Glycerol, hydroxymethylfurfural (5-HMF), furfural (2-furaldehyde), levulinic acid (HPLC/RID)
- Nitrogen-containing organics, including amides and N-heterocyclic compounds (pyrazine, methyl pyrazine, 2-pyrrolidinone, 1-methyl 2-pyrrolidinone, and 2-piperidinone), phenolic compounds (GC/MS)





Batch biochemical assays:

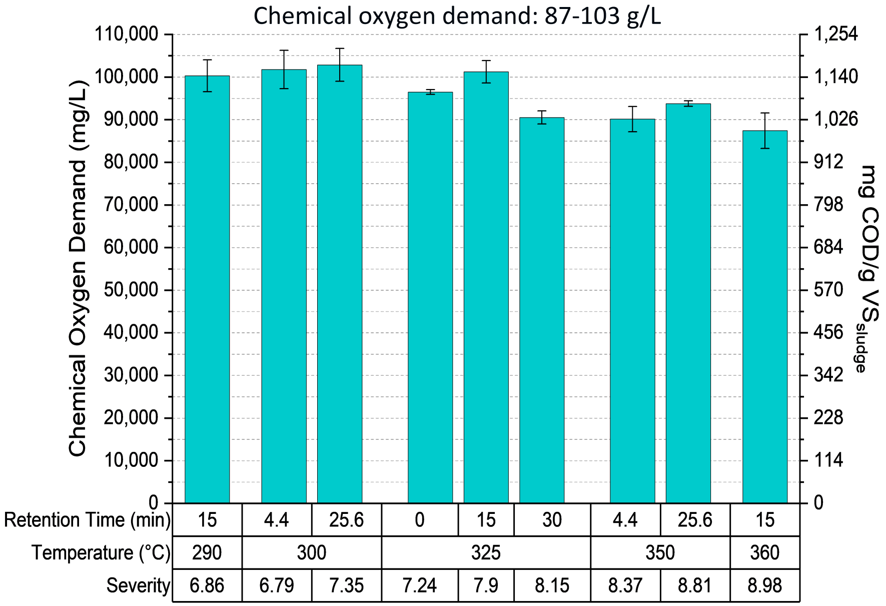
- Aerobic online real-time respirometry assays
    - Five-day biochemical oxygen demand (BOD_5)
    - Ultimate biochemical oxygen demand (UBOD)
    - Aerobic biodegradability index (BOD_5/COD)
- Mesophilic or thermophilic biochemical methane potential (BMP) assays
- Anaerobic biodegradability (%) (Specific BMP/Theoretical BMP of 0.35 L/g COD)
- Mesophilic or thermophilic biochemical hydrogen potential (BHP) assays

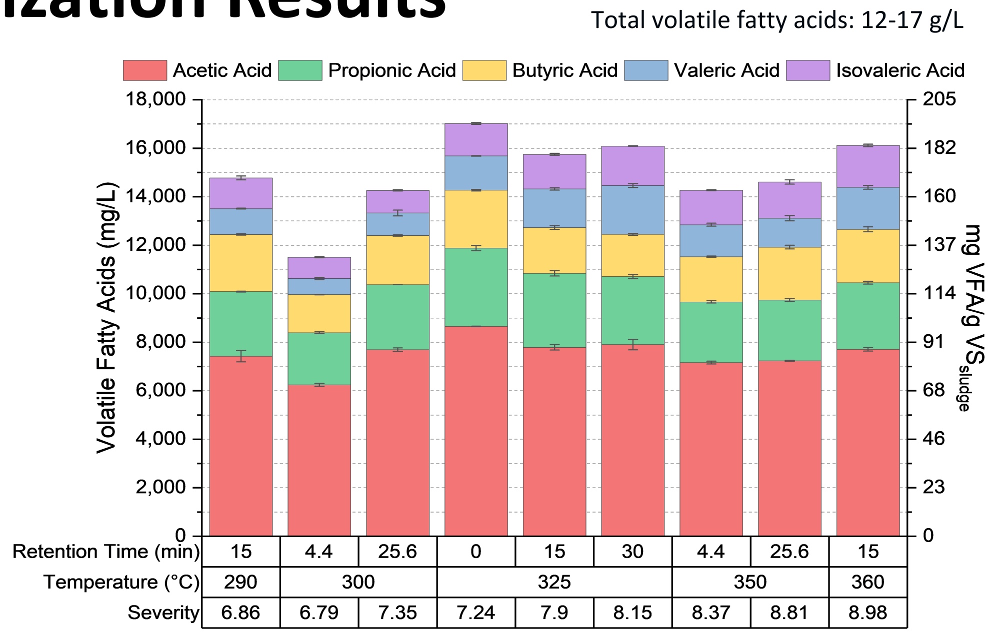


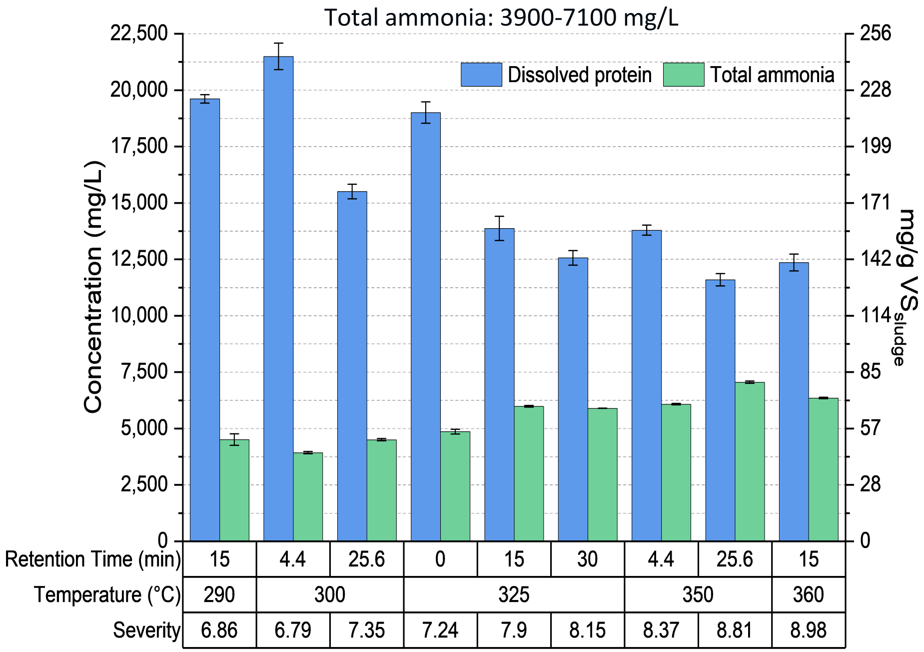
Continuous-flow reactor studies:

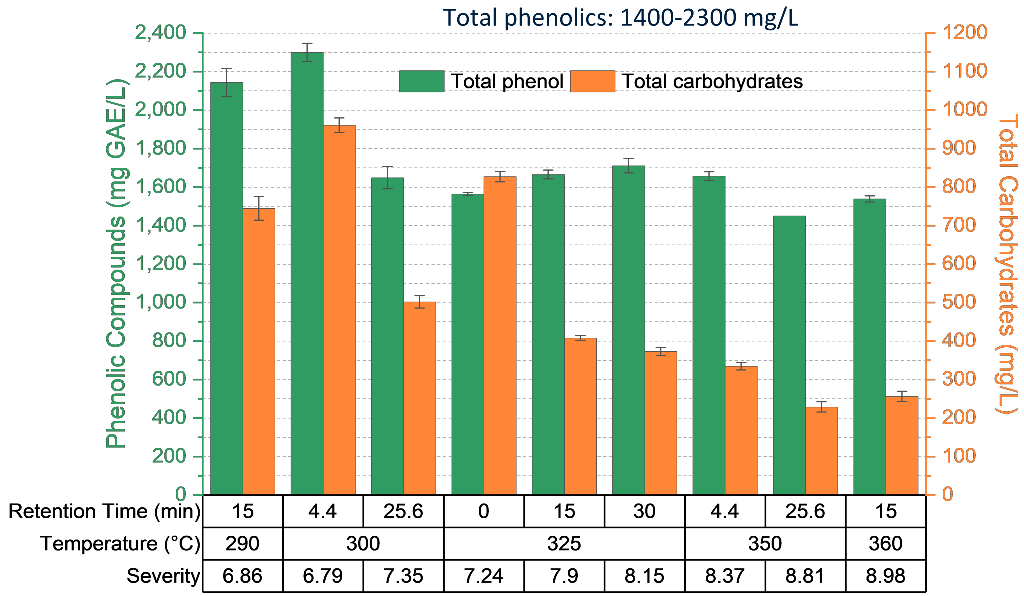
- Mesophilic and thermophilic anaerobic digestion and co-digestion
- Activated sludge process operation

HTL Aqueous Characterization Results



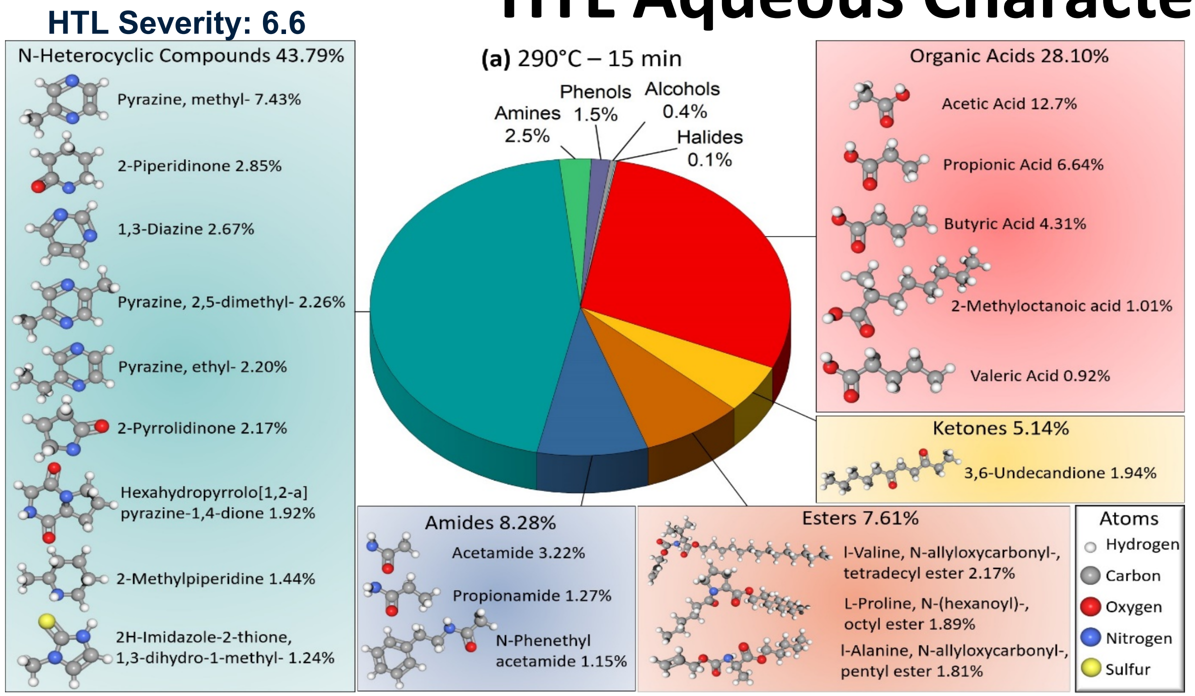


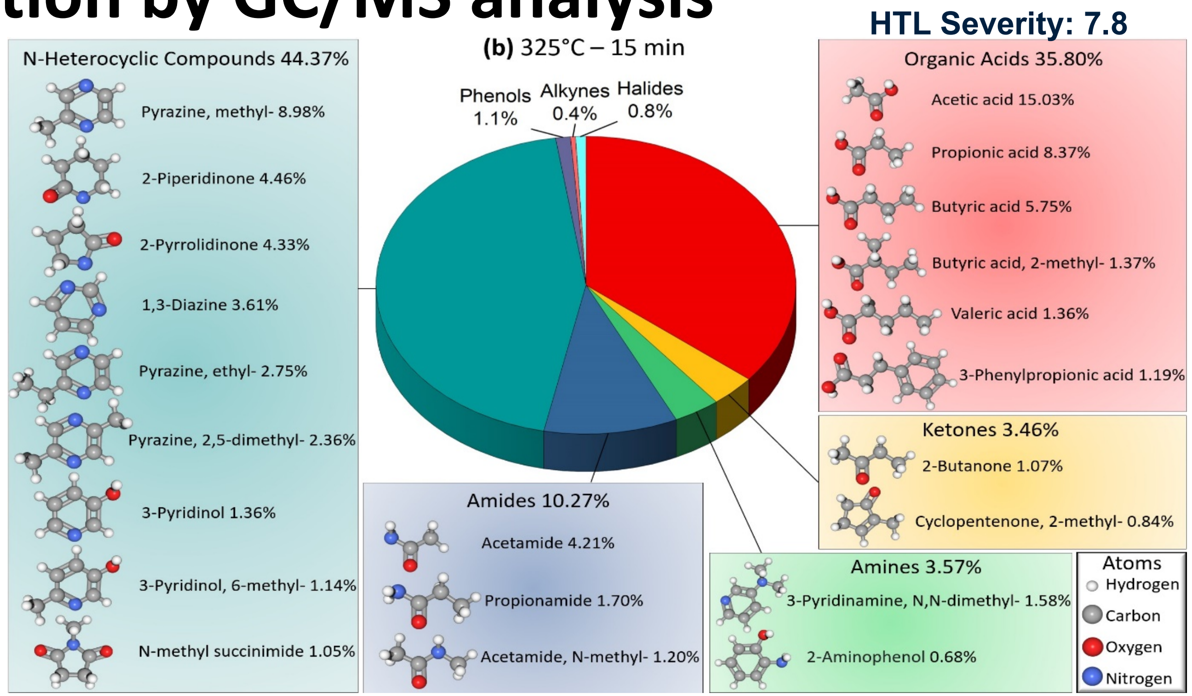


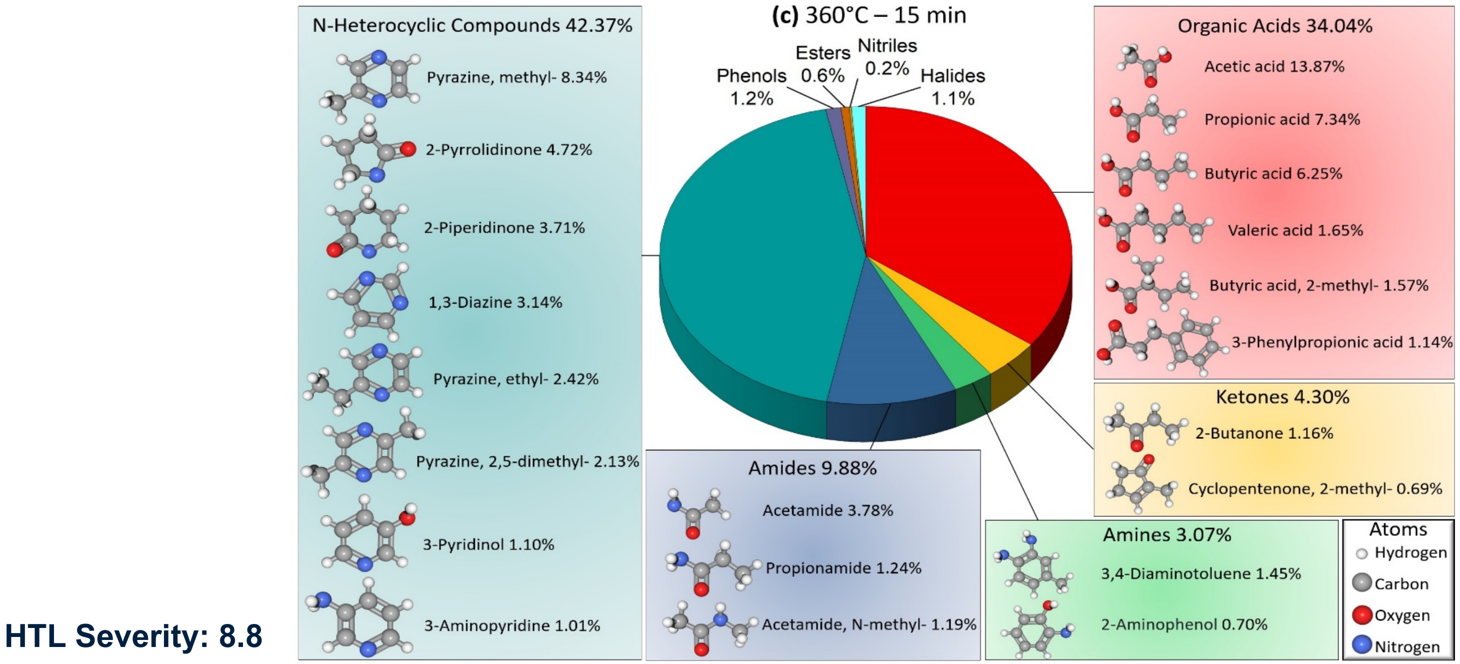


Basar, I.A., Liu, H., Eskicioglu, C., 2023. Chem. Eng. Journal, *467, 143422*.

HTL Aqueous Characterization by GC/MS analysis



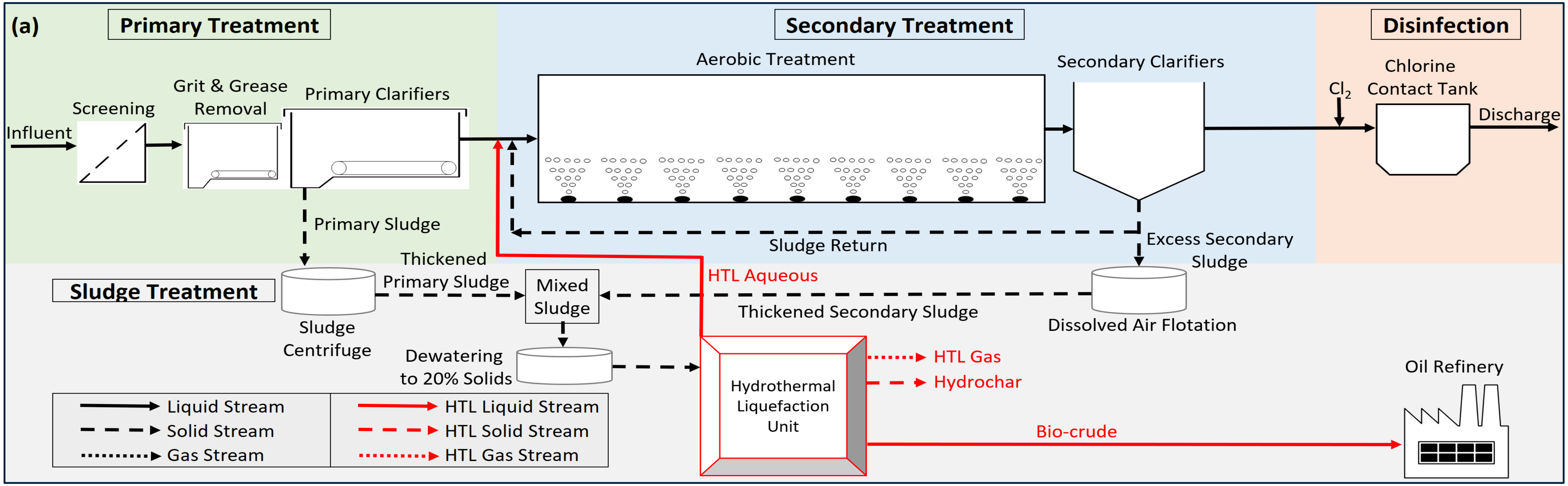


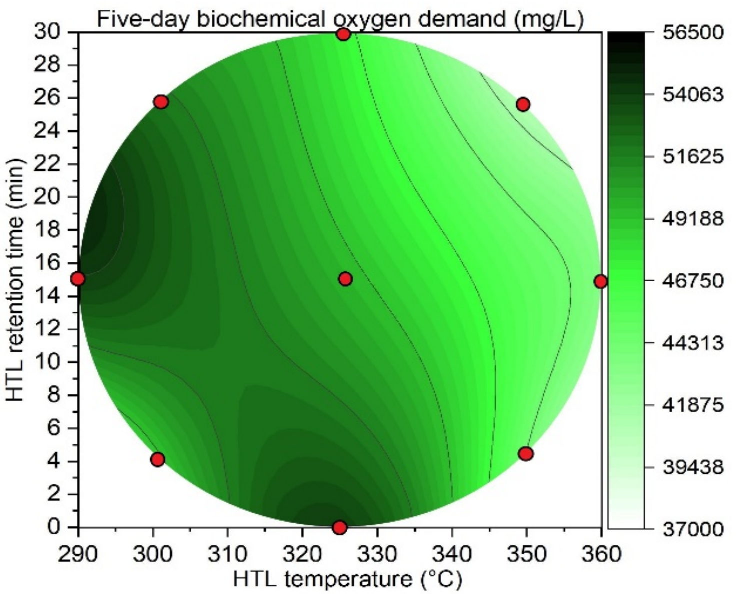


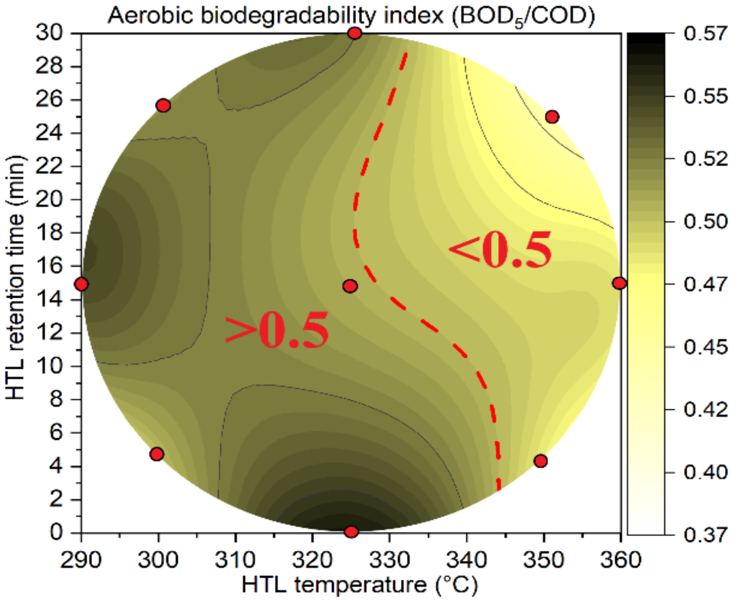
- **N–heterocyclic** compounds is the **most abundant** at all **3 HTL severities**!
- Form during Maillard reactions of reducing **sugars** and **amino acids**
- High cytotoxicity and low biodegradability!

Basar, I.A., Liu, H., Eskicioglu, C., 2023. Chem. Eng. Journal, *467, 143422*.

Onsite Aqueous Treatment Scenario 1: Aerobic Treatment







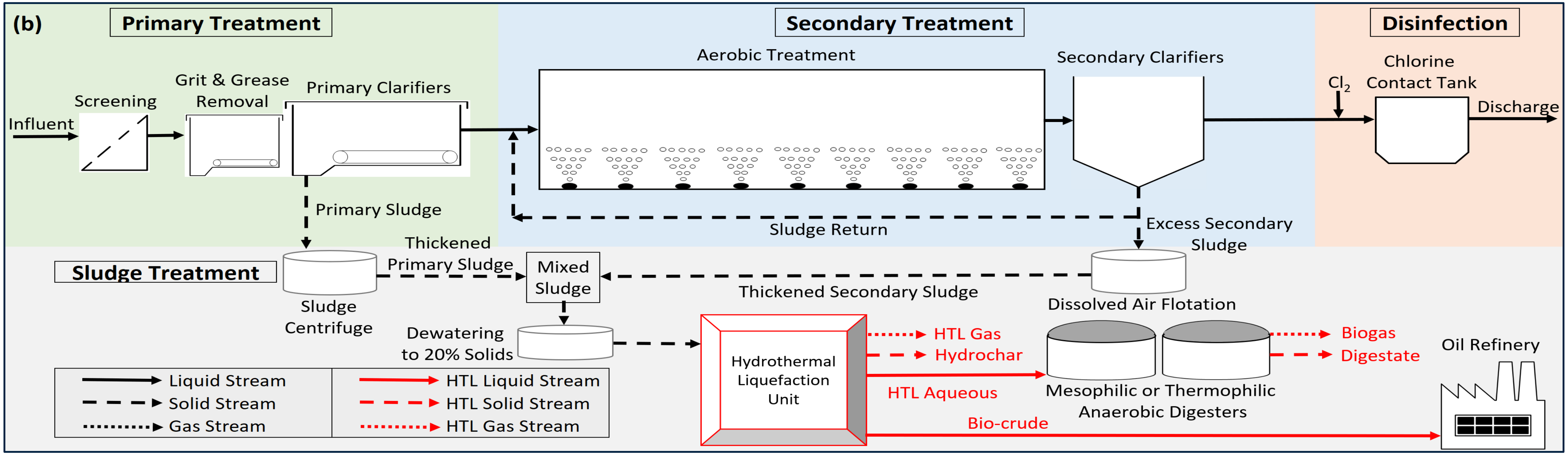
44-56% aerobic (20°C) degradability

T<340°C found to be readily aerobically biodegradable (index > 0.5).

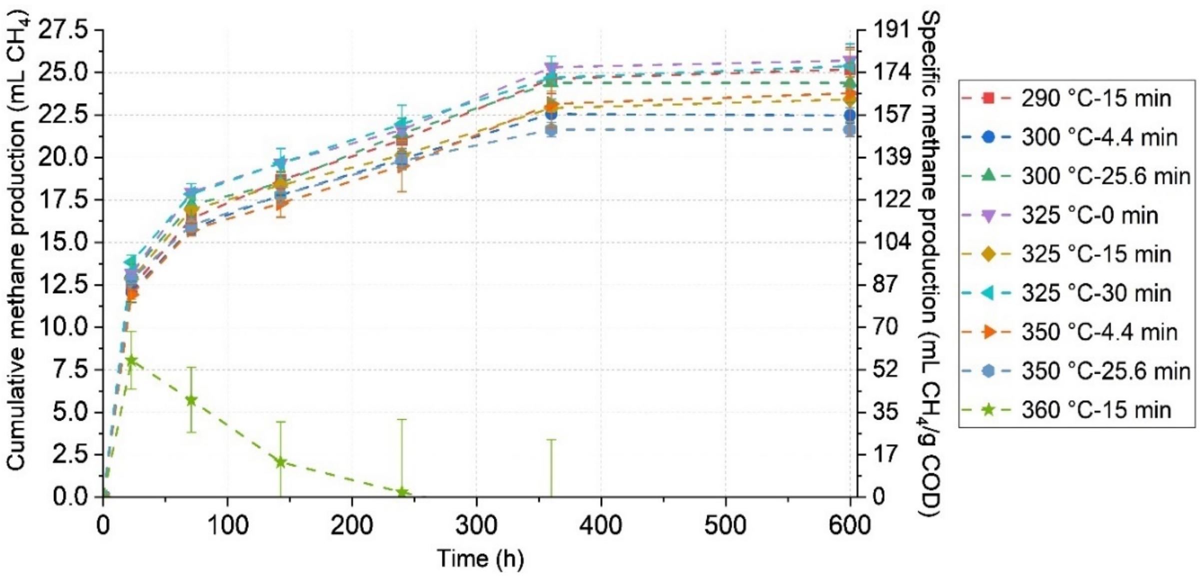
As HTL **intensity increases**, the extent of aerobic **biodegradability decreases** due to increase of inhibitory compounds in aqueous.

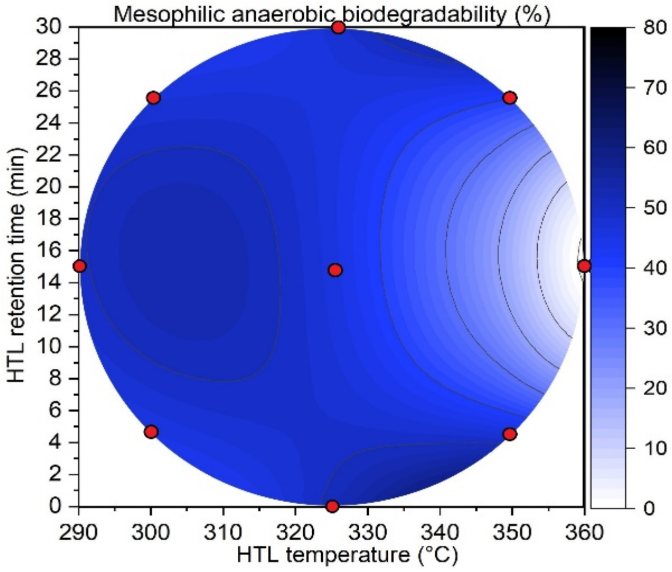
Basar, I.A., **Stokes, A.** Eskicioglu, C., 2024. Water Res., *252, 121206*

Onsite Aqueous Treatment Scenario 2: Mesophilic Anaerobic Treatment



BMP assay: Food to Microorganism Ratio: 0.25 g $COD_{aqueous}$ /g $VS_{inoculum}$





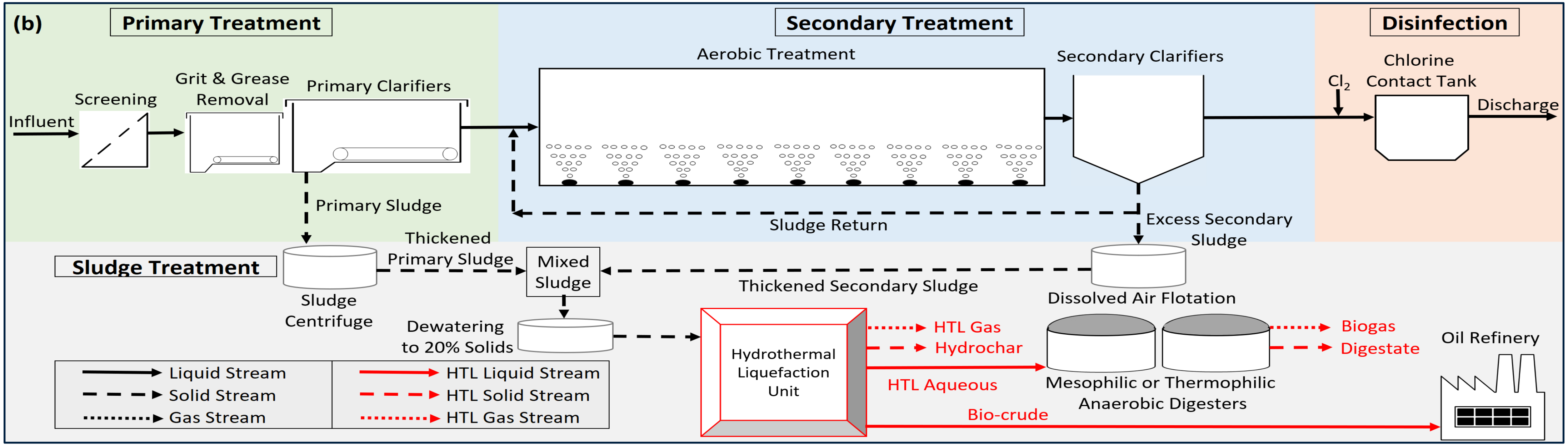
As HTL **intensity increases,** anaerobic **biodegradability decreases, similar to aerobic assays.**

5-50% mesophilic (35°C) degradability.

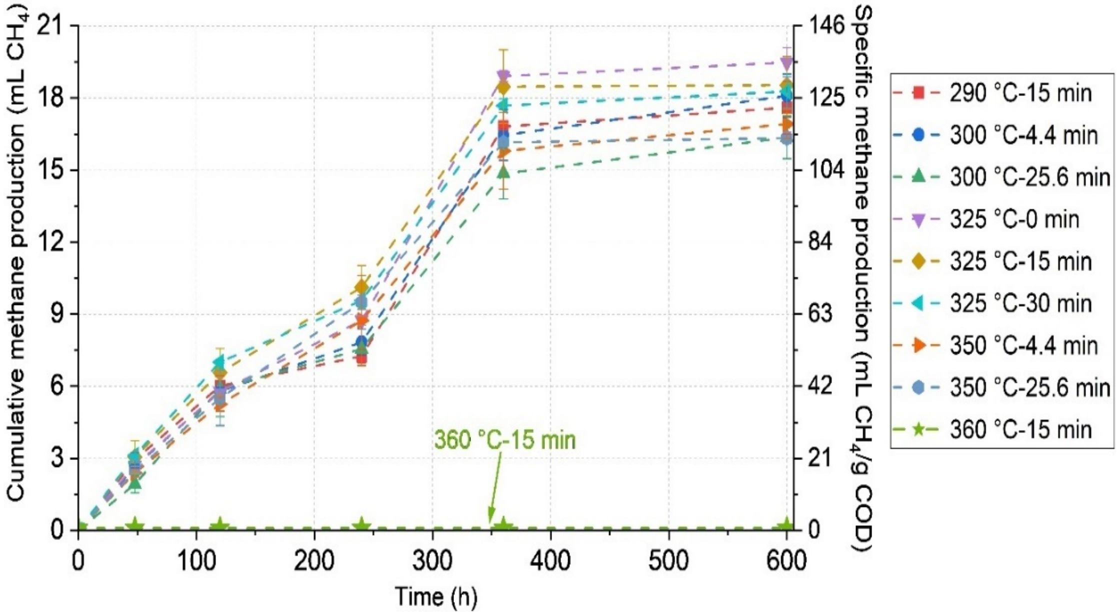
T=360°C unsuitable for AD.

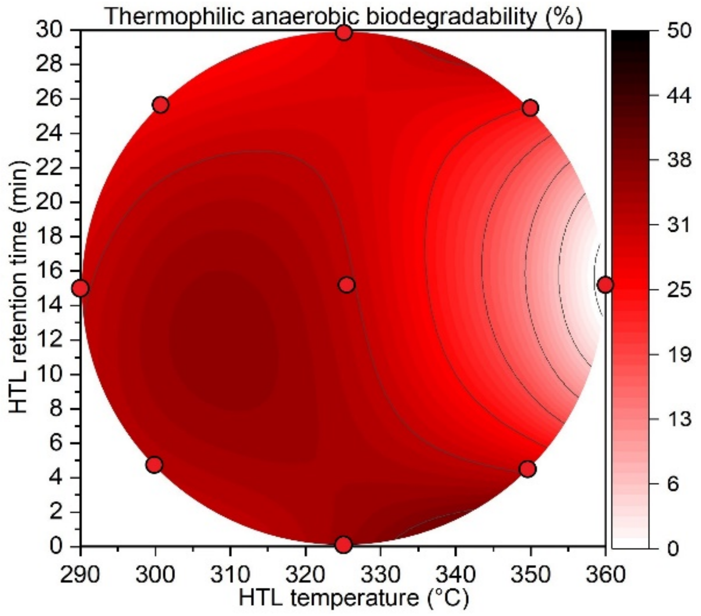
Basar, I.A., Stokes, A. Eskicioglu, C., 2024. Water Res., *252, 121206*

Onsite Aqueous Treatment Scenario 3: Thermophilic Anaerobic Treatment



BMP assay: Food to Microorganism Ratio: 0.25 g $COD_{aqueous}$ /g $VS_{inoculum}$





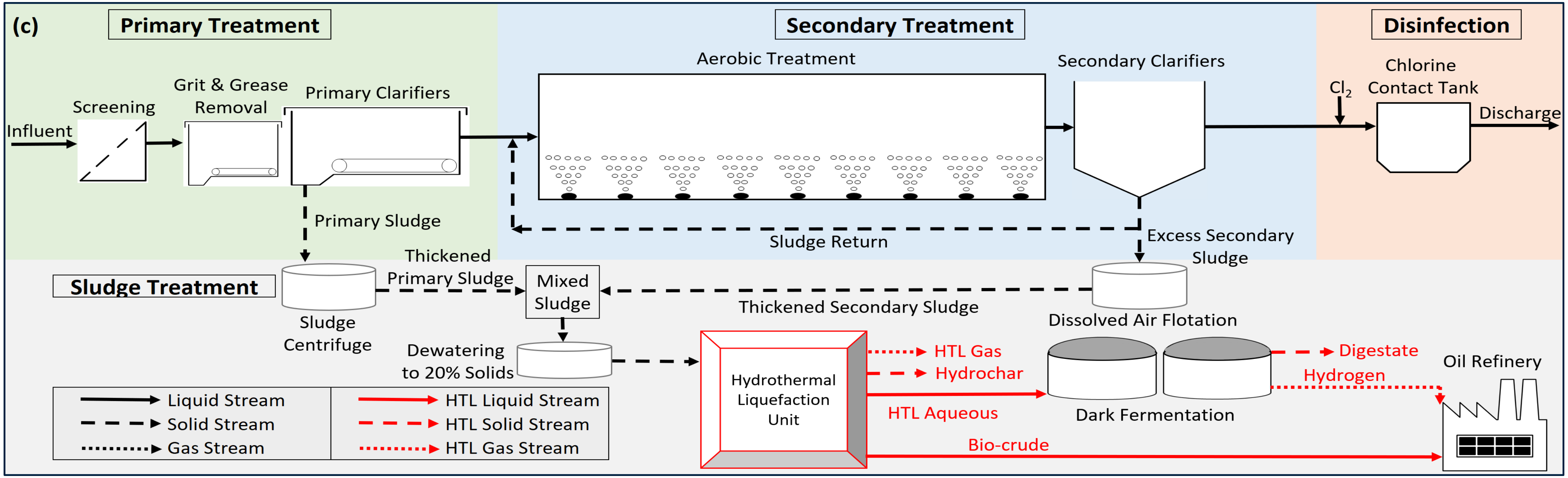
2-35% thermophilic (55°C) degradability.

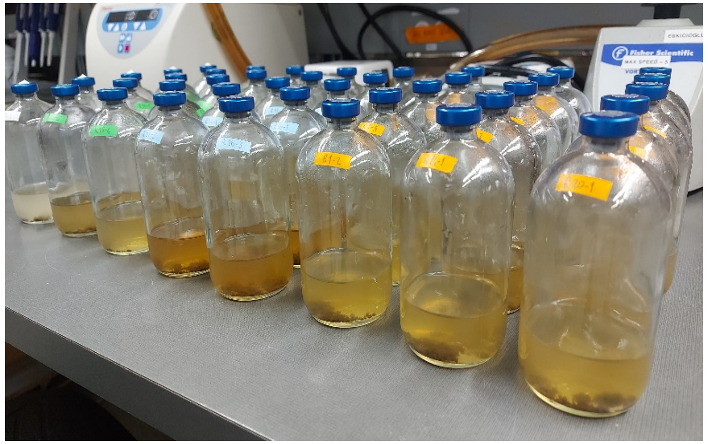
Thermophilic cultures are more sensitive to HTL inhibitors due to narrower microbial diversity.

T=360°C unsuitable for AD.

Basar, I.A., **Stokes, A**. Eskicioglu, C., 2024. Water Res., *252, 121206*

Onsite Aqueous Treatment Scenario 4: Dark Fermentation Treatment





Biochemical Hydrogen Potential (BHP) assays

Food to Microorganism Ratio: 10 g $COD_{aqueous}$ /g $VSS_{inoculum}$

No hydrogen could be detected in mesophilic (35°C) BHP assays utilizing HTL aqueous due to:

- Low readily biodegradable sugars left in HTL aqueous
- High total ammonium nitrogen
- Presence of other inhibitory compounds

Basar, I.A., **Stokes, A**. Eskicioglu, C., 2024. Water Res., *252, 121206*

Other HTL Aqueous Treatment Research at Bioreactor Technology Group

HTL aqueous pre-treatment for detoxification **and enhanced biological treatment**:

- *Adsorption* of HTL aqueous by GAC, biochar, hydrochar + biological treatment[1]
- *Ammonia stripping/recovery* from HTL aqueous + biological treatment[2]
- *Ozone treatment* of HTL aqueous + biological treatment
- *Hydrogen peroxide* treatment of HTL aqueous + biological treatment

Long-term (> 1 year) continuous-flow **bioreactor assessment of HTL aqueous**:

- Anaerobic co-digestion of HTL aqueous with municipal sludge, dewatering centrate, sludge[3]
- Returning HTL aqueous to activated sludge process for co-treating with domestic wastewater[4]

[1]**Aktas, K.,** 2024., *M.A.Sc. Thesis, University of British Columbia, Canada.*

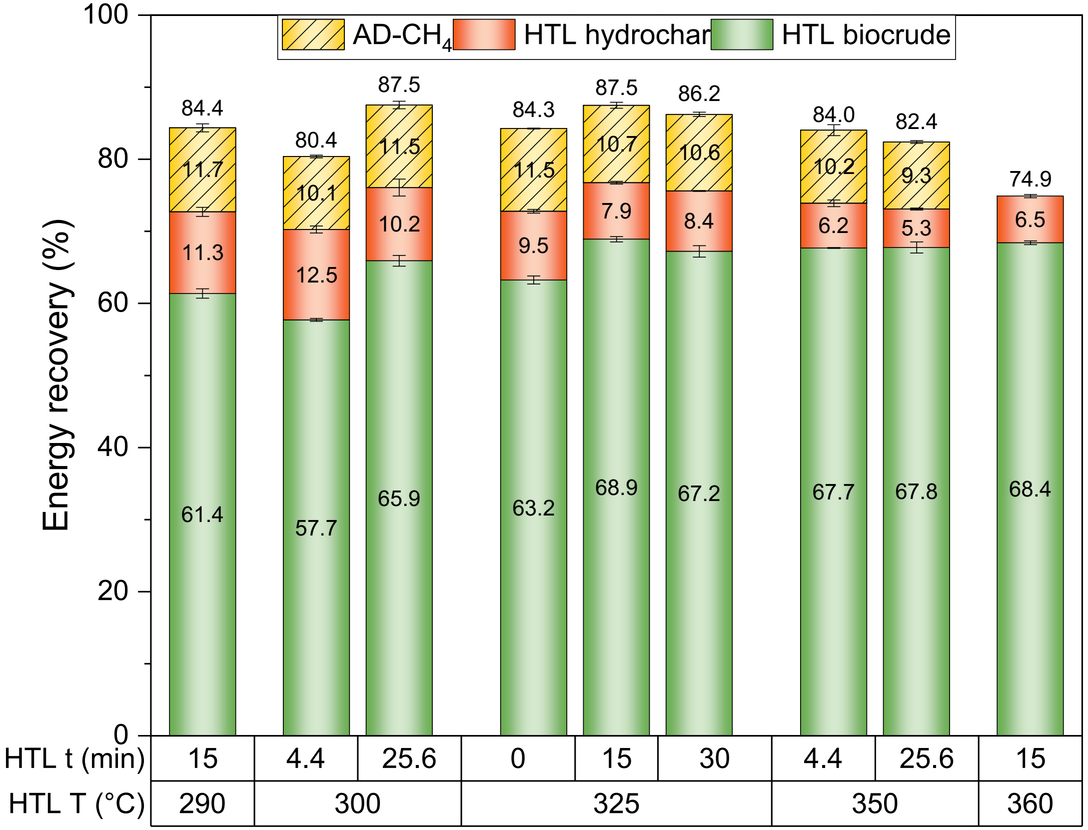
[2]**Cox, A**., 2024., *M.A.Sc. Thesis, University of British Columbia, Canada.*

[3]**Azarmina, N**., 2023., *M.A.Sc. Thesis, University of British Columbia, Canada.*

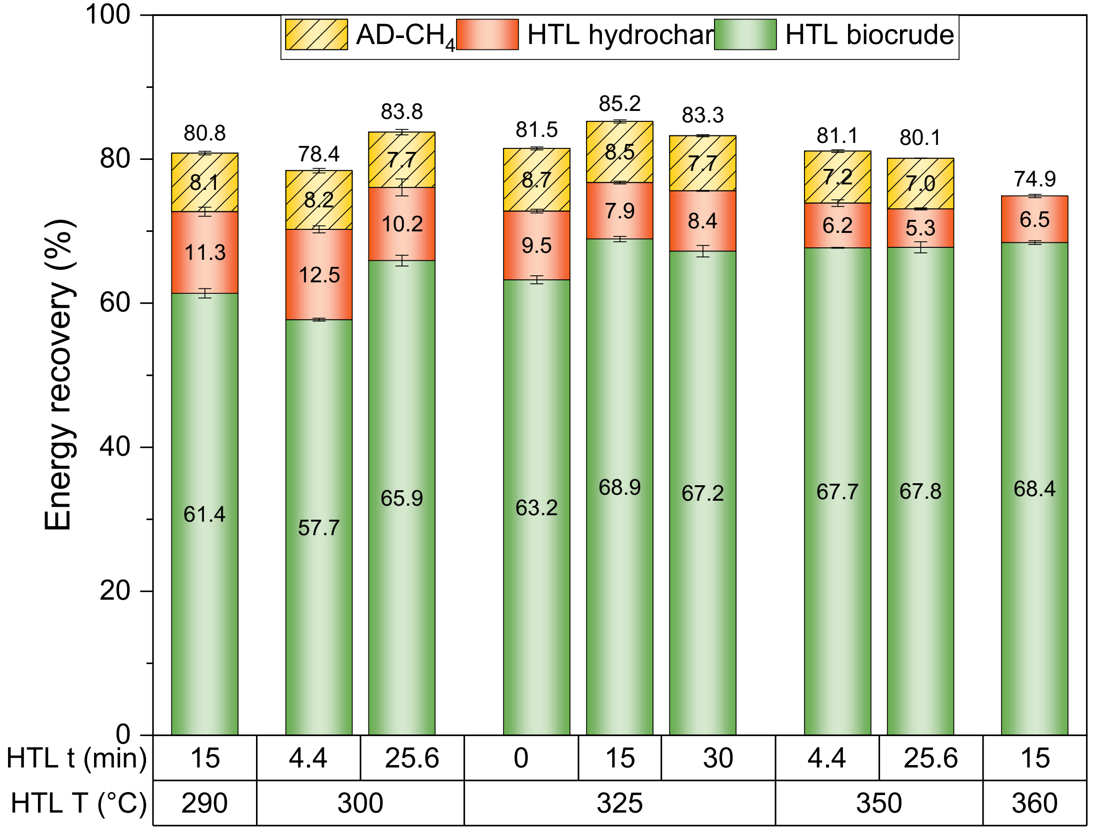
[4]**Basar, I. A.**., 2024., Ph.D. *Thesis, University of British Columbia, Canada.*

Energy Recovery from Mixed Sludge by HTL Coupled with Anaerobic Digestion

HTL - Mesophilic (35°C) AD



HTL - Thermophilic (55°C) AD



- **Up to 88% energy can be recovered as various biofuels from mixed sludge by using HTL coupled with mesophilic AD.**

$$Energy\ recovery\ (\%) = \frac{Mass_{product} \times HHV_{product}}{Mass_{sludge} \times HHV_{sludge}}$$

Feedstock: Dewatered mixed sludge to 20% TS by wt. Mixed sludge had a PS:SS mixing ratio of 48:52% TS by wt.
PS: Primary sludge, SS: Secondary sludge, AD: anaerobic digestion, HTL: hydrothermal liquefaction.
T: reaction temperature, t: residence time, HHV: higher heating value.

Liu, H., Basar, I.A., Lyczko, N., Nzihou, A., Eskicioglu, C., 2023: WEFTEC 2023 - 96th Annual Water Environment Federation Technical Exhibition and Conference. Water Environment Federation. https://doi.org/10.2175/193864718825159036

Summary of Results

- In a range of 290-360^{o}C, 0-30 min, the optimum HTL conditions for maximum biocrude recovery from dewatered mixed sludge were identified as 325-342^{o}C and 11-20 min.
- HTL aqueous contains high levels of COD, VFAs, ammonia along with a wide range of N-heterocyclic and phenolic compounds limiting its aerobic (20^{o}C), mesophilic (35^{o}C) anaerobic and thermophilic (55^{o}C) anaerobic biodegradability of 56%, 50% and 35%, respectively.
- HTL aqueous is unfit for biohydrogen production.
- As HTL severity increases, the extent of aerobic and anaerobic biodegradability decreases due to increase of inhibitory compounds in aqueous.
- Thermophilic cultures are less tolerant to HTL aqueous, than their mesophilic counterparts due to reduced microbial diversity at elevated temperatures.
- Total energy recovery from mixed sludge could reach 88% if the HTL aqueous phase was successfully utilized in mesophilic digesters.

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Thank You