Upcycling of Biowastes for Energy, Chemicals, and Materials: A Circular Economy Approach

Principal Investigator : Prof. Animesh Dutta

Organization: University of Guelph, Guelph, Ontario

Presentation date: April 28, 2022
Location: Guelph, ON

Acknowledgement

- Canadian Agricultural Partnership
- Biomass Cluster holder: BioFuelNet Canada
- Partners:
  1. Cinder Power Developments Inc.
  2. Custom Steam Solutions Inc.
  3. Shrimp Canada
  4. IGPC Ethanol

Our Ultimate Goal is to Develop

"A wide variety of renewable products including bio-carbon, renewable chemicals, bio-methane, and bio-fertilizers from a variety of **non-food sustainable agri-food wastes** feedstocks."

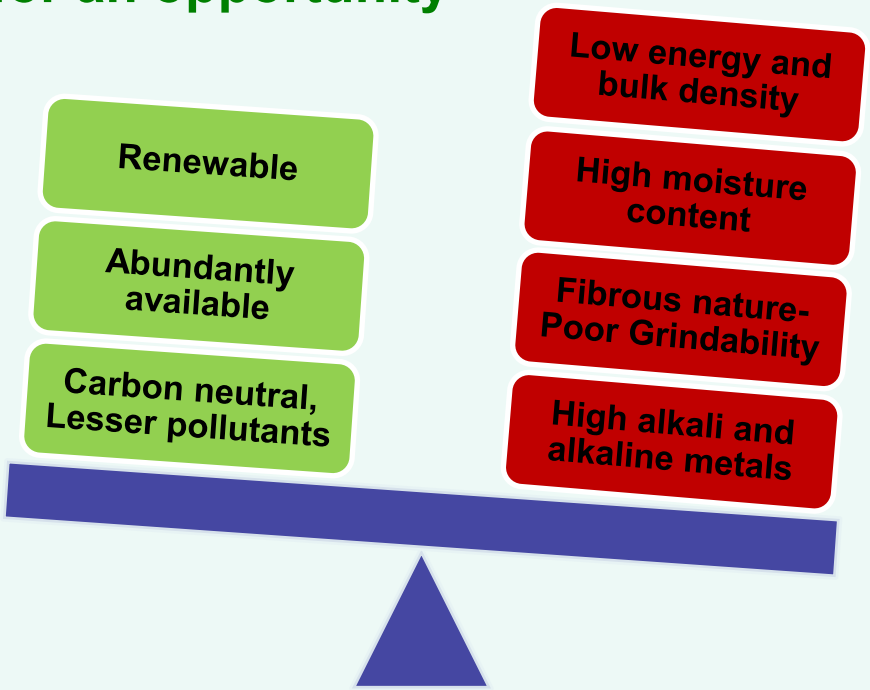
Meeting Biomass Canada Cluster's Goal by

- Valorization of agricultural and food wastes (crop residues, greenhouse, and food processing wastes)
- Developing green processes and products value chain
- Strengthening sustainability and bioeconomy of Canadian agriculture and agri-food sector

Project Overview

Theme: "Waste is a resource - waiting for an opportunity"

"Agri-food wastes is not regarded as an ideal replacement for fuel and materials application"



- Hydrothermal Carbonization (HTC) processing where biomass is treated with hot compressed water instead of drying exhibits unique physicochemical properties
- HTC products from low quality agri-food residue can be a potential newer value chain

Research Questions:

- Can we produce industrial grade biocarbon from this low quality biomass (low alkali metals, higher HHV, and higher grindability) for energy and materials applications?
- Will there be any industrial grade biochemical as a co-product from HTC Process Water (HTCPW)?

Approach

Hypothesis:

1. Changing HTC processing conditions (time, temperature, feedstocks sizing, etc.) will generate recipes for biocarbon of required morphological properties for various applications. **(help eliminate some of the key barriers to Agri-food waste stream)**
2. Two steps thermo-catalytic process will be able to **generate high value carbon materials**
3. By applying this HTC process water into AD (Anaerobic Digestion) system, the hydrolysis process will be accelerated, which is the main limiting factor for AD system (**help eliminate some limiting factors for AD system**)

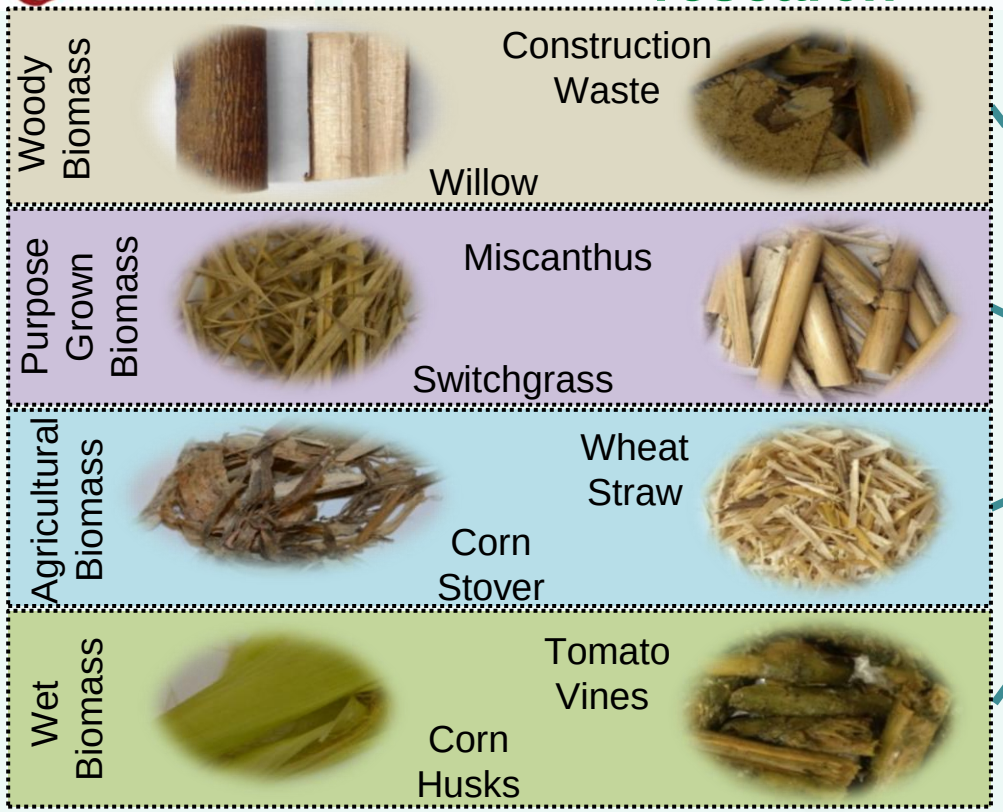
Approach to establish of these hypothesis includes:

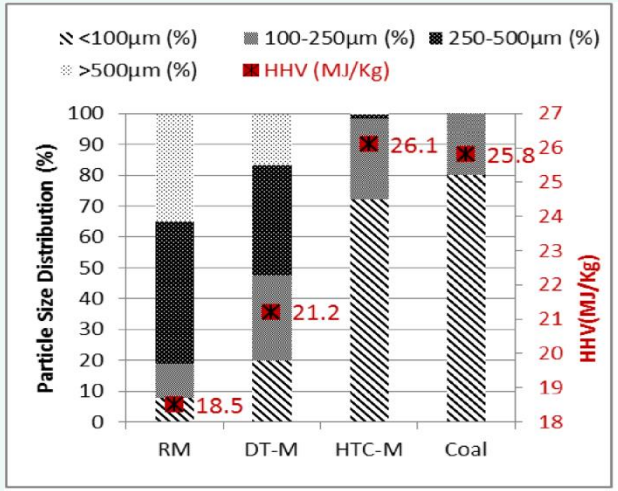
1. We defined milestones with
   - HTC Process design and development
   - Feedstock processing and characterizations (HTC & AD)
   - Process development/refinement
2. Identified critical deliverable
   - Life cycle assessment (LCA) and life cycle costing (LCC)

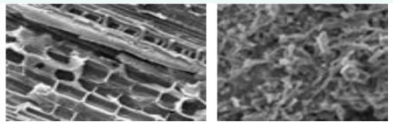
2 - Technical Accomplishments/ Progress/Results

Objectives	Deliverables & Status 2021-2022
1. Preprocess greenhouse residues, energy crops, crop residues, municipal green bin (i.e., food waste)	*Completed earlier*
2. Characterize hydrochar and process water	HTC & Surface characterization of the biochar - *Completed*
3. Effectiveness of hydrochar in various treatments	Hydrochar for activated carbon, water retention experiments, and nutrient recovery potentials – *Study Completed, Data processing in progress*
4. Effectiveness of process water in anaerobic digestion (AD)	Application of liquid form HTC in to anarobic digester - *Completed*
5. Potential use of biogas and hydrochar in CHP	Biomethane separation and purification studies for RNG is completed. – *data processing in progress*
6. Investigate the environmental and economic implications	*Schedule for 2022-2023*

Biocarbon development research

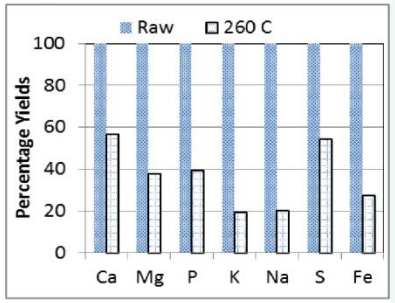






RM: difficult to grind

HTC-M: Easy to grind



Bio-carbon
- Soil amendment

Bio-carbon
- Heat and power production

Charcoal
- Metallurgy applications

Activated Carbon
- Wastewater treatment
- Energy storage

- **HTC can be an ideal pre-treatment method to remove some of the barriers.**
- **Depending upon applications, it may require further processing**

Technical Accomplishments: Publications on HTC technology development and product characterization

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Energy

Volume 214, 1 January 2021, 119020

Development of a mathematical model for hydrothermal carbonization of biomass: Comparison of experimental measurements with model predictions

Mohammad Heidari [a], Shakirudeen Salaudeen [a], Precious Arku [a], Bishnu Acharya [b], Syeda Tasnim [a], Animesh Dutta [a]

ELSEVIER

Energy

Volume 165, Part B, 15 December 2018, Pages 370-384

Biocarbon, biomethane and biofertilizer from corn residue: A hybrid thermo-chemical and biochemical approach

Subhash Paul, Animesh Dutta, Fantahun Defersha

scientific reports

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nature > scientific reports > articles > article

Article | Open Access | Published: 08 March 2021

Integrated hybrid architecture of metal and biochar for high performance asymmetric supercapacitors

Omid Norouzi, S. E. M. Pourhosseini, Hamid Reza Naderi, Francesco Di Maria & Animesh Dutta

Scientific Reports **11**, Article number: 5387 (2021) | Cite this article

2220 Accesses | **12** Citations | **1** Altmetric | Metrics

Springer Link

Original Article | Published: 06 August 2020

Product evaluation of hydrothermal carbonization of biomass: semi-continuous vs. batch feeding

Mohammad Heidari, Omid Norouzi, Kevin MacDermid-Watts, Bishnu Acharya, Yongsheng Zhang & Animesh Dutta

Biomass Conversion and Biorefinery **12**, 15–25 (2022) | Cite this article

479 Accesses | **10** Citations | Metrics

Springer Link

Climate Change and Green Chemistry of CO2 Sequestration pp 231–262 | Cite as

Biomass-Based CO_2 Adsorbents for Biogas Upgradation with Pressure Swing Adsorption

agyan P. Garnaik, Ranjan R. Pradhan, Yi Wai Chiang & Animesh Dutta

Chapter | First Online: 11 May 2021

257 Accesses

Part of the Green Energy and Technology book series (GREEN)

ELSEVIER

Chemical Engineering Journal

Volume 410, 15 April 2021, 128323

Design of a ternary 3D composite from hydrochar, zeolite and magnetite powder for direct conversion of biomass to gasoline

Omid Norouzi [a, b], Mohammad Heidari [a], Francesco Di Maria [b], Animesh Dutta [a]

Open Access | Feature Paper | Article

Numerical Comparison of a Combined Hydrothermal Carbonization and Anaerobic Digestion System with Direct Combustion of Biomass for Power Production

by Mohammad Heidari [1], Shakirudeen Salaudeen [1], Omid Norouzi [1], Bishnu Acharya [2] and Animesh Dutta [1,*]

[1] School of Engineering, University of Guelph, Guelph, ON N1G 2W1, Canada

[2] School of Sustainable Design Engineering, University of Prince Edward Island, Charlottetown, PE C1A 4P3, Canada

* Author to whom correspondence should be addressed.

Processes **2020**, *8*(1), 43; https://doi.org/10.3390/pr8010043

Received: 13 November 2019 / Revised: 14 December 2019 / Accepted: 21 December 2019 / Published: 1 January 2020

(This article belongs to the Special Issue Anaerobic Digestion Processes)

ELSEVIER

Volume 11, June 2022, 100056

Technologies for the production of renewable natural gas from organic wastes and their opportunities in existing Canadian pipelines

Omid Norouzi, Mohammad Heidari, Animesh Dutta

Open Access | Article

Miscanthus to Biocarbon for Canadian Iron and Steel Industries: An Innovative Approach

by Trishan Deb Abhi, Omid Norouzi, Kevin Macdermid-Watts, Mohammad Heidari, Syeda Tasnim and Animesh Dutta *

School of Engineering, University of Guelph, Guelph, ON N1G 2W1, Canada

* Author to whom correspondence should be addressed.

Academic Editor: Prasad Kaparaju

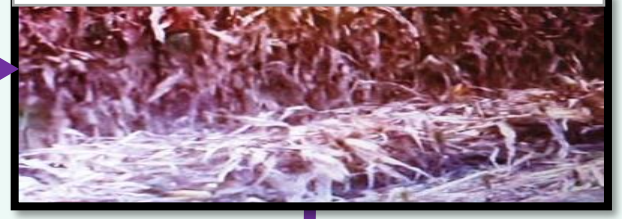
Energies **2021**, *14*(15), 4493; https://doi.org/10.3390/en14154493

Received: 15 June 2021 / Revised: 20 July 2021 / Accepted: 23 July 2021 / Published: 25 July 2021

(This article belongs to the Special Issue Carbonization of Biomass for Energy Production)

Example 1: Bioenergy and biofertilizer from hydrothermal treated corn residue: a circular economy concept

Corn residue



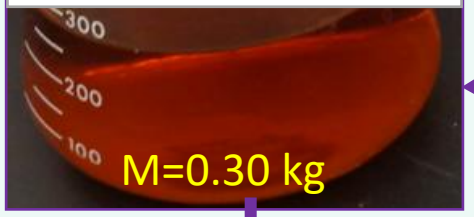
Reference: Energy, Vol 165, Part B, 2018, Pages 370-384

$M=1\ kg_{dry}$; E=18.13 MJ

Hydrothermal process

M loss = 0.23 kg

Liquid (HTPW)



Biocarbon for different application

M=0.47 kg; E=10.91 MJ

AD process

Biogas

Biomethane

E = 3.35 MJ

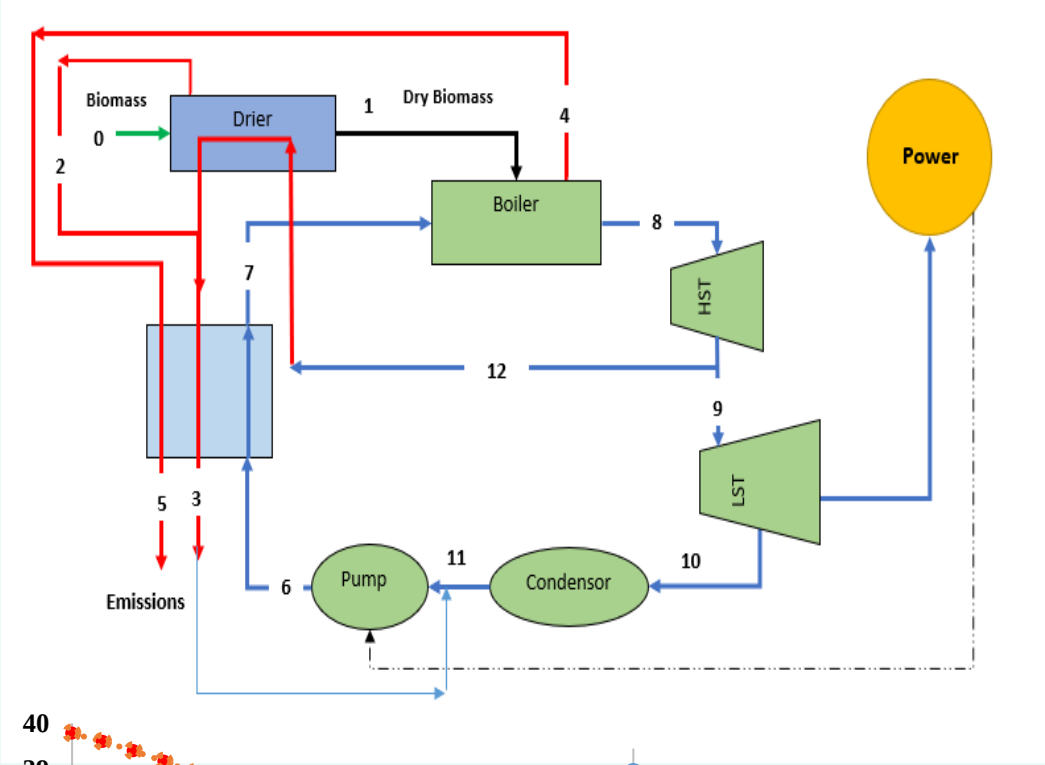
Digestate (Biofertilizer)

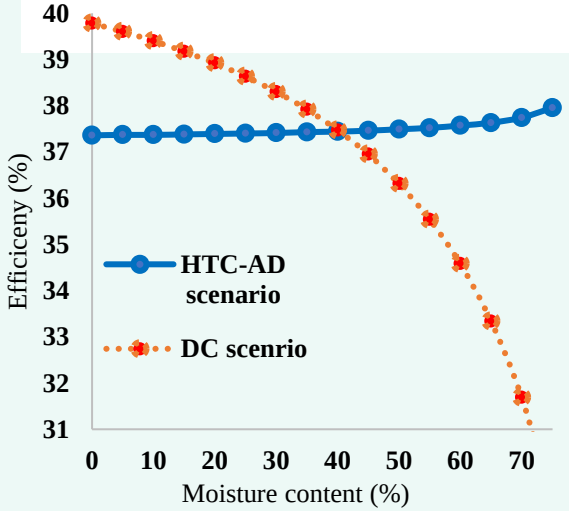
Recovery N=31%, P=23%, K=26%, S=19%

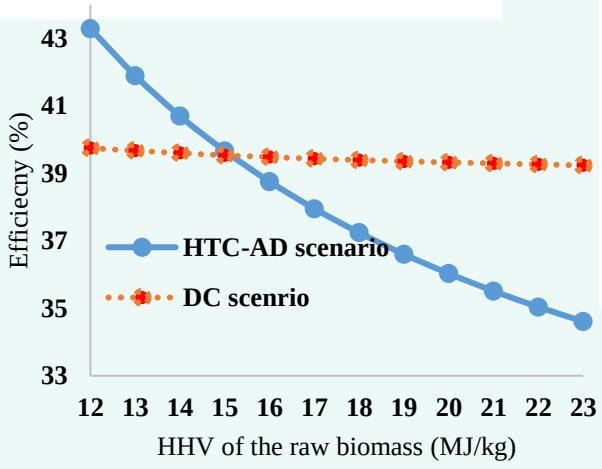
Overall energy recovery efficiency=79%

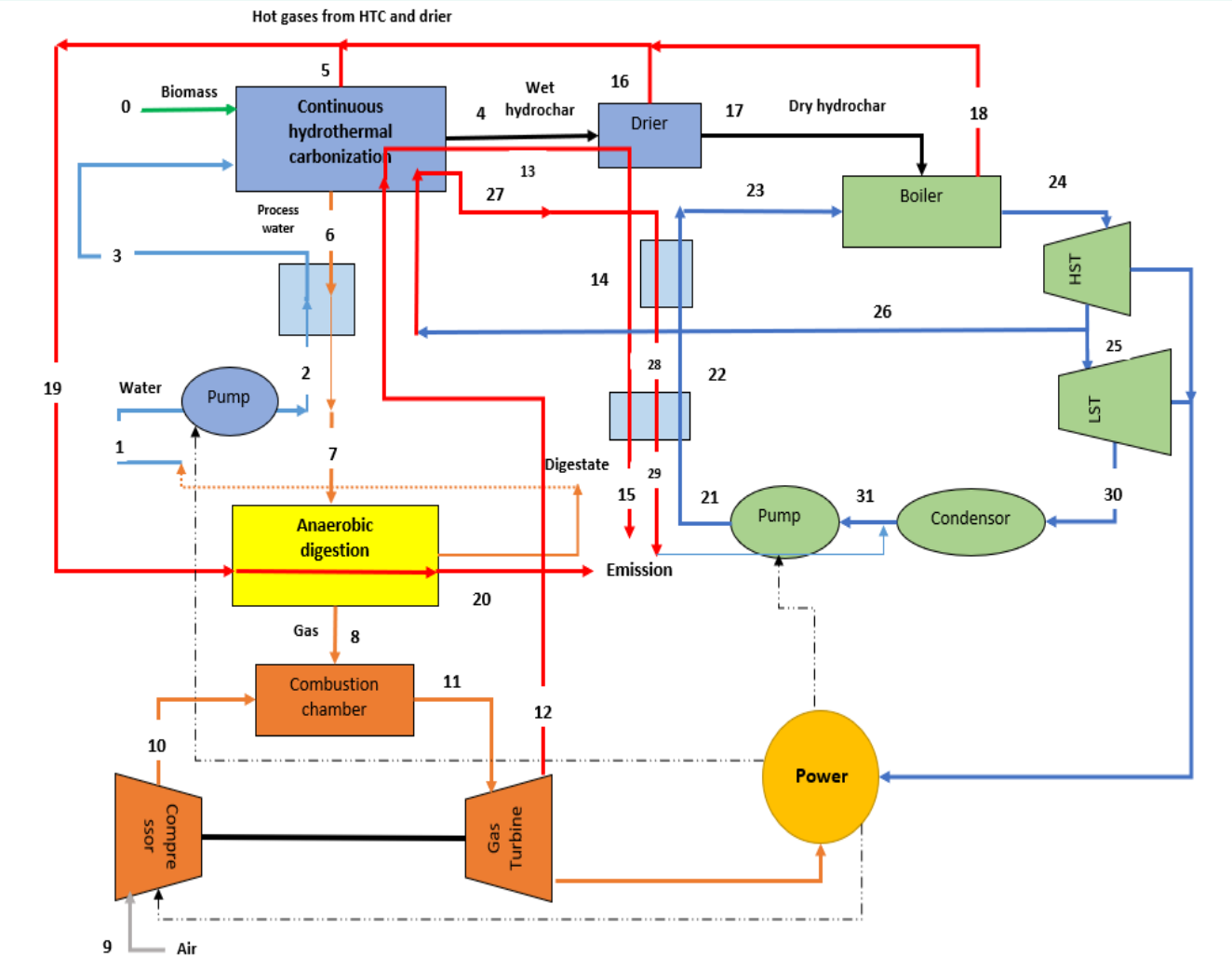
Case Study 1: Numerical analysis of an integrated HTC-AD system for power generation

Ref: Processes 2020, 8(1), 43



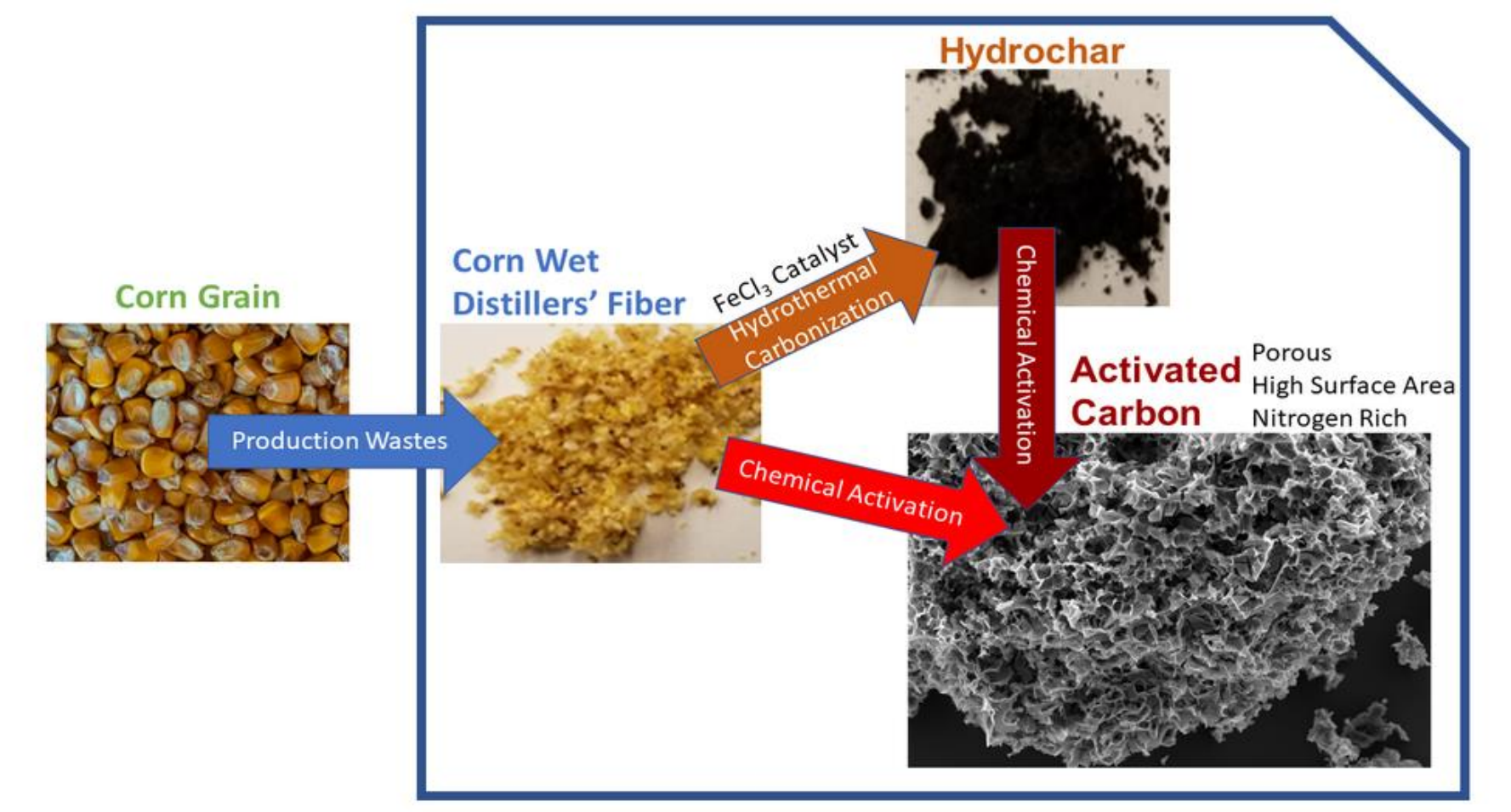






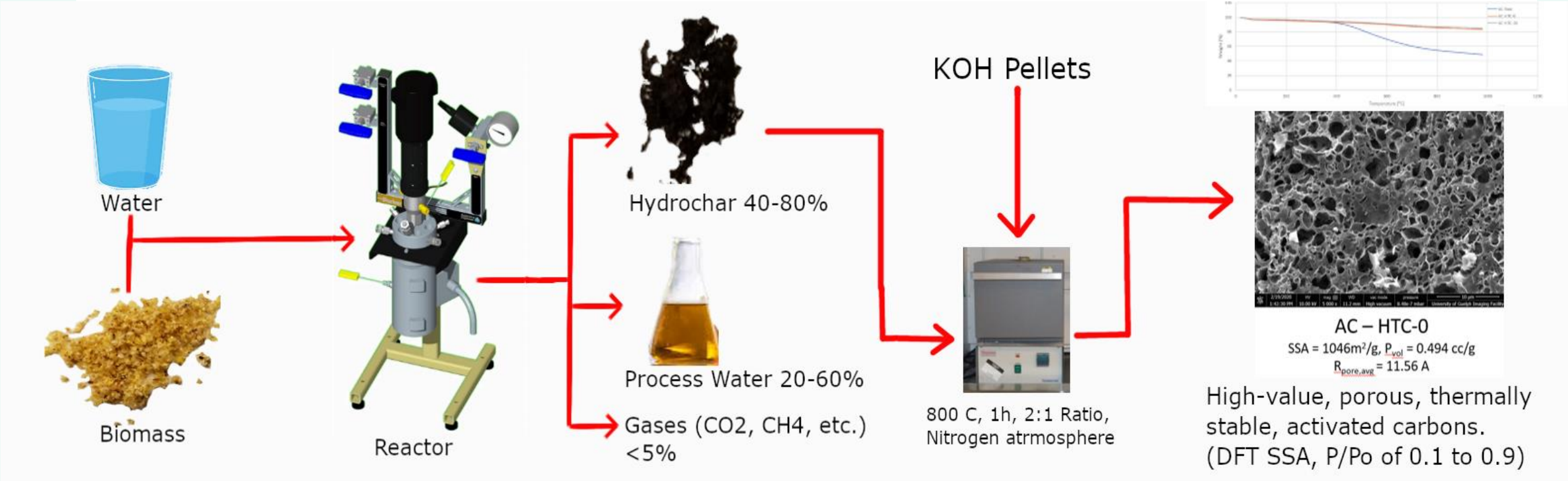
HTC-AD scenario shows a better performance compared to DC one when the moisture content of the biomass is over 40%

Ex. 2: A Tunable Approach for Activated Carbon Production from Low Value Biomass



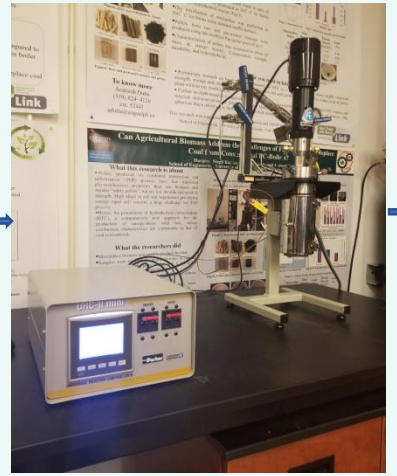
Ex. 2 Continued: A Tunable Approach for Activated Carbon Production from Low Value Biomass

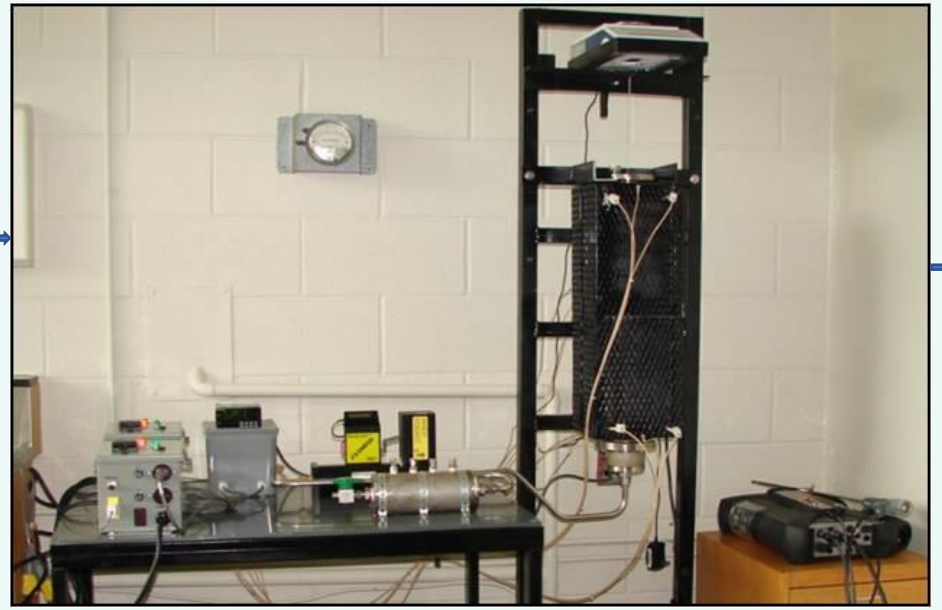
- Valuable, high quality activated carbons can be produced through a 2-step HTC and chemical activation procedure.
- Applications in heavy metal removal, water filtration, gas storage, super capacitors, and many more.



Ref: ACS Omega Journal, 6, 23, May, 2021, page: 14874-14886
Title: Effects of $FeCl_3$ Catalytic Hydrothermal Carbonization on Chemical Activation of Corn Wet Distillers' Fibre

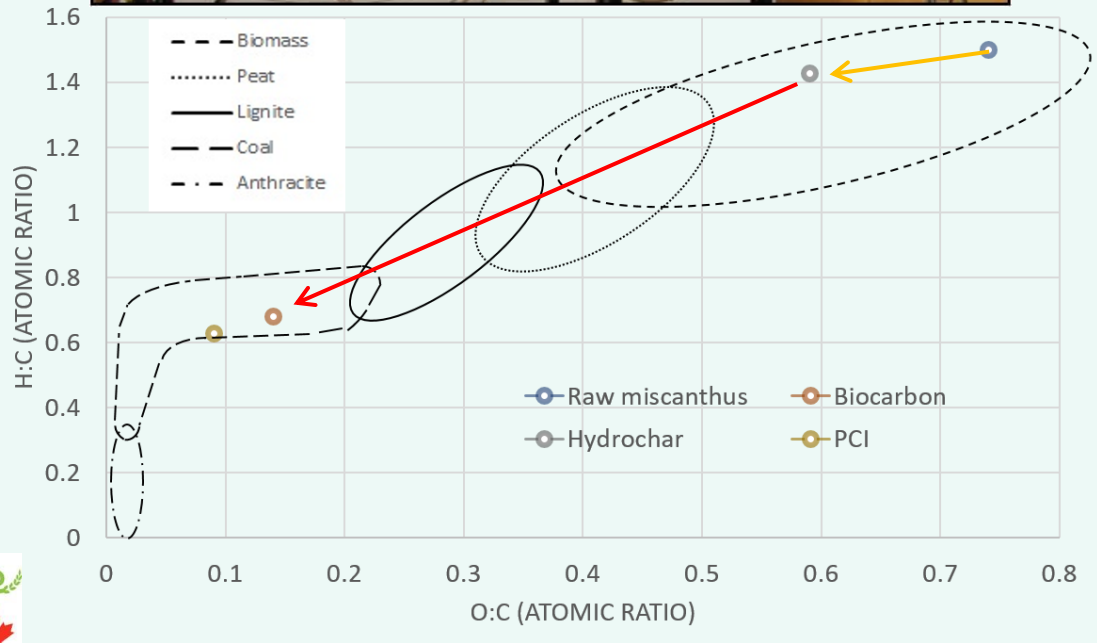
Ex. 2 Continued: Miscanthus/Switchgrass to Biocabon for Iron and Steel Industries: A Tunable Approach





Properties	Raw Switchgrass	Torrefied-290
%C	**44.76 ± 2.04**	**64.28 ± 2.42**
%H	6.04 ± 0.62	4.34 ± 0.69
%N	0.66 ± 0. 08	0.68 ± 0.13
%S	0	0
%O	**44.09 ± 1.87**	**23.58 ± 1.87**
HHV (MJ/Kg)	**17.13 ± 1.49**	**26.04 ± 1.91**
%VM	84.3 ± 3.18	50.35 ± 2.72
%Ash	**4.45 ± 0.23**	**7.12 ± 0.38**
%FC	11.25 ± 0.8	42.53 ± 1.83

Hydrochar	
C(%)	**52.2**
H(%)	6.2
N(%)	0.05
S(%)	0
O(%)	**41.31**
Ash(%)	**0.24**
FC(%)	15.1
VM(%)	84.66
HHV (MJ/Kg)	**20.37**

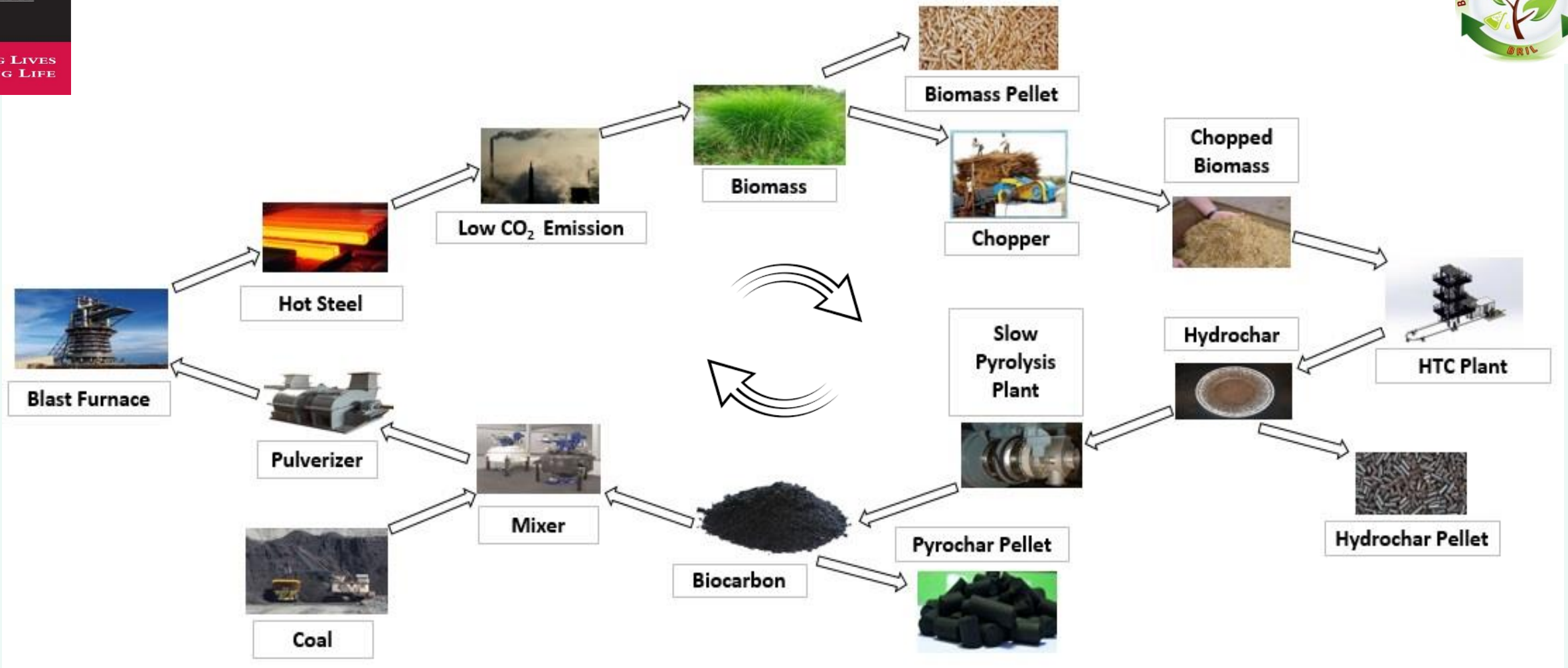


Biocarbon	
C(%)	**79.67**
H(%)	4.5
N(%)	0.35
S(%)	0
O(%)	**14.69**
Ash(%)	**0.79**
FC(%)	63.71
VM(%)	35.5
HHV (MJ/Kg)	**32.59**

PCI coal	
C(%)	**77.66**
H(%)	4.1
N(%)	1.76
S(%)	0.3
O(%)	**9.53**
Ash(%)	**6.65**
FC(%)	56.94
VM(%)	36.41
HHV (MJ/Kg)	**32.07**

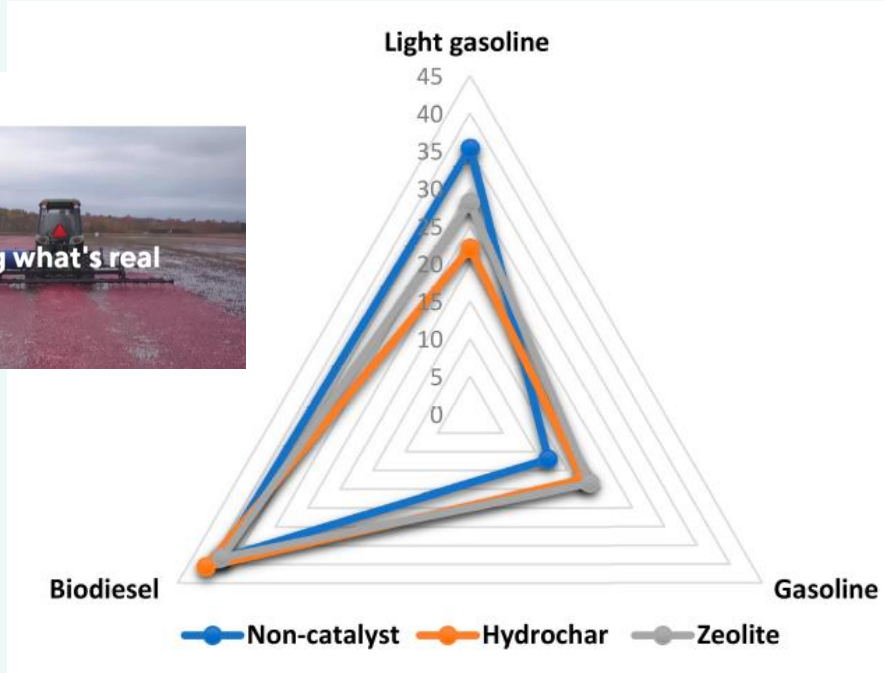
Ref: Energies, 14,(5) July 2021, Pages 4493

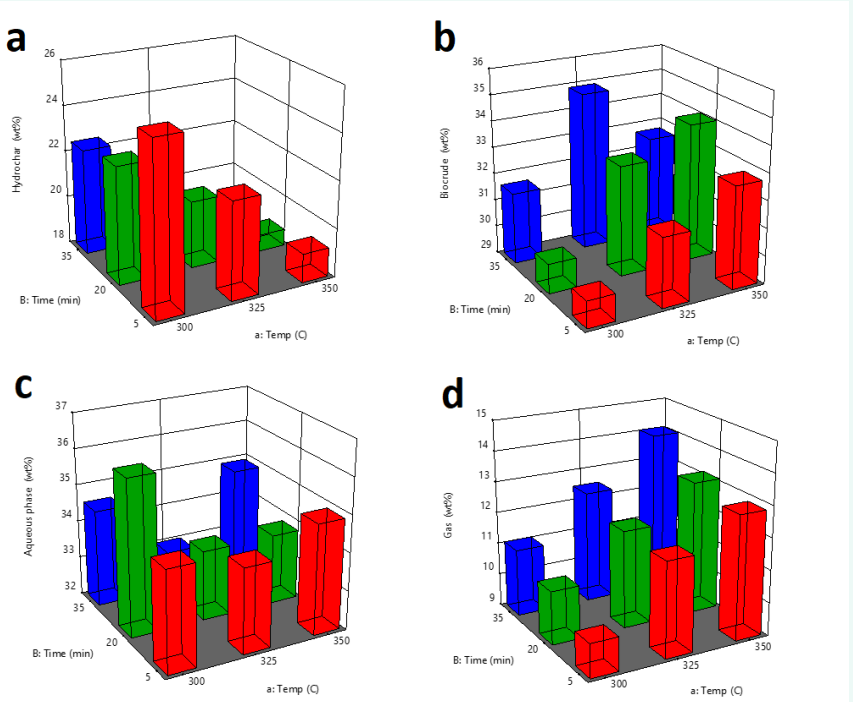
Ex. 2 Continued: Overall Approach Industry relevance

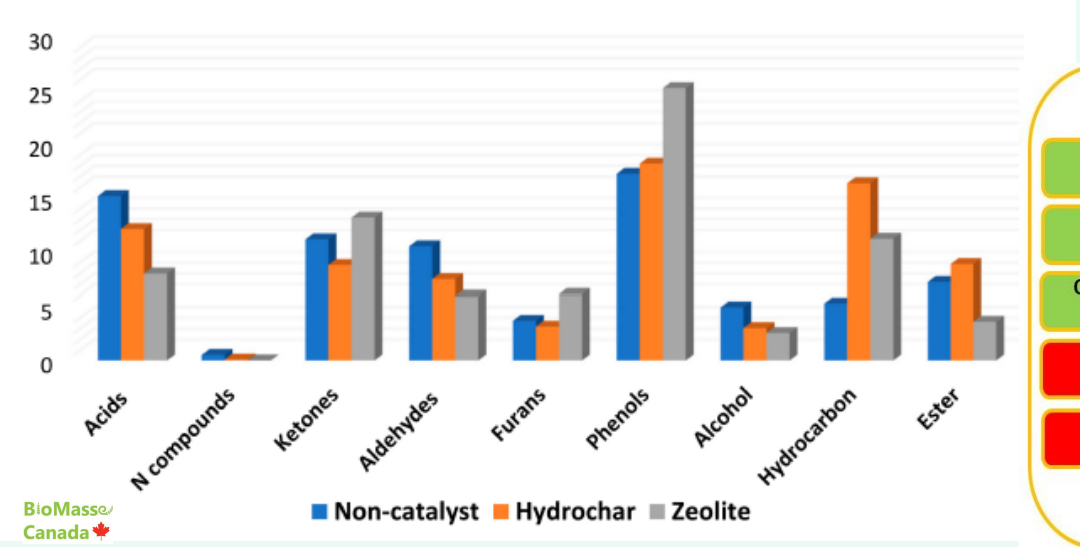


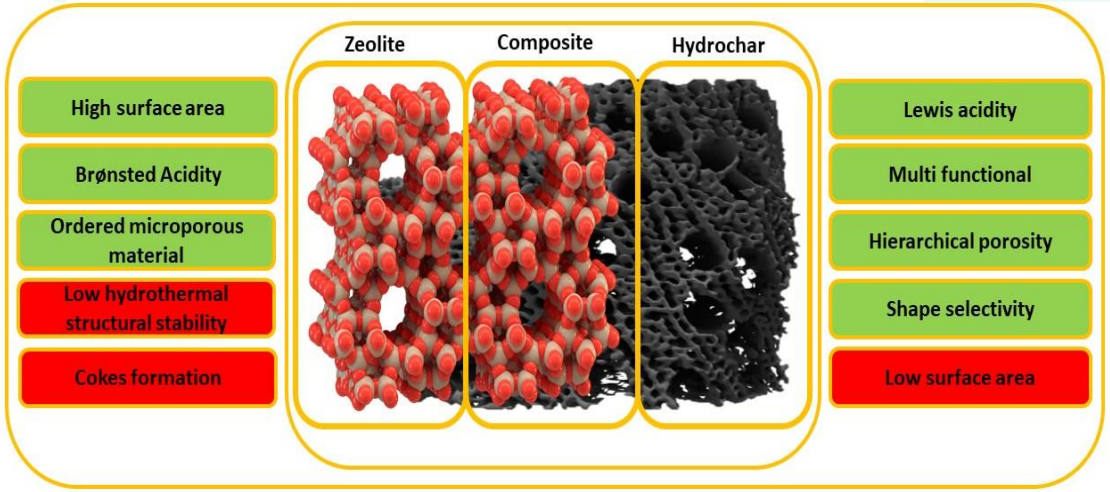
- Integrated HTC and slow pyrolysis of high ash low grade biomass
- Biocarbon with less ash content and good combustion behavior
- Partial replacement of fossil carbon in blast furnace iron making process
- Reduction of GHGs emission

Case Study 3: New Insights for the Future Design of Composites Composed of Hydrochar and Zeolite from Cranberry Pomace. Ref: Energies 13 (24), 6600, 2020





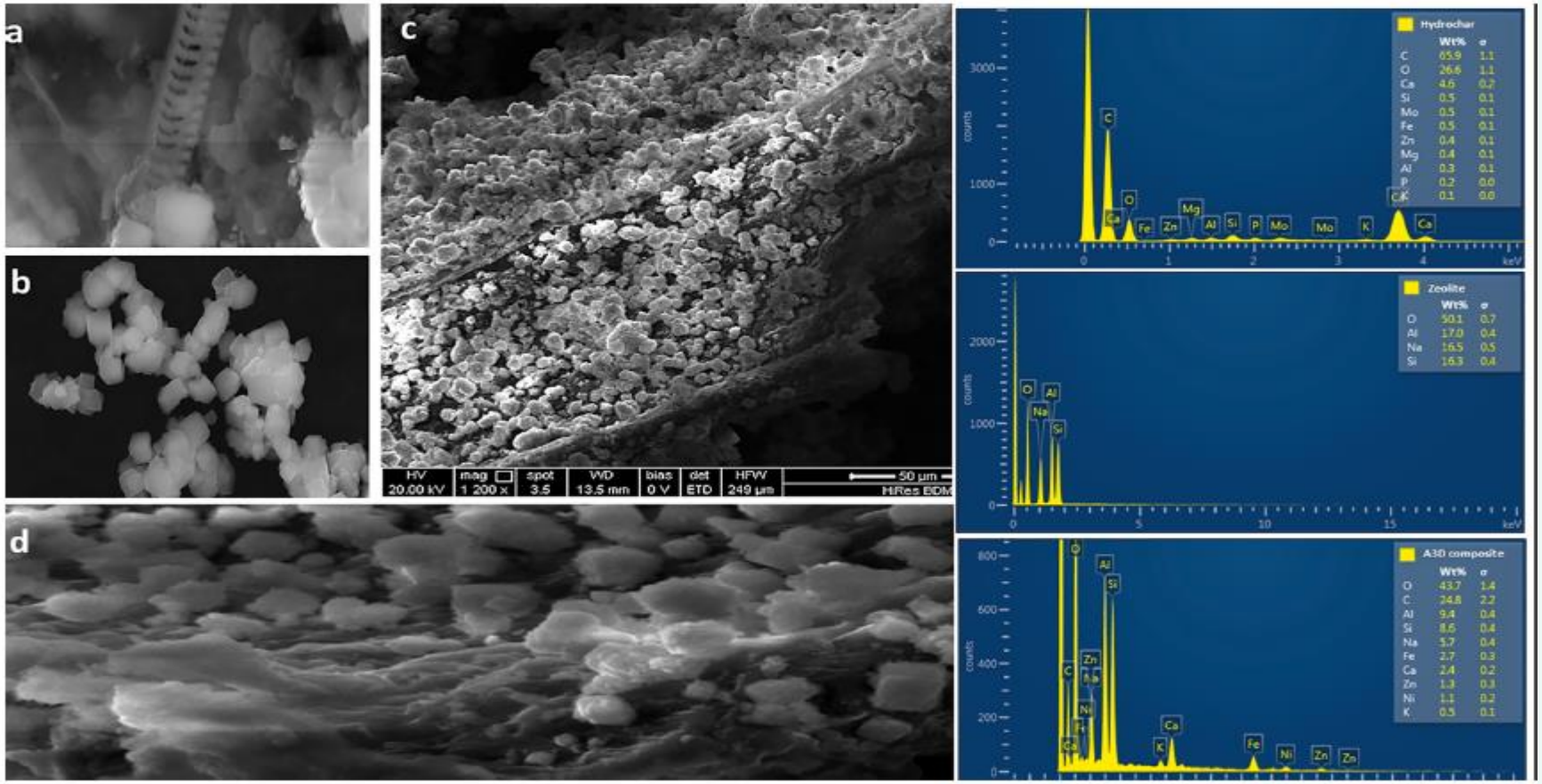




A catalyst based on hydrochar and zeolite (hydrochar/zeolite composite) can resolve present limitations and challenges by:

- Creating meso/macropores into the micropores structure of the zeolite;
- Increasing the number of accessible active sites for macromolecules;
- Enhancing the thermal stability of the zeolite;
- Creating 3D interconnected structure using activated hydrochar

Case Study 3: Design of a ternary 3D composite from hydrochar, zeolite and magnetite powder for direct conversion of biomass to gasoline

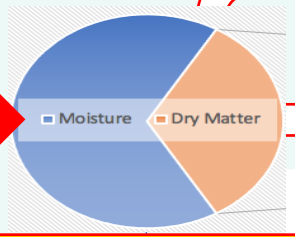


- We have synthesized a zeolite-hydrochar composite using a simple one-step hydrothermal liquefaction (HTL) process.
- hierarchically structured porosity of the composite facilitates diffusion of macromolecules and their derivatives inside the composite and improves the accessibility to lewis acid sites.
- The chemical interaction of hydrochar/zeolite was confirmed by XRD and SEM-EDS analyses

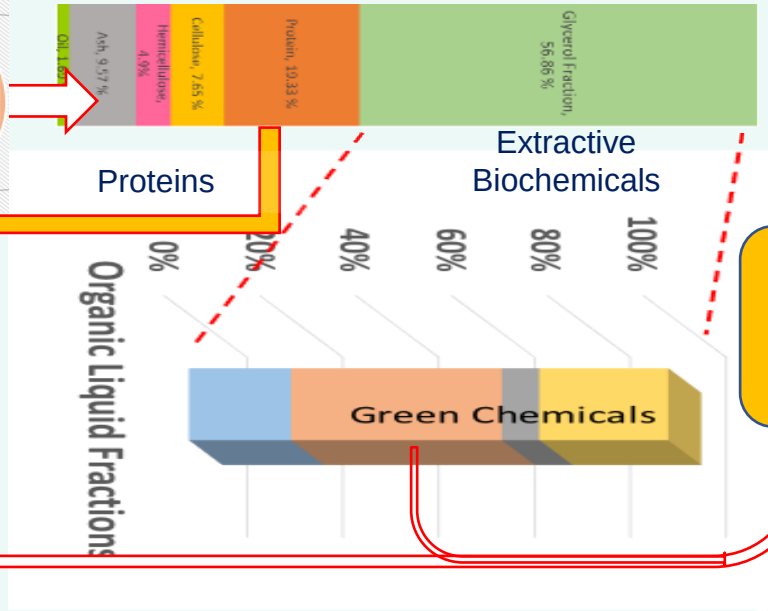
Technical Accomplishments

Establishment of Biorefinery Product Stream for Bioprocess Wastes

Non-lignocellulosic Agri-food process wastes



Fractionation of the macromolecules



Proteins

Extractive Biochemicals

Toxic residue / organic extracts

Hydrothermal Carbonization

Adopted and Established Biorefinery Approach

Protein Concentrate

Functional Peptides for Feed

Amino acids

Adsorbent / Fertilizer

Bio carbon

Technical Accomplishments: PUBLICATIONS: Biorefinery of Corn CDS

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Food Chemistry

Available online 21 April 2022, 133036

In Press, Journal Pre-proof

Exploration of corn distillers solubles from selective milling technology as a novel source of plant-based ACE inhibitory protein hydrolysates

Sonu Sharma [a], Ranjan Pradhan [a, b], Annamalai Manickavasagan [a], Mahendra Thimmanagari [c], Animesh Dutta [a]

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Food and Bioproducts Processing

Volume 127, May 2021, Pages 225-243

Evaluation of nitrogenous pyrolysates by Py–GC/MS for impacts of different proteolytic enzymes on corn distillers solubles

Sonu Sharma [a], Ranjan Pradhan [a, c], Annamalai Manickavasagan [a], Mahendra Thimmanagari [b], Animesh Dutta [a]

Springer Link

Review Article | Published: 23 May 2020

Characterization of ultrasonic-treated corn crop biomass using imaging, spectral and thermal techniques: a review

Sonu Sharma, Ranjan Pradhan, Annamalai Manickavasagan & Animesh Dutta

Biomass Conversion and Biorefinery (2020) | Cite this article

ELSEVIER

Food and Bioproducts Processing

Volume 124, November 2020, Pages 354-368

Application of analytical pyrolysis to gain insights into proteins of condensed corn distillers solubles from selective milling technology

Sonu Sharma [a], Ranjan Pradhan [a, c], Annamalai Manickavasagan [a], Mahendra Thimmanagari [b], Animesh Dutta

Springer Link

Original Article | Published: 16 July 2021

Valorization and potential of condensed corn distillers solubles fractions from selective milling technology

Sonu Sharma, Ranjan Pradhan, Annamalai Manickavasagan, Mahendra Thimmanagari & Animesh Dutta

Biomass Conversion and Biorefinery (2021) | Cite this article

Industrial Crops & Products

Production of antioxidative protein hydrolysates from corn distillers solubles: process optimization, antioxidant activity evaluation, and peptide analysis

--Manuscript Draft--

Manuscript Number:	INDCRO-D-21-05665
Article Type:	Research Paper
Section/Category:	Biorefinery, valorization of byproducts
Keywords:	corn distillers solubles, protein, peptide, antioxidant, alcalase.

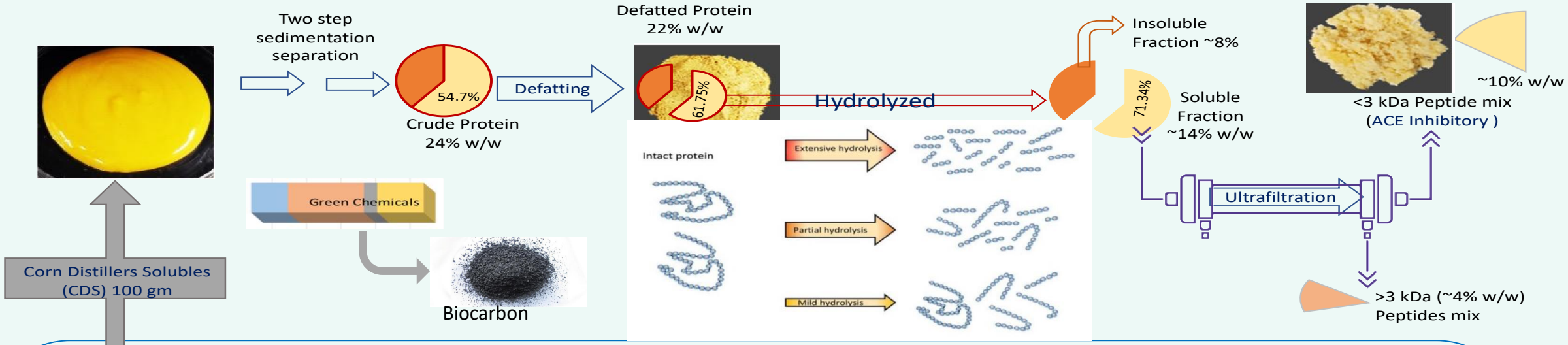
Food & Function

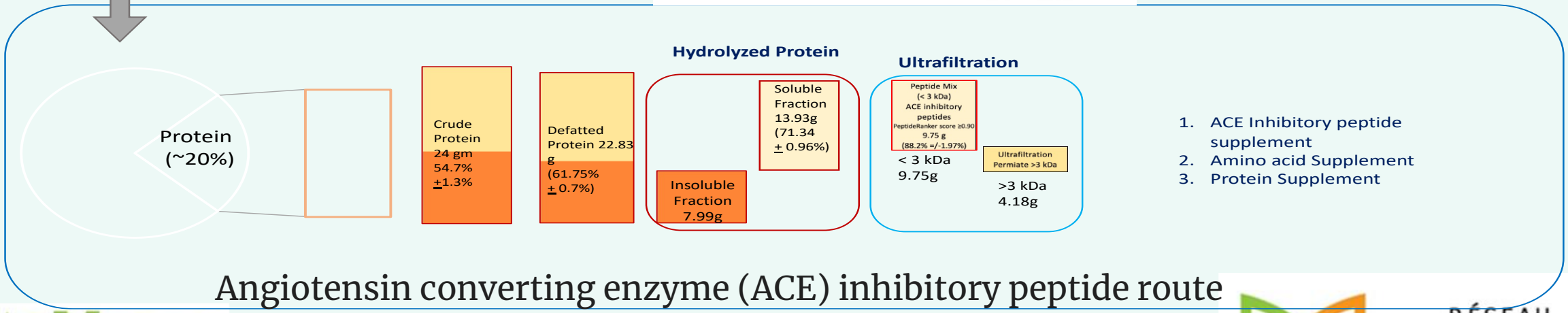
Corn distillers solubles as a novel bioresource of bioactive peptides with ACE and DPP-IV inhibition activity: characterization, in-silico evaluation, and molecular docking

Journal:	*Food & Function*
Manuscript ID	FO-ART-12-2021-004109
Article Type:	Paper
Date Submitted by the Author:	03-Dec-2021
Complete List of Authors:	Sharma, Sonu; University of Guelph, Pradhan, Ranjan; University of Guelph, Engineering Manickavasagan, Annamalai; University of Guelph Thimmanagari, Mahendra; OMAFRA Dutta, Animesh; University of Guelph, Engineering

Technical Accomplishments

Protein Fraction Valorization Route



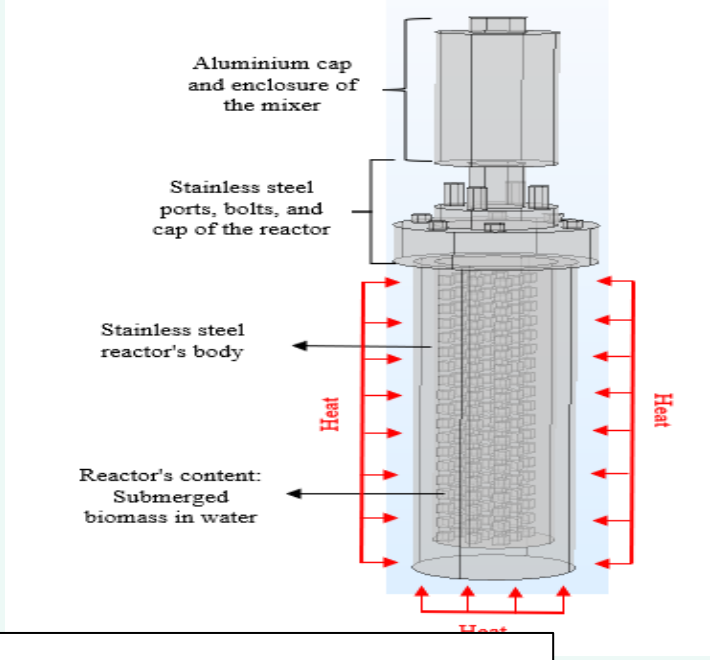


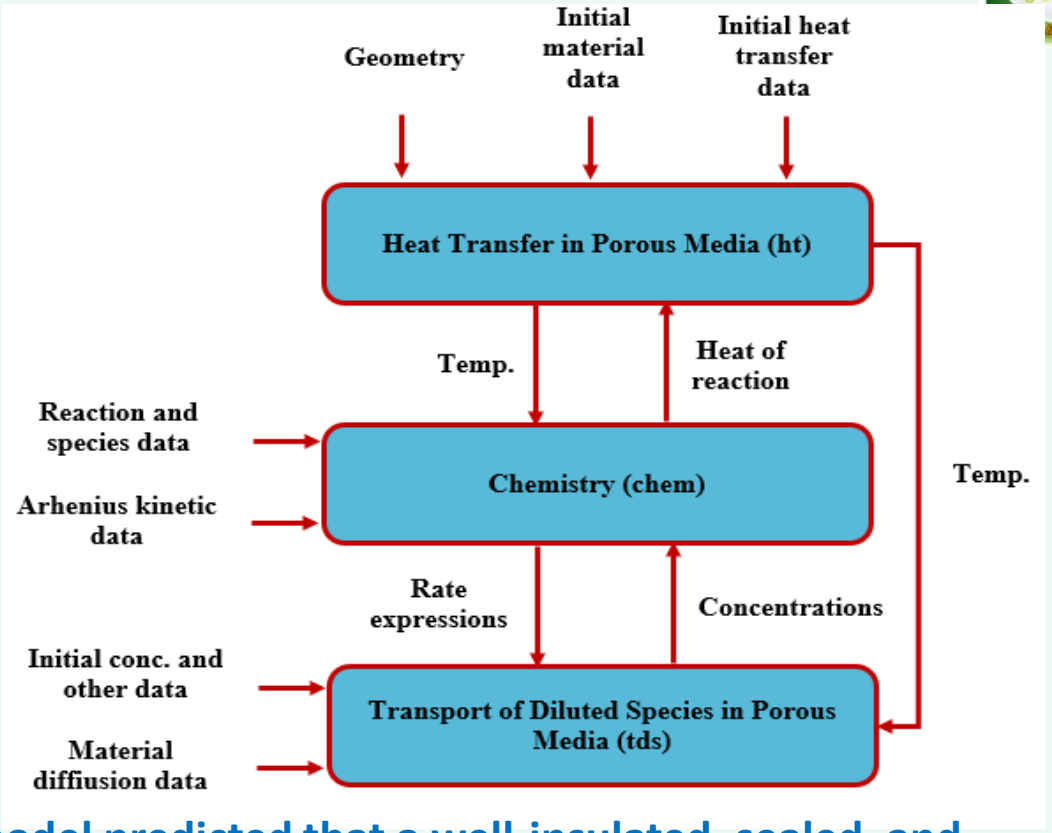
1. ACE Inhibitory peptide supplement
2. Amino acid Supplement
3. Protein Supplement

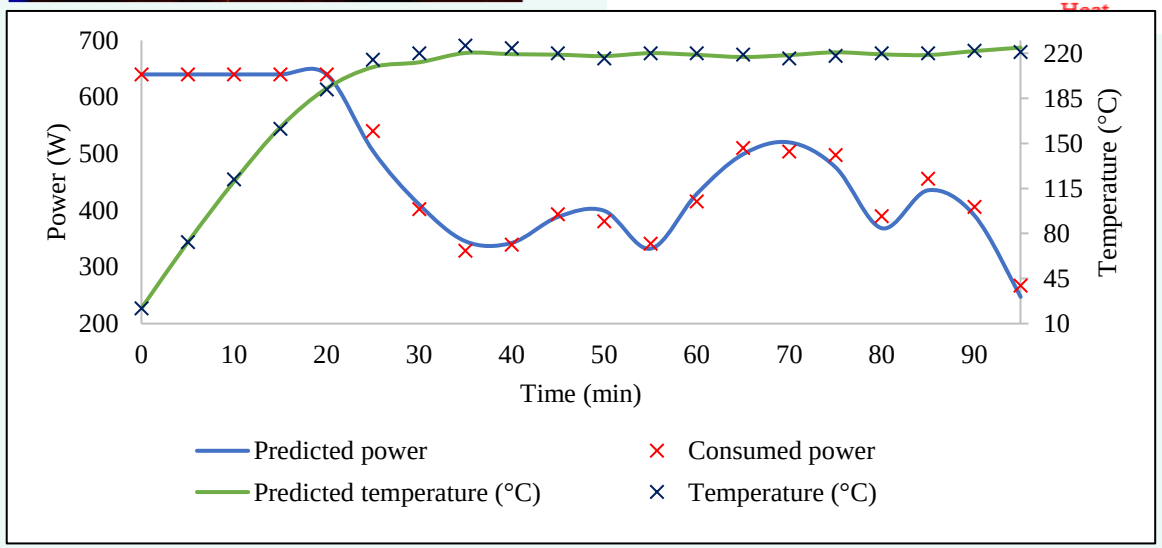
Angiotensin converting enzyme (ACE) inhibitory peptide route

Technical Progress, Future Work and Conclusion

Design and Development for Continuous HTC: Energy requirements







- The model predicted that a well-insulated, sealed, and continuous reactor can decrease the power consumption significantly when aqueous phase is recycled for heat integration and recovery.
- The developed model can potentially be used as a first step in designing an industrial reactor for hydrothermal conversion of biomass, which may attractthis investors and policy makers for commercialization of technology.

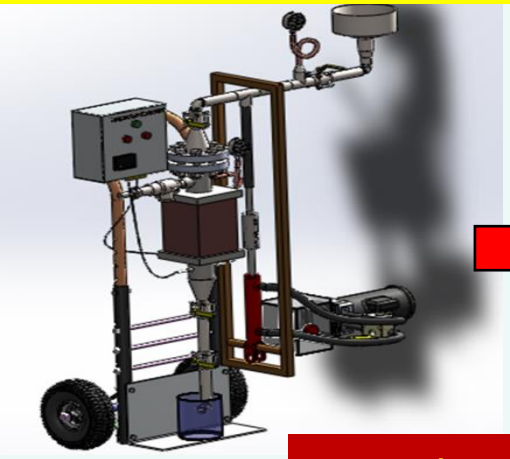
Ref: Energy, Vol 214, 2021, 119020

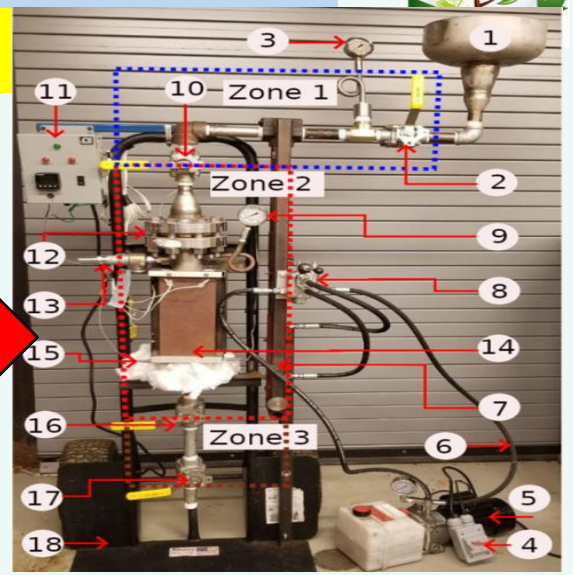
Technical Progress

Lab scale continuous hydrothermal carbonization (HTC) reactor

A lab-scale continuous hydrothermal carbonization (HTC) reactor is developed and validated.

Conceptual Design





Complete

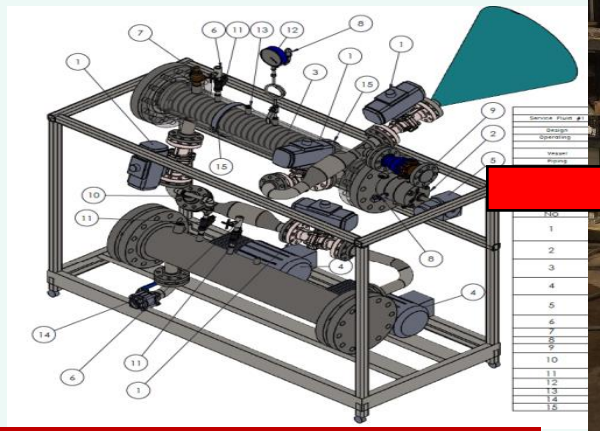
Ref: Biomass Conversion and Biorefinery (2020)

Continuous HTC is favorable due to the enhancement of primary carbonization and suppression of secondary carbonization; higher qualities of the hydrochar can be obtained.

Pilot scale continuous hydrothermal carbonization (HTC) reactor

A continuous pilot scale HTC reactor is developed. The process was validated with laboratory scale trials.

Conceptual Design



Commissioned

3 – Relevance: Contributions to three goals and objectives of the BMC and to overall national biomass / bioeconomy goals

Overall Mandate: Valorization of Agricultural and Food Wastes: A Closed-Loop Circular Economy Concept to Address Climate Change, Biogas Production, Wastewater Management, and Soil Health

1. Mobilize Canada's agricultural sector to commoditize biomass for bioenergy and bioproducts, to benefit agricultural producers in all regions of Canada
   - Established sustainable technological advancement for **scaling-up HTC technology**
2. Canadian farmers to earn additional revenues from residues, biomass crops grown
   - Value addition to agri-food processing wastes/contaminations corn processing using biorefinery and circular economy approach
3. Emerging carbon credit markets

   Potentials emerged for biocarbon and biocoke
   - Carbon storage in soil via biochar may be pursued for carbon credit
   - Substitution of bio-carbon for PCI coal may attract green steel production
   - Bio-carbon based energy storage materials for future

3 – Relevance to the industry

Collaboration Developed with Industries

1. Custom Steams collaborated to jointly scale-up semicontinuous HTC system.

2. Continental carbon partnered with us to extend support for application of activated carbon produced from local bioresources

3. IGPC Ethanol participates for enhancing value added materials to accommodate contaminated corn procurements for processing

Recent graduates Trishan, Eniola, Kevin, Omid, and Haidari are working in energy industries in Ontario and developed partnership with those industries.

4 - Critical Success Factors

Critical success factor

- Commercial viability of HTC depends on Scaling-up of HTC plant

Potential challenges

- Logistics of bioresources to processing plants
- Regulatory and operational limits of HTC reactors

Demonstrate commercial viability of biomass

- Bio-carbon and Activated Carbon as a commercial commodity likely to be integrated into Canadian business and compensate the biomass producers
- Biorefinery value chain likely to attract revenue and business model sustainability

5. Future Work

Plan to do through the end of the project

- Upgrade biocarbon for productivity and higher value applications
- Reach out to stake holders for green chemicals established through biorefinery
- Develop Factsheets for potential bioproducts and carbon products

Highlight upcoming key milestones –

- Lifecycle and techno-economic assessments

To address and deal with commercialization issues

- Engage stake holders with a Knowledge Transfer and Translation (KTT) activity

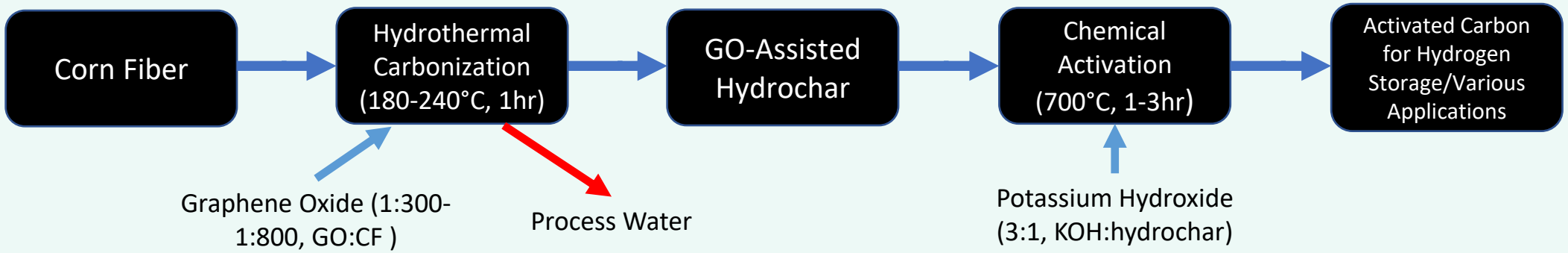
FUTURE DIRECTION (3-5 YEARS):

COMMERCIAL GRADE ACTIVATED CARBON FOR HYDROGEN STORAGE FROM GRAPHENE OXIDE ASSISTED HYDROTHERMAL CARBONIZATION OF CORN FIBER

New Process Development: Process overview and advantages

- **Conventional 2-Stage Process Path:**

- **Proposed 2-Stage Process (GO Assisted HTC With KOH Activation):**



Advantages:

Corn fiber is high in moisture and nitrogen content[1]:

Low-value by-product of corn ethanol industry[1]

Suitable for HTC, enhancement of H_2 storage properties from N_2 functionality[2]

Addition of GO ($C_{140}H_{42}O_{20}$):

Act as catalyst during HTC, enhance morphology of hydrochar[3,4]

Promote HTC reactions and facilitate carbonization[4]

HTC for carbonization step

Enhances pore formation and degree of carbonization[6]

Reduction in ash content and impurities[6]

Chemical Activation with KOH

Promote formation of micropores[7]

Higher surface area[7]

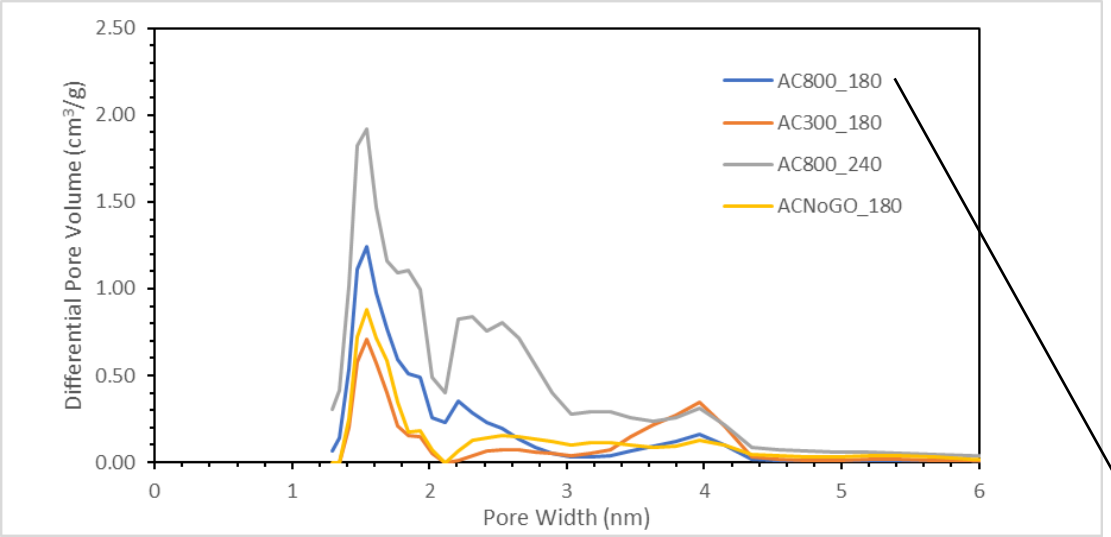
Product Metrics and Objectives

➢ Pore size and distribution

- Most important for physical H_2 adsorption in porous materials[7,8]
- Nanoporous material (pore width sizes in range of 0.7-1.5nm will be most effective for H_2 storage)[7]
- Kinetic diameter of H_2 molecule is 0.28nm, should be at least double[8]

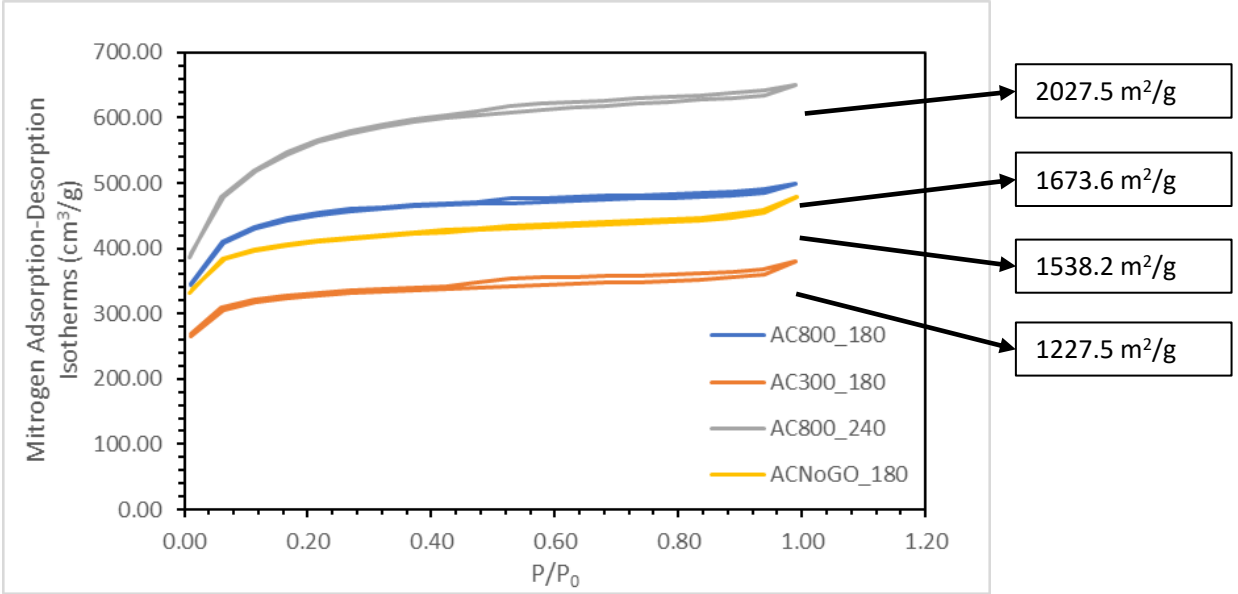
➢ Specific Surface Area

- BET surface area above ~1500m²/g[7]
- Type-1 N_2 Adsorption Isotherm



Initial pore size distribution results from prepared activated carbons.

*Note for sample ID: AC800_180 corresponds to activated carbon produced with 1:800 GO:CF ratio and HTC temperature of 180°C



Initial N_2 adsorption-desorption isotherms from prepared activated carbons

Summary

Key points to take away

1) **Approach**: Target the recovery of value from every co-product of agri wastes conversion by utilizing the outputs of one process as the input to another, leading to zero-waste solutions.

2) **Technical accomplishments**: Develop a pilot scale semicontinuous HTC reactor, a modified two step processing pathway, a concept of HTC-AD integration, and biorefinery paths to addressed sustainable routes for agri wastes valorization

3) **Relevance:** Mobilize Canada's agricultural sector by converting agri wastes to commodity chemicals and potential revenue and carbon credit generation

4) Major **challenge** anticipated is with scaling-up of the HTC to commercial scale

5) **Future Work** will continue for lifecycle of the process and products established

6) Engage with stake holders' for potential **technology transfer**

BRIL TEAM

Thank You for Your Time

Acknowledgement

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Shrimp Canada
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