Hydrothermal Carbonization: A Thermochemical Pathway to Convert Wastes to Conversion-ready Feedstocks

FLORIDA TECH
FLORIDA'S STEM UNIVERSITY™

Presenter: Toufiq Reza

Assistant Professor of Chemical Engineering

Biomedical and Chemical Engineering and Sciences

Florida Institute of Technology, Melbourne, FL 32901

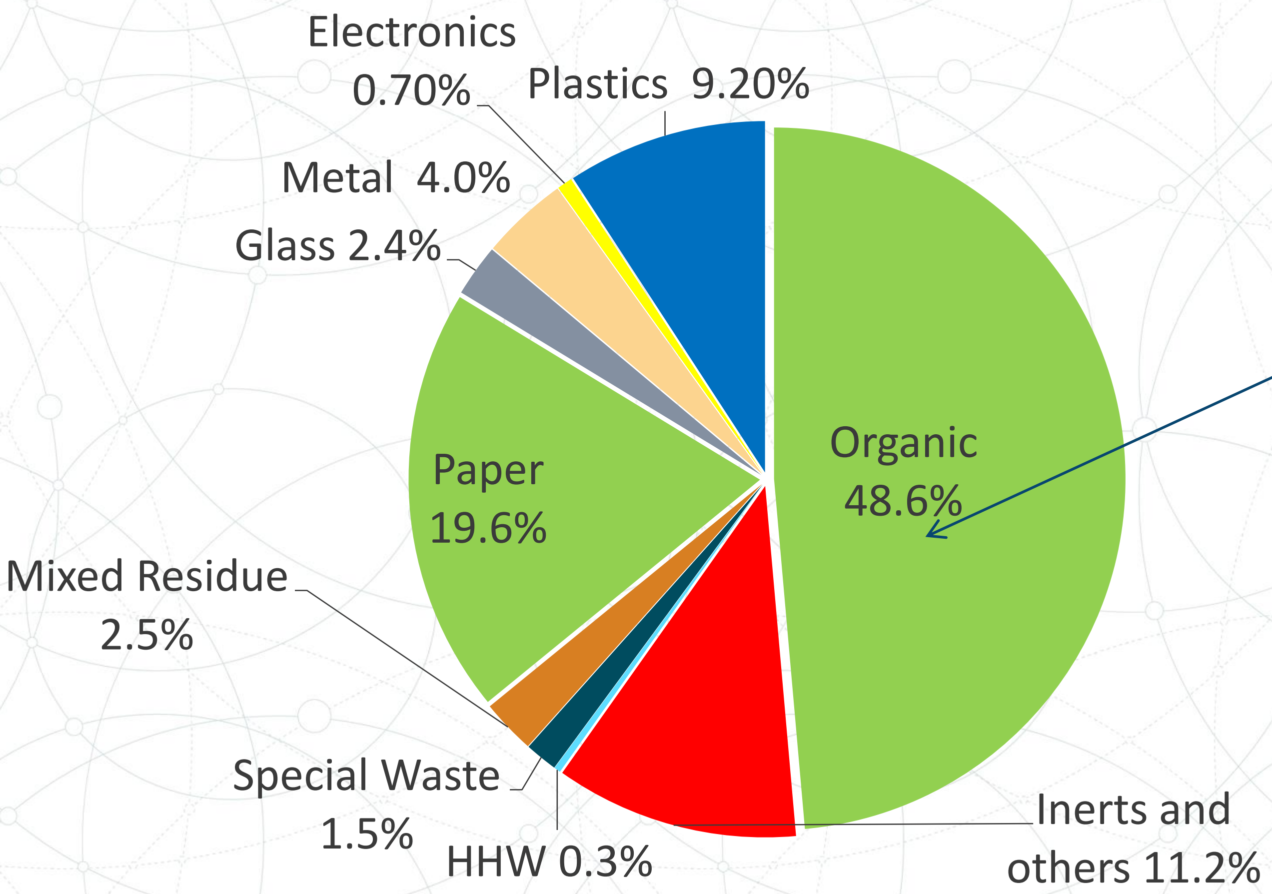
BETO Workshop

Advancing the Bioeconomy: From Waste to Conversion-Ready Feedstocks

Arlington, VA

February 19, 2020

Heterogeneity of MSW
Example: California



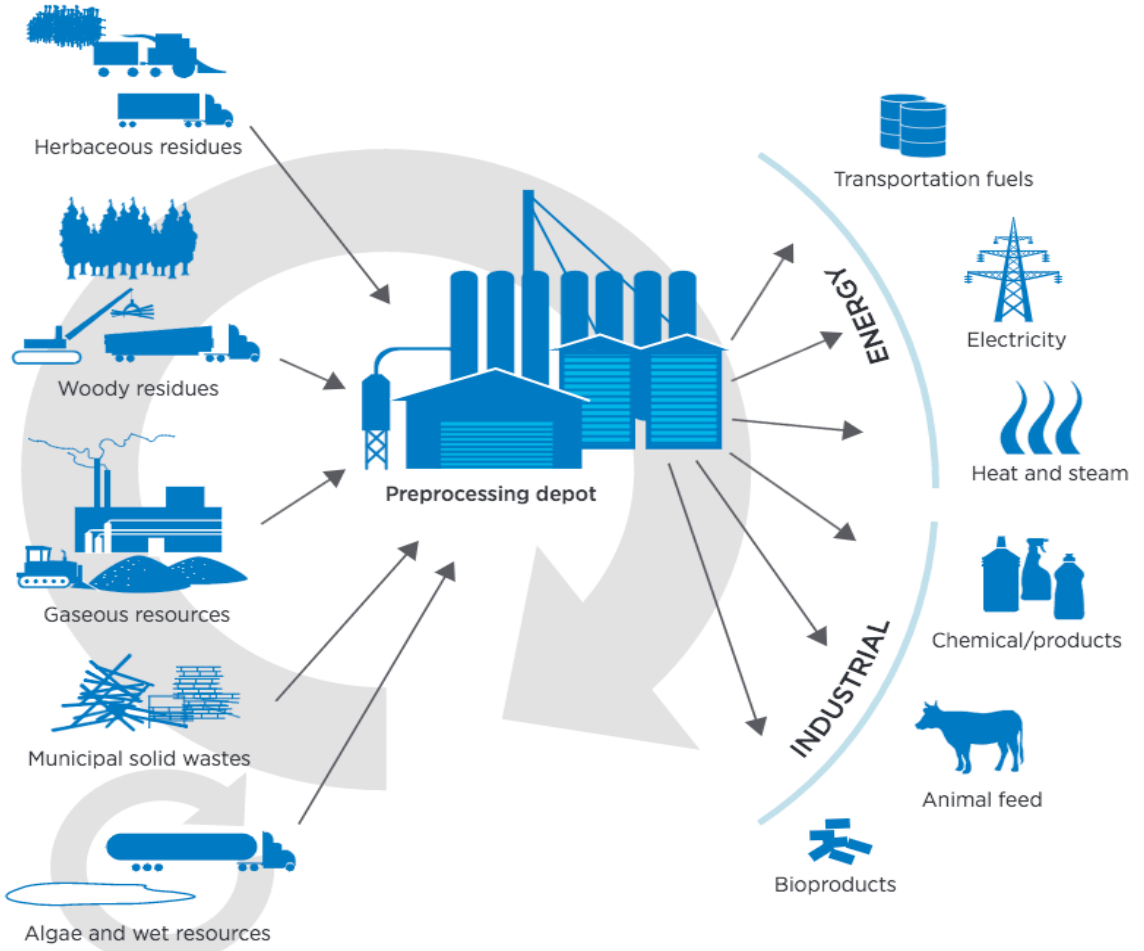
"Organic waste" is :

- food waste
- green waste
- pruning waste
- wood waste
- food-soiled paper waste mixed in with food waste

Associates, E. S. *Waste characterization study. Prepared San Francisco Department of the Environment.*; **2006**.

Problems associated with MSW

1. Heterogeneous
2. High water content
3. Poor mechanical dewaterability
4. High ash content
5. Low bulk density
6. Low friability
7. Contaminated with organic and inorganic contaminants



Preprocessing of diverse biomass concept proposed by INL

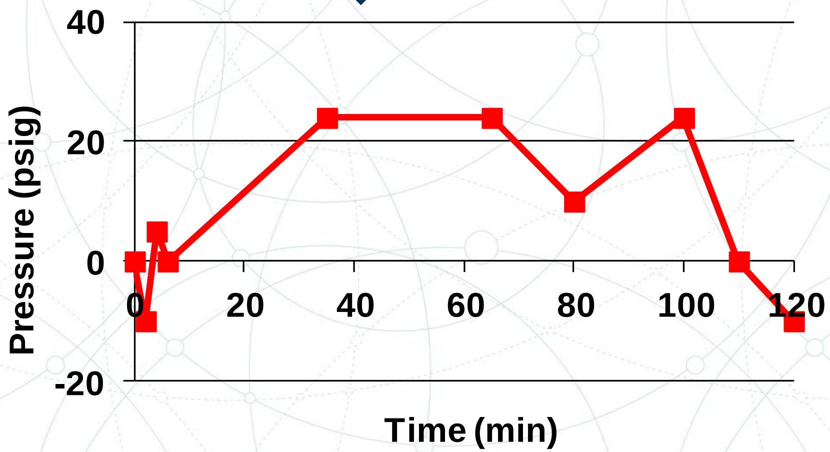
Billion ton update: Biomass Supply for a Bioenergy and Bioproducts Industry; OAK RIDGE NATIONAL LABORATORY: 2016

Sorting/Metal Recovery

Materials Recovery

- **More than 300 facilities in the US**
- **Operated by Waste Management, Republican Services, and Waste connections**
- **Primarily designed for recycle metals and glass**
- **Organic fraction of waste is still a liability**

Feedstock (unsorted MSW) preparation



Holtman, K. M. et. al. *Waste Management & Research* **2015.**

Size separated autoclave products

Biogenic fraction
MSW pulp (<3/8”)

Non-biogenic fraction
(1”+)

Comparison of Various Pretreatment Processes

- **Energy Input (KWh t^{-1})**
- **Autoclave/thermal hydrolysis, grinding/mechanical, and microwave**
- **Grinding or physical homogenization takes lower energy for further enhancement**
- **Microwave is the most energy extensive route**

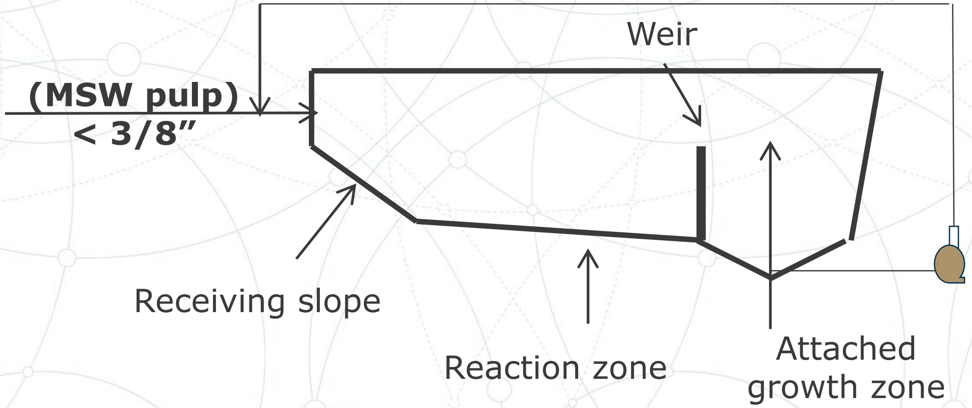
Fan, Y.V.et.al. *J of Env Manag.* 2018, 223, 888-897

FLORIDA TECH

Anaerobic Digestion

USDA pilot AD system

1500 gal high solids anaerobic digester (20 % solids)



back

front

VS content increases, NVS content decreases

Mass and H_2O balance

87 dry lb TS

- 63 lb VS
- 24 lb NVS
- 2440 lb H2O (293 gal)

157,800 L CH_4

511 gal H_2O (4262 lbs)

Anaerobic Digestion

4689 lb wet pulp

- 1630 lb TS
- 1214 lb VS
  - -473 lb cellulose
  - -176 lb hemicelllose
  - -406 lb sCOD
  - -145 lb acid insoluble mat'l (i.e., lignin)
- 416 lb NVS
- 3059 lb H2O (367 gal)

3144 lb wet digestate

- 825 lb TS
- 520 lb VS
  - -77 lb cellulose
  - -54 lb hemicellulose
  - - 80 lb dissolved solids
  - - 240 lb lignin
  - - 69 lb est. biomass/others
- 306 lb NVS
- 2319 lb H2O (367 gal)

817 gal H_2O (6814 lbs)

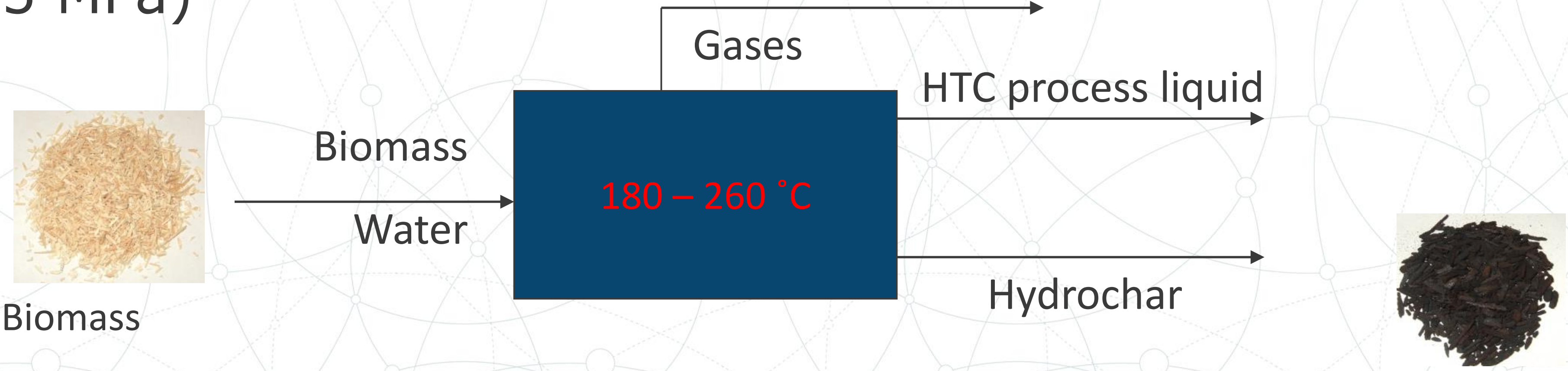
Holtman, K. M. et.al. *Bioresource Technology* **2015.**

FLORIDA TECH

Hydrothermal Carbonization

Hydrothermal Carbonization

- Hot compressed water (180 – 260 °C)
- Short contact time (< 20 min)
- High Pressure : vapor pressure of liquid water (1-5 MPa)



- M. Toufiq Reza, ProQuest, UMI Dissertation Publishing, July 2012. ISBN: 1249074398.
- J.G. Lynam, C.J. Coronella, W. Yan, M.T. Reza, V.R. Vasquez ", Bioresource Technology, 2011, 102, 6192-6199.
- J. G. Lynam, M. T. Reza, V. R. Vasquez, C. J. Coronella, Fuel 99:271-273 (2012)
- J. G. Lynam, M. T. Reza, Wei Yan, and Charles J. Coronella, In preparation for Bioresource Technology.

Advantages of HTC

1. Wet process
2. Enhance homogenization
3. Decontaminate wastes
4. Non-catalytic process
5. Straightforward process
6. Hydrophobic hydrochar resulting in ease of filtering
7. Soil amendment, and production of NPK fertilizer

Input

Wet biomass

HTC

Output

Hydrochar

A. A. Peterson, et. al. Energy Environ. Sci., vol. 1, no. 1, 2008, pp. 32–65, 2008.

Hydrochars

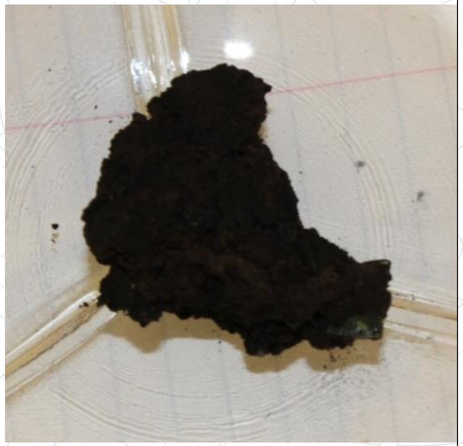
(a) Raw dry MSW digestate

(b) HTC 250 C 30 min MSW digestate hydrochar

(c) HTC 250 C 2 h MSW digestate hydrochar

(d) HTC 300 C 30 min MSW digestate hydrochar

(a) Raw dry MSW pulp

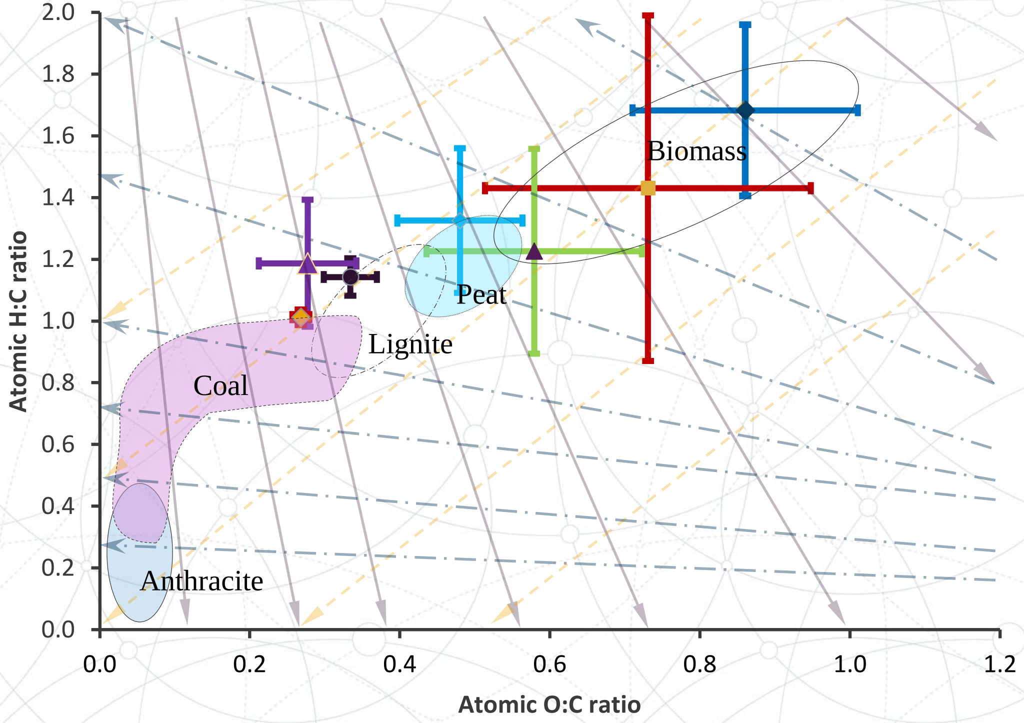


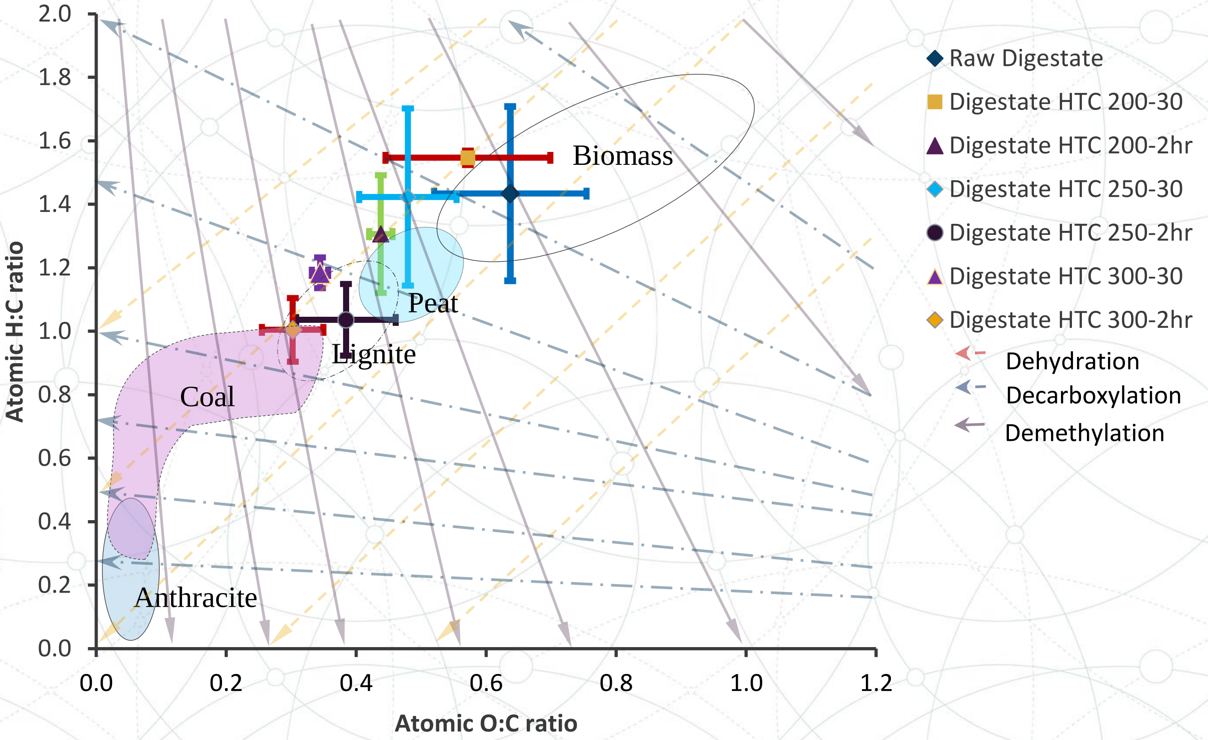
(b) HTC 250 C 30 min MSW pulp hydrochar

(c) HTC 250 C 2 h MSW pulp hydrochar

(d) HTC 300 C 30 min MSW pulp hydrochar

Van-Krevelen Diagram





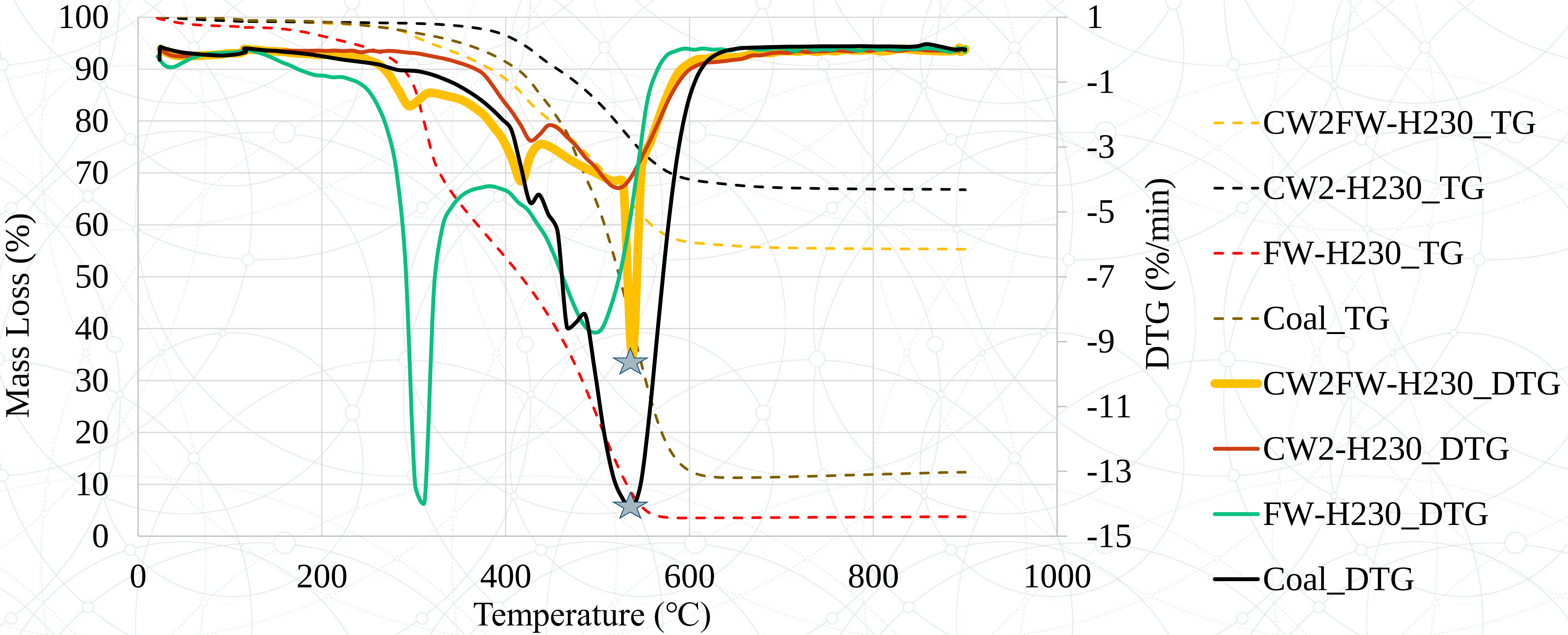
Reza, M.T. et al. ACS Sus Chem Engr, 2016, 4 (7), 3649-3658

Grindability

- Specific case for fibrous biomass
- HTC could improve grindability several times even when biomass is treated at 200 °C

Sharma, H.B. et al. Waste Management, Volume 91, Pages 108-119

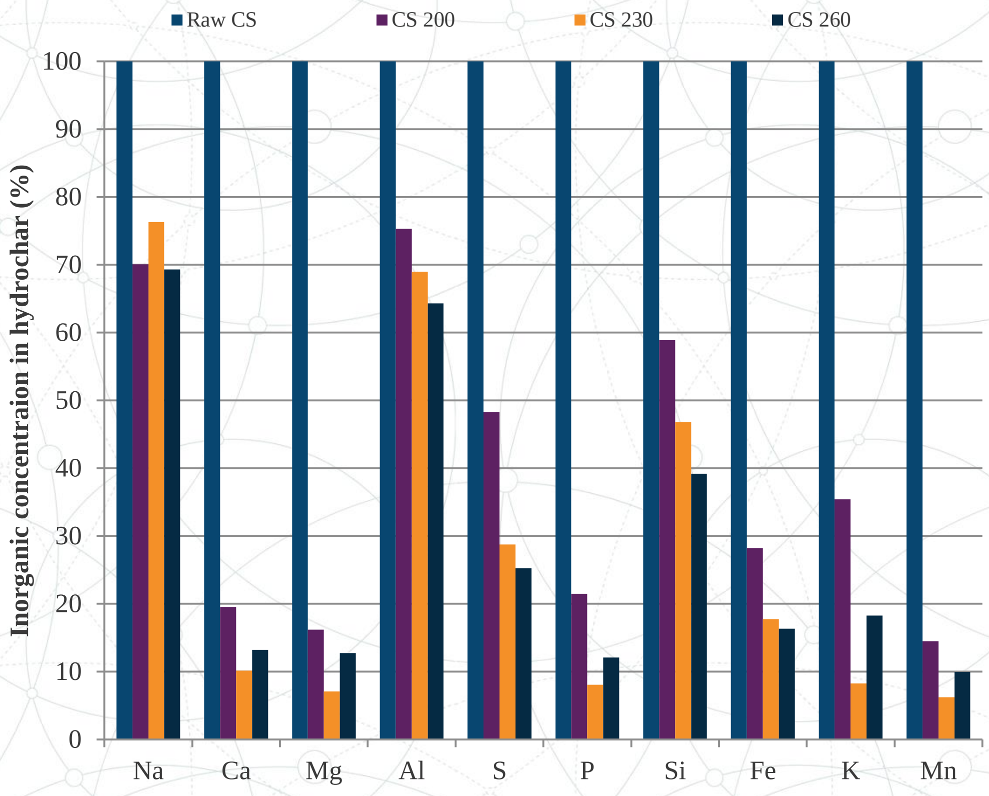
Combustion Characteristics

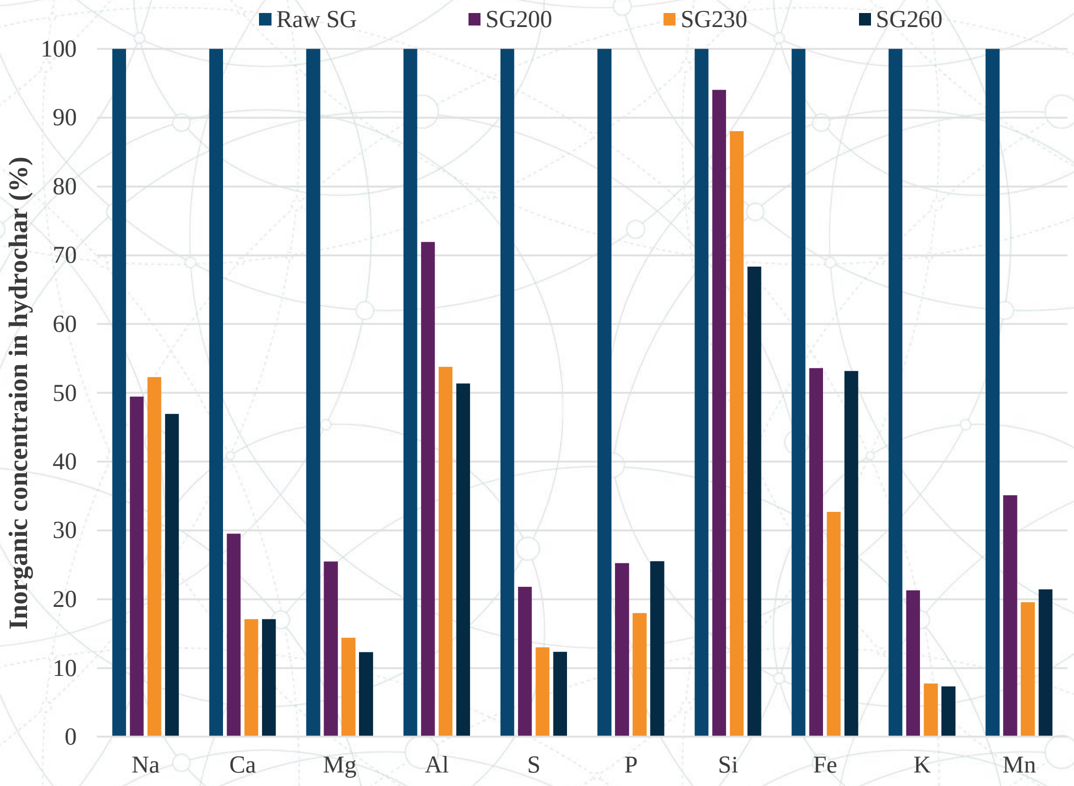


Combustion mass loss curves and DTG curves for untreated and HTC treated samples at 230 °C

Reza, M.T. et al. Waste and Biomass Valorization, under-review

Inorganics Leached From Biomass



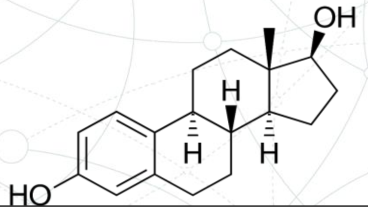


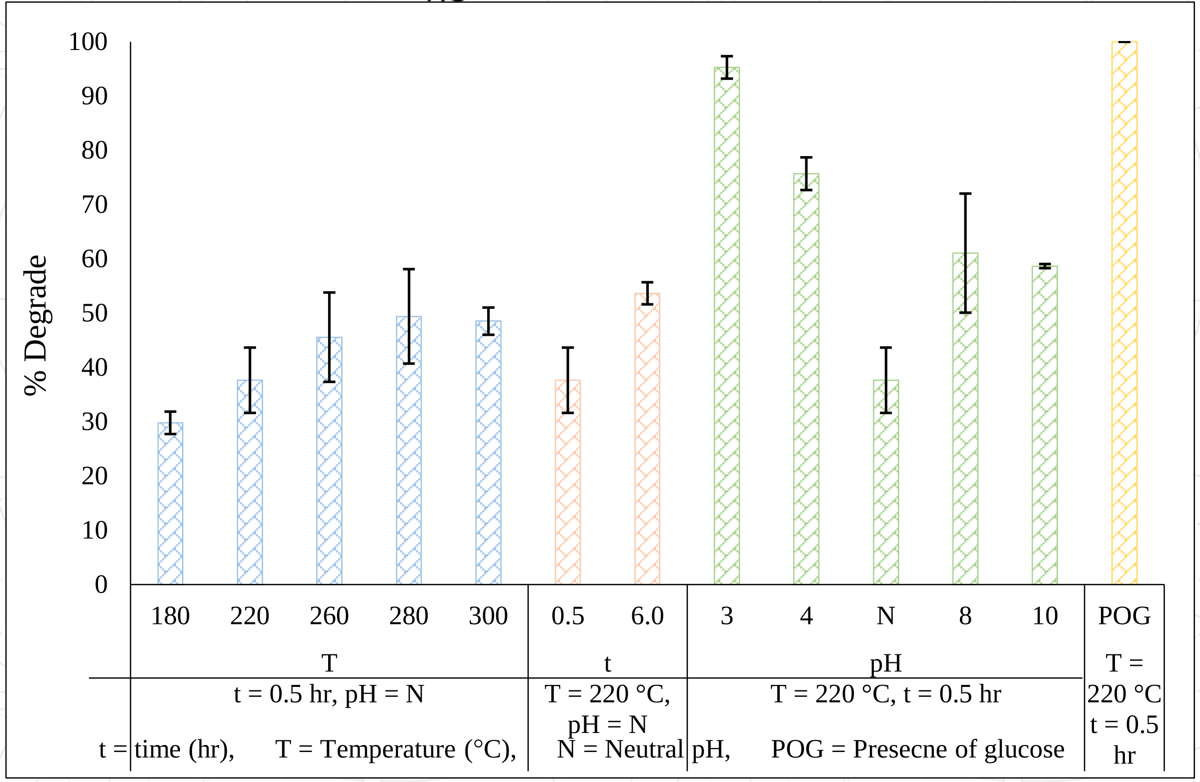
Leaching of specific inorganic elements during MHP at different temperatures for corn stover (left) and switch grass (right). Note that inorganic elements present in raw biomass is considered as 100%.

FLORIDA TECH

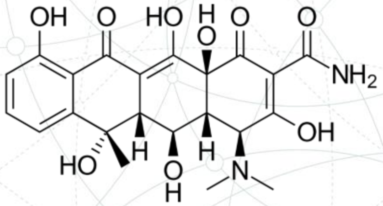
Degradation of Organic Contaminants

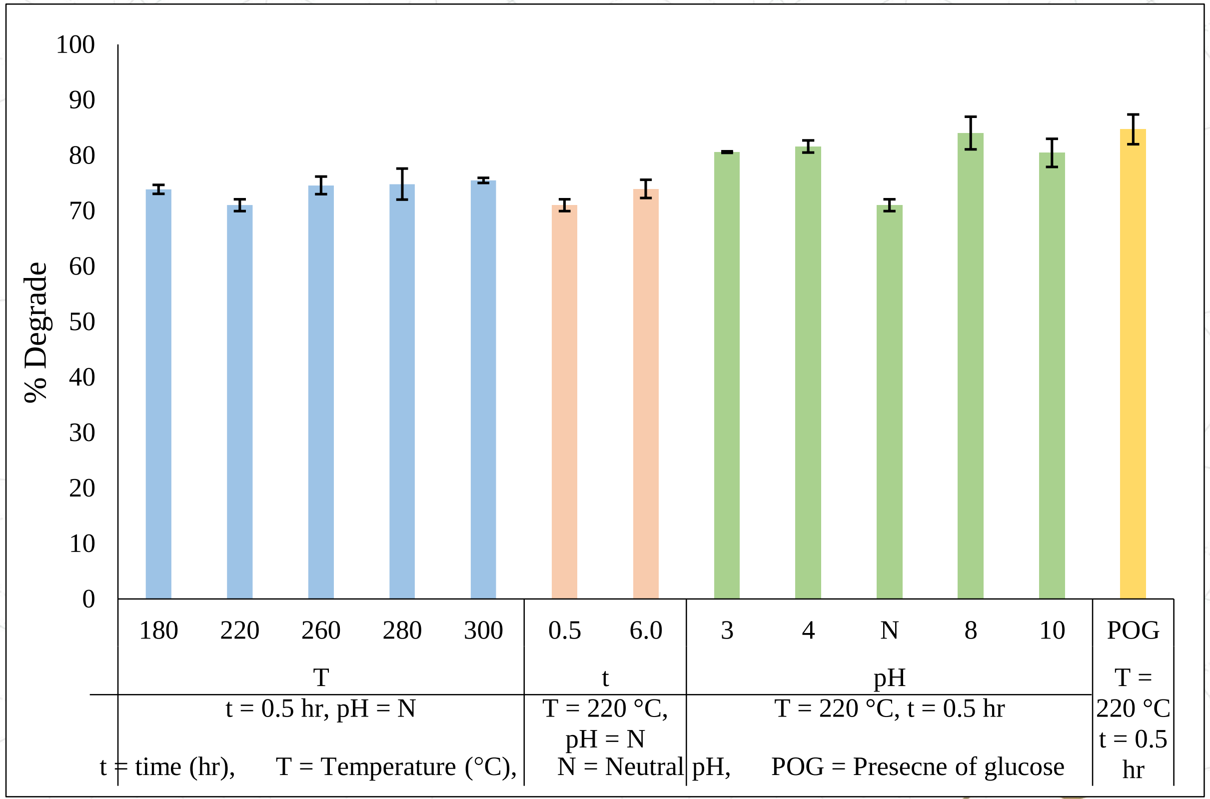
Estradiol





Oxytetracycline

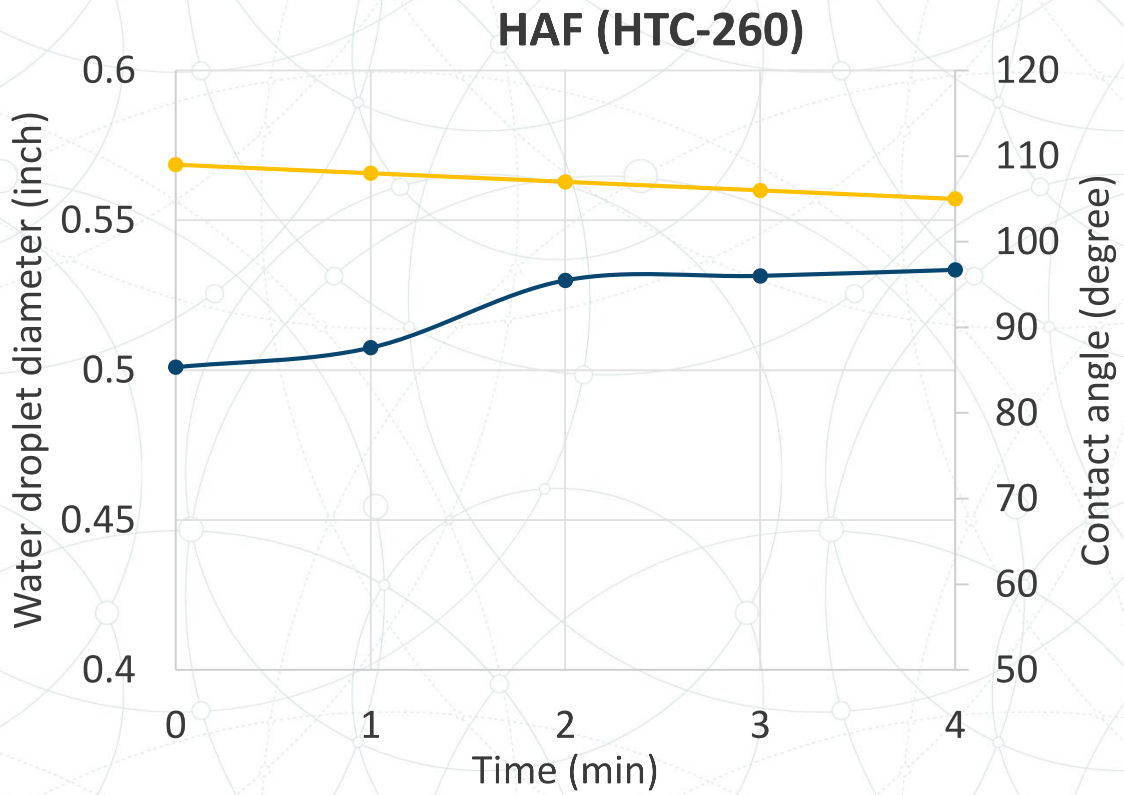


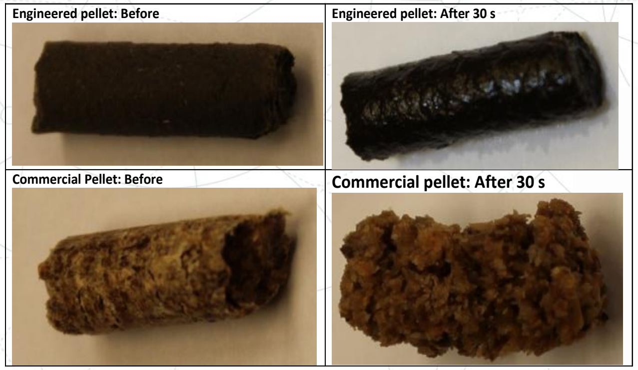


Saha, N. et al. SN Applied Science, under-review

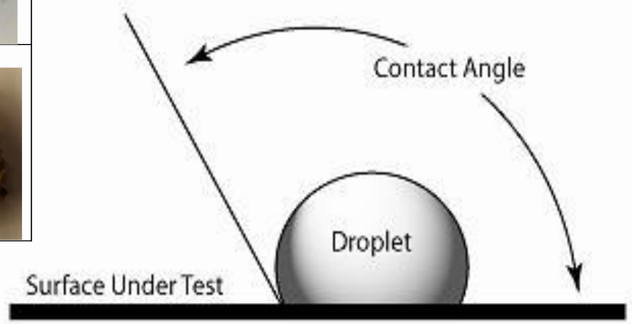
Dewaterability and Hydrophobicity

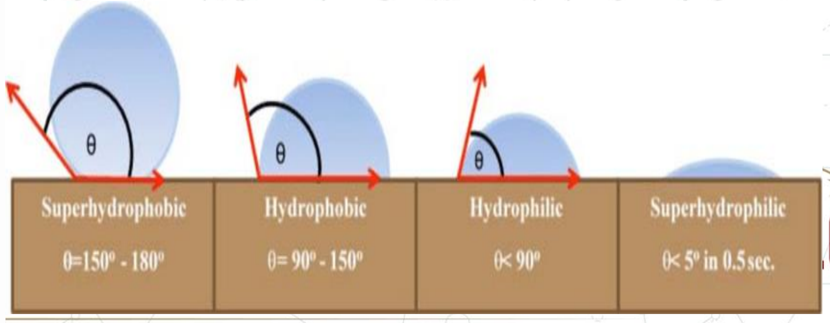
Sample	Initial dry matter (DM %)	After Centrifugation (DM%)	After Mechanical Pressing (DM %)
Sewage Sludge 1	30		37±0.5
Hydrochar_1_205_7	20	26	52±5.5
Sewage Sludge 2	10	21	30±1.4
Hydrochar_2_205_7	11	28	70±8.0





Escala, H.B. et al. Energy Fuels, 2013, 27,1, 454-460

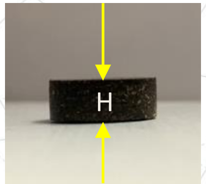




ORIDA TECH

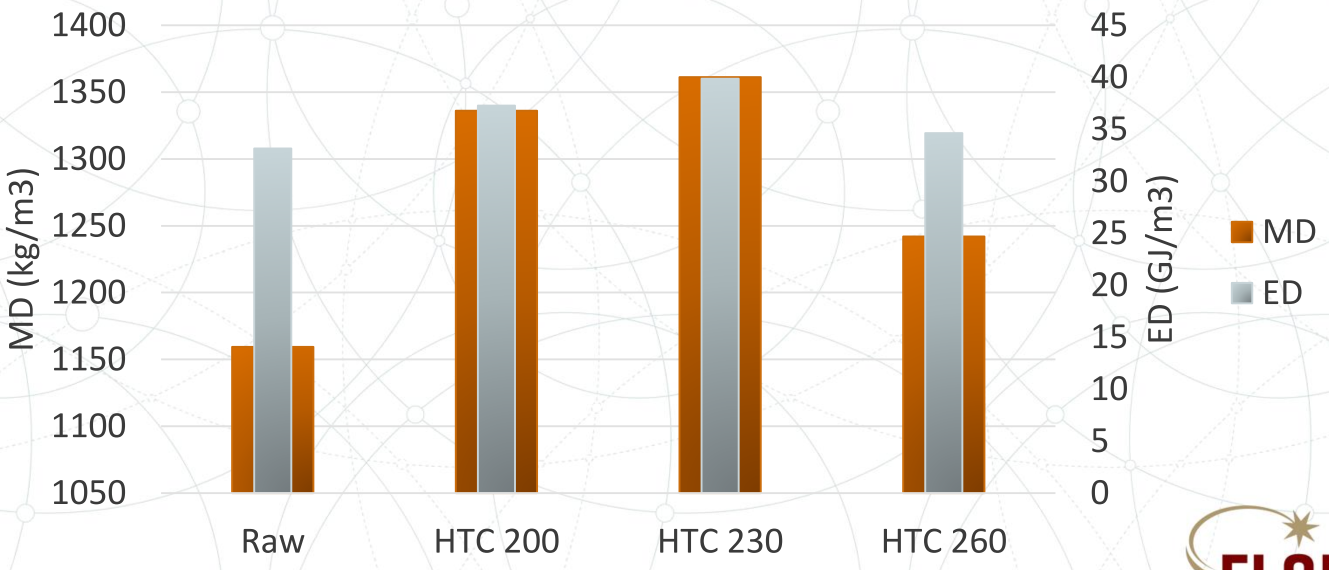
Mass and Energy Densification

Component	Density Range (kg/m^3)	Typical value (kg/m^3)
Food waste	120-480	290
Paper	30-130	85
Glass	160-480	195
Metal	120-1200	320
Uncompact MSW	90-180	130
Truck Compact	180-450	300
Well Compact MSW	600-750	600



$$MD = \frac{\text{weight of the pellet}}{\textit{volume of the pellet}}$$

$$EY = \text{MD of the pellet} \times \text{HHV of the pellet}$$

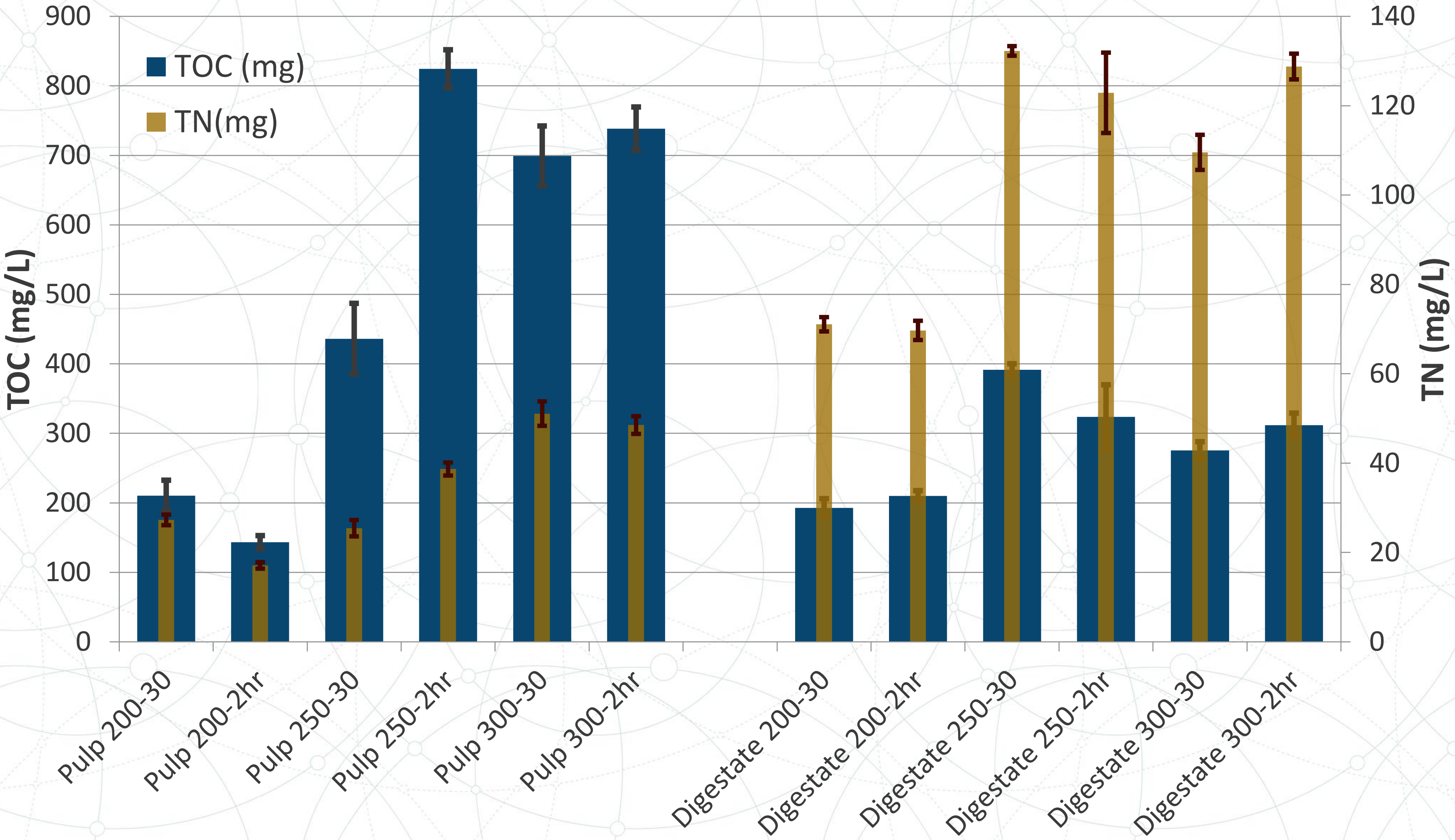


https://slideplayer.com/slide/10213265/

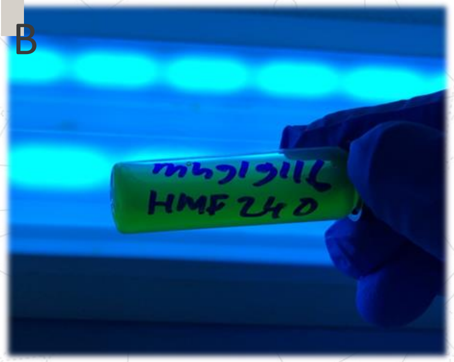
MY: Mass Yield EY: Energy Yield MD: Mass Density ED: Energy Density

FLORIDA TECH

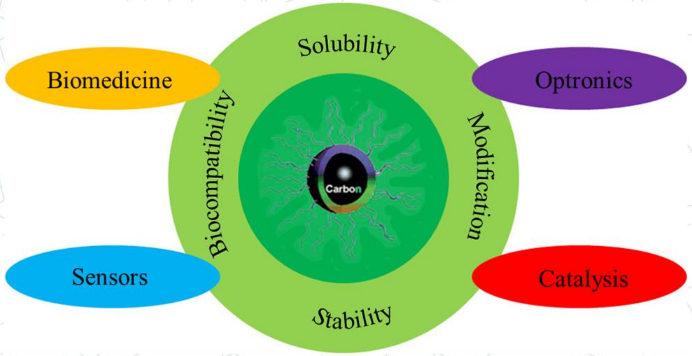
HTC Process Liquid



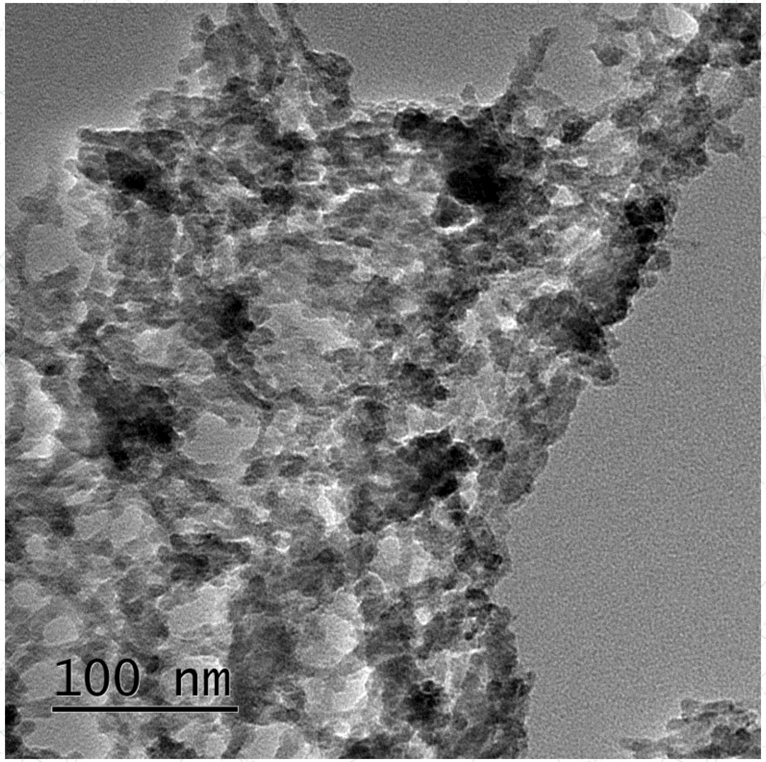
Carbon Quantum Dots from HTC process liquid

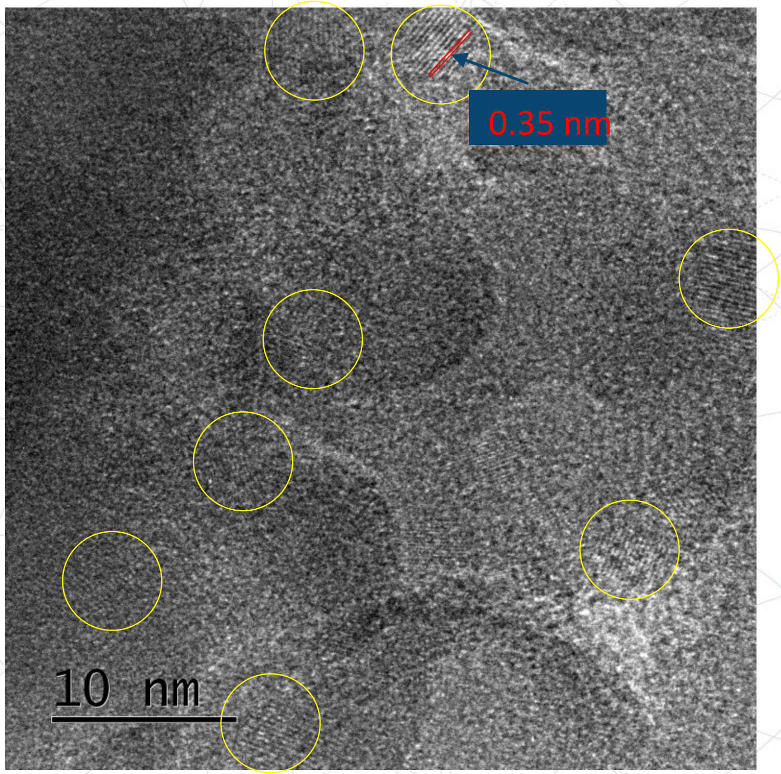


A) CQDs under daylight; B) CQDs under UV light



Applications based on superioir properties of carbon quantum dots.





- Graphene CQDs are $400-600 per liter with ~0.1% concentration (w/v)
- Global medical imaging market is $34.1 B in 2017
- Catalyst Market Size Expected To Reach $34.3 Billion By 2024
- The global optronics market will attain revenues of $5.05bn in 2015

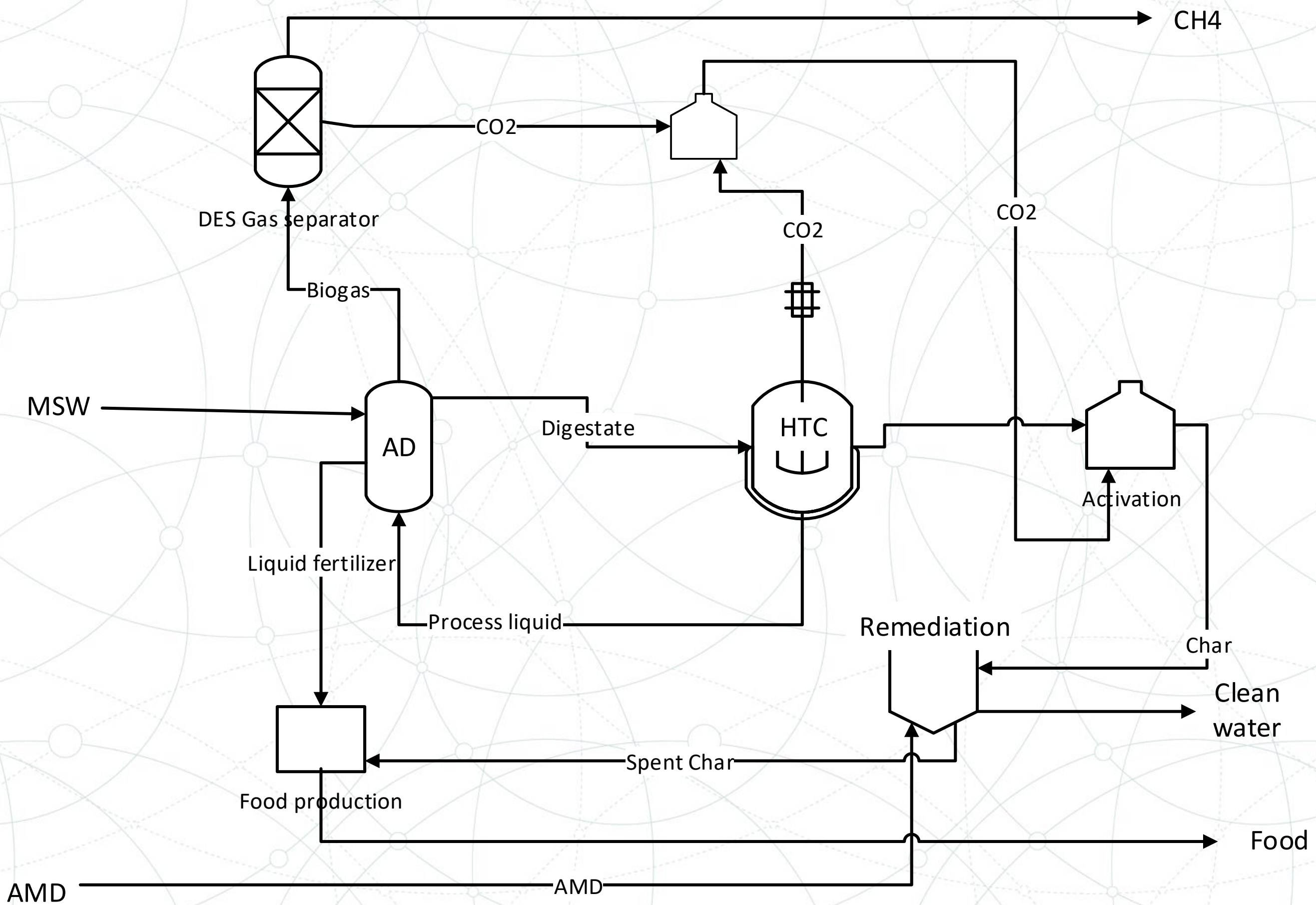
FLORIDA TECH

Ongoing Research

NSF-INFEWS

Title: INFEWS/T2: Organic Waste Lifecycles at the Interface of Food, Energy and Water Systems (OWL-FEWs)

Collaborator and Lead: Ohio University



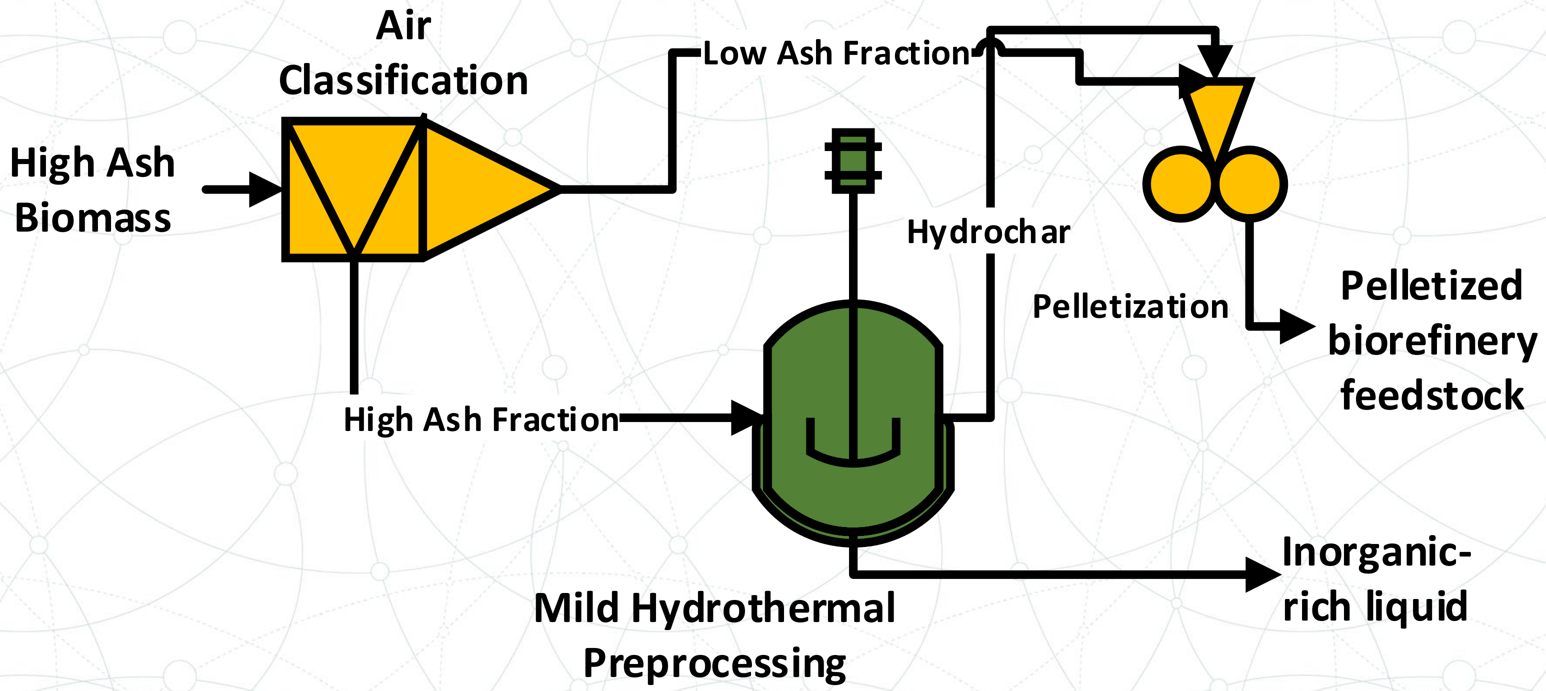
Ongoing Research

USDA-NIFA-AFRI

Award no: 2019-67019-29288

Title: Development and Optimization of Mild Hydrothermal Preprocessing for High Ash Biomass into Pelletized Biorefinery Feedstocks

Collaborator: INL

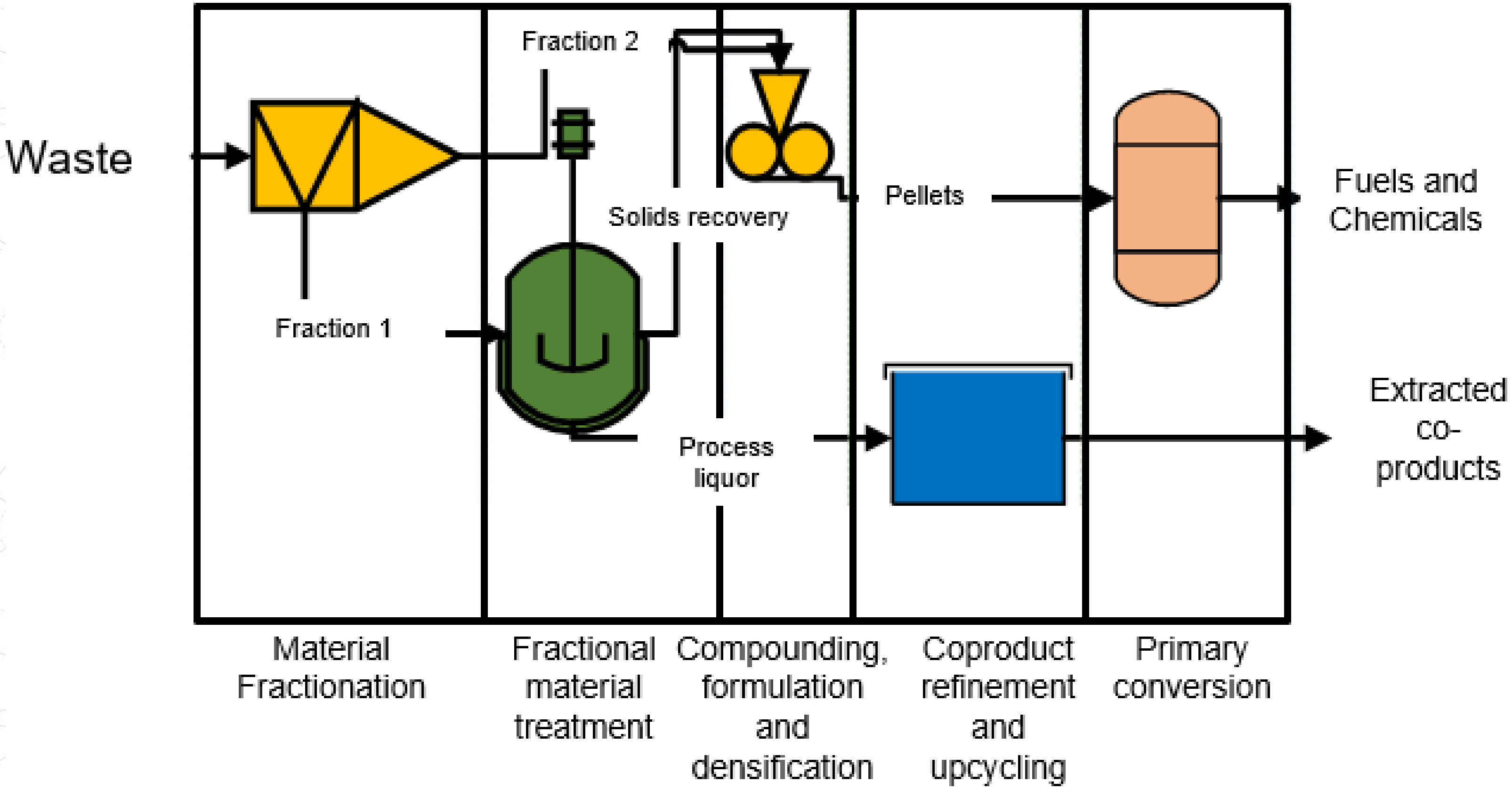


Future Research

EERE/BETO

Title: Decontaminated Pelletized Biorefinery Feedstocks Processing from Non-recyclable Municipal Solid Waste

Collaborator: Universities, National Labs, and Industries



Conclusions

- MSW is heterogeneous, contains high moisture, inorganic and organic contaminants, and have low density
- Sorting/materials recovery/preprocessing will be required to separate recyclables from MSW
- Organic-rich fraction could be benefitted by hydrothermal carbonization as it will
  - Increase hydrophobicity
  - Enhance friability
  - Increase density
  - Reduce inorganic content on the solid phase
  - Decontaminate from emerging organic pollutants
- Future research will require to integrate HTC with other technologies (e.g., AD, air classification, pelletization) to produce a homogeneous and decontaminated feedstock for conversion processes

FLORIDA TECH

Acknowledgements

United States Department of Agriculture
National Institute of Food and Agriculture

Award no: 2019-67019-29288

NSF 1856058

ACS PRF 60342-DNI9

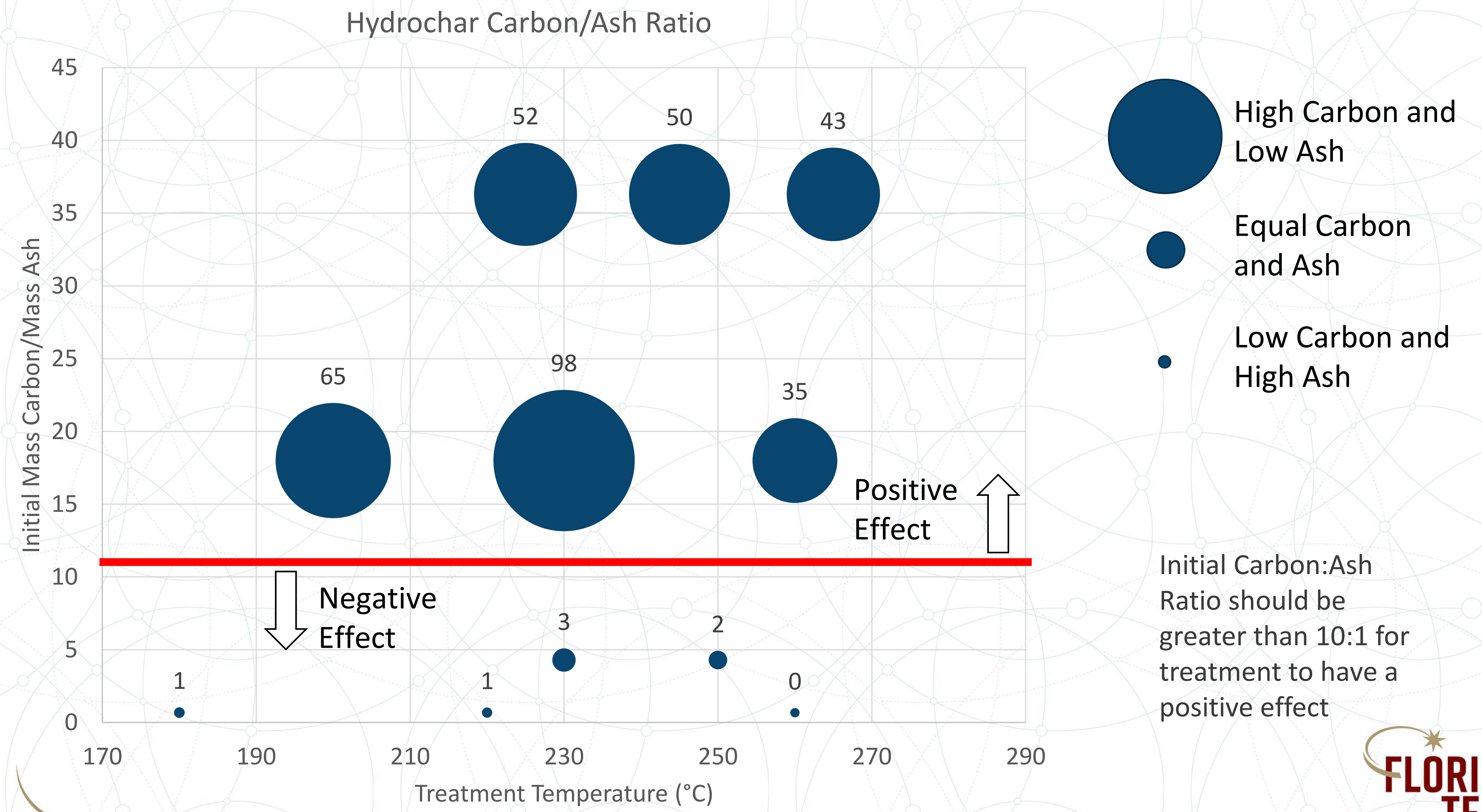
USDA-ARS: Drs. Bill Orts, Diana Franqui

Thank you.

treza@fit.edu; website: www.research.fit.edu/reza

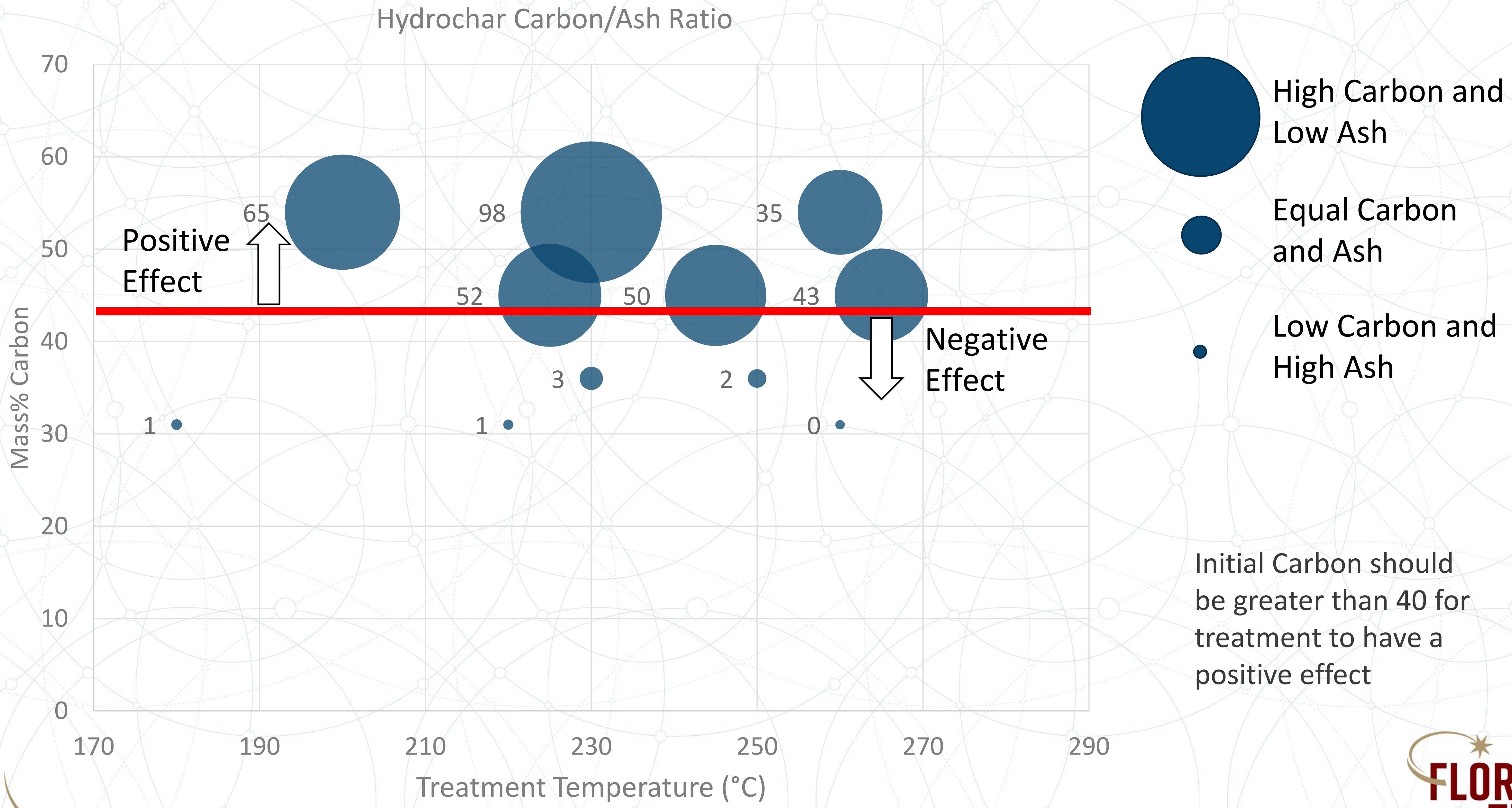
FLORIDA TECH

FLORIDA'S STEM UNIVERSITY™



Initial Carbon:Ash Ratio should be greater than 10:1 for treatment to have a positive effect

FLORIDA TECH

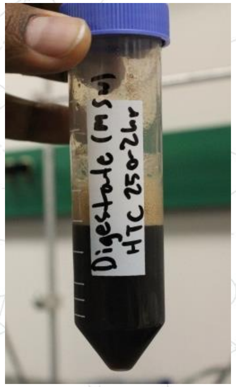


Initial Carbon should be greater than 40 for treatment to have a positive effect

HTC Process Liquid

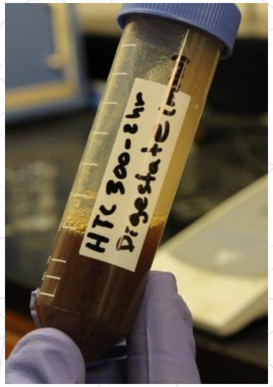
- Dark in color
- OFMSW derived ones are acidic
- Digestate derived ones are slightly basic
- Have high TOC
- Strong odor

(a) HTC 250 C 30 min digestate process liquid

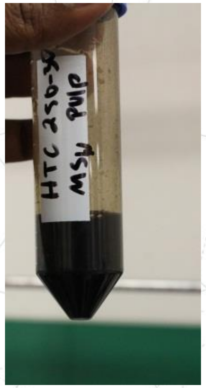


(b) HTC 250 C 2 h digestate process liquid

(c) HTC 300 C 30 min digestate process liquid



(d) HTC 300 C 2 h digestate process liquid



(e) HTC 250 C 30 min pulp process liquid

(f) HTC 250 C 2 h pulp process liquid

(g) HTC 300 C 30 min pulp process liquid

(h) HTC 300 C 2 h pulp process liquid

Reza Research Group

Core Research

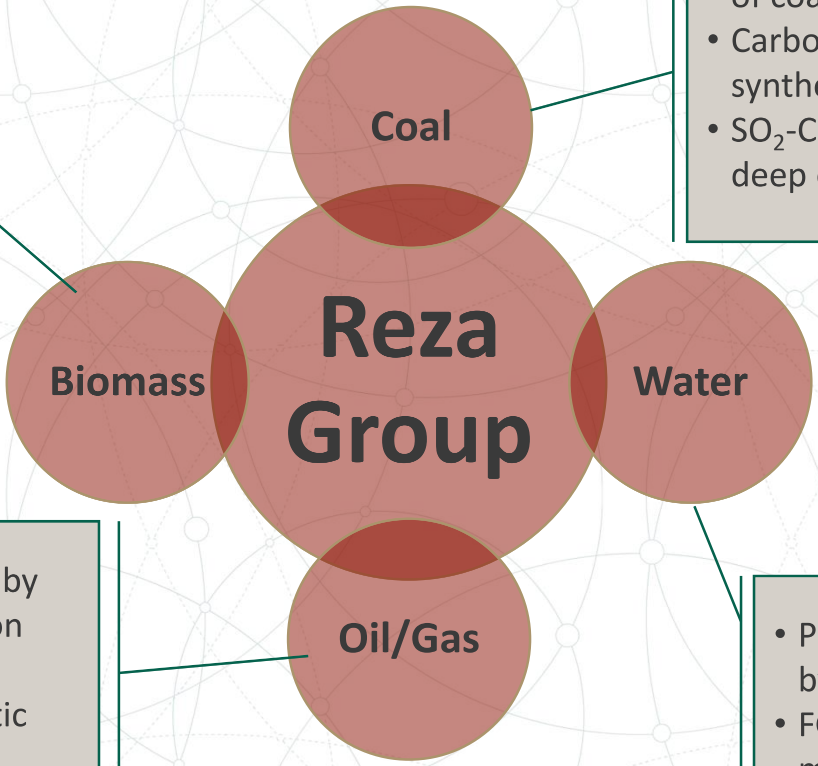
- Deep Eutectic Solvents (DES)
- Hydrothermal Carbonization (HTC)

Personnel

- Graduate Students: 5
- Undergraduate students: 10

Funding agencies

- USDA-AFRI-Agricultural Wastes
- NSF-INFEWS- Food Waste
- ACS-PRF – Refinery waste



Biomass

- **Hydrothermal carbonization (HTC)**
- CO_2 gasification of biochar

Coal

- Hydrothermal upgrading of coal waste-biomass
- Carbon quantum dots synthesis from Ohio coal
- SO_2-CO_2 co-capture by deep eutectic solvents

Oil/Gas

- Enhanced shale porosity by hydrothermal degradation
- Adsorption of BTX from aliphatics by deep eutectic solvents

Water

- Produced water treatment by deep eutectic solvents
- FGD wastewater quality monitoring by ion selective electrodes