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Organization: University of Guelph, Guelph, Ontario

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.
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)?
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

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

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

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

Biomass-Based CO₂ Adsorbents for Biogas Upgradation with Pressure Swing Adsorption.

Technologies for the production of renewable natural gas from organic wastes and their opportunities in existing Canadian pipelines.
Example 1: Bioenergy and biofertilizer from hydrothermal treated corn residue: a circular economy concept


- **Bioenergy**
  - **Biogas**
    - **Biocarbon** for different application
      - M=0.47 kg; E=10.91 MJ
      - E = 3.35 MJ
  - **Liquid (HTPW)**
    - M=0.30 kg
    - M loss = 0.23 kg
  - **AD process**
    - M=1 kg, E=18.13 MJ

- **Biofertilizer**
  - **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
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.


Title: Effects of FeCl$_3$ Catalytic Hydrothermal Carbonization on Chemical Activation of Corn Wet Distillers’ Fibre
Ex. 2 Continued: Miscanthus/Switchgrass to Biocarbon for Iron and Steel Industries: A Tunable Approach

<table>
<thead>
<tr>
<th>Properties</th>
<th>Raw Switchgrass</th>
<th>Torrefied-290</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C</td>
<td>44.76 ± 2.04</td>
<td>64.28 ± 2.42</td>
</tr>
<tr>
<td>%H</td>
<td>6.04 ± 0.62</td>
<td>4.34 ± 0.69</td>
</tr>
<tr>
<td>%N</td>
<td>0.66 ± 0.08</td>
<td>0.68 ± 0.13</td>
</tr>
<tr>
<td>%S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>%O</td>
<td>44.09 ± 1.87</td>
<td>23.58 ± 1.87</td>
</tr>
<tr>
<td>HHV (MJ/Kg)</td>
<td>17.13 ± 1.49</td>
<td>26.04 ± 1.91</td>
</tr>
<tr>
<td>%VM</td>
<td>84.3 ± 3.18</td>
<td>50.35 ± 2.72</td>
</tr>
<tr>
<td>%Ash</td>
<td>4.45 ± 0.23</td>
<td>7.12 ± 0.38</td>
</tr>
<tr>
<td>%FC</td>
<td>11.25 ± 0.8</td>
<td>42.53 ± 1.83</td>
</tr>
</tbody>
</table>

Hydrochar

<table>
<thead>
<tr>
<th>Properties</th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>S(%)</th>
<th>O(%)</th>
<th>FC(%)</th>
<th>VM(%)</th>
<th>HHV (MJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>52.2</td>
<td>6.2</td>
<td>0.05</td>
<td>0</td>
<td>41.31</td>
<td>15.1</td>
<td>84.66</td>
<td>20.37</td>
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</table>

Biocarbon

<table>
<thead>
<tr>
<th>Properties</th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>S(%)</th>
<th>O(%)</th>
<th>FC(%)</th>
<th>VM(%)</th>
<th>HHV (MJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI coal</td>
<td>79.67</td>
<td>4.5</td>
<td>0.35</td>
<td>0</td>
<td>14.69</td>
<td>63.71</td>
<td>35.5</td>
<td>32.59</td>
</tr>
</tbody>
</table>

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/macro pores 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.
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

Green Chemicals

Organic Liquid Fractions

40% 50% 60% 70% 80% 90% 100%

Hydrothermal Carbonization

Toxic residue / organic extracts

Bio carbon

Adsorbent / Fertilizer

Amino acids

Functional Peptides for Feed

Protein Concentrate

Adopted and Established Biorefinery Approach

Biogas

Bio carbon
Technical Accomplishments: PUBLICATIONS: Biorefinery of Corn CDS

- Characterization of ultrasonic-treated corn crop biomass using imaging, spectral and thermal techniques: a review
  
  Sonu Sharma, Ranjan Pradhan, Annamala Manickavasagan, Mahendra Thimmanagari, Animesh Dutta
  
  Biomass Conversion and Biorefinery (2020) | Cite this article

- Application of analytical pyrolysis to gain insights into proteins of condensed corn distillers solubles from selective milling technology
  
  Sonu Sharma, Ranjan Pradhan, Annamala Manickavasagan, Mahendra Thimmanagari, Animesh Dutta

- Valorization and potential of condensed corn distillers solubles fractions from selective milling technology
  
  Sonu Sharma, Ranjan Pradhan, Annamala Manickavasagan, Mahendra Thimmanagari, Animesh Dutta
  
  Biomass Conversion and Biorefinery (2021) | Cite this article
Angiotensin converting enzyme (ACE) inhibitory peptide route

Technical Accomplishments

Protein Fraction Valorization Route

- Two step sedimentation separation
- Defatting
- Crude Protein 24% w/w
- Defatted Protein 22% w/w
- Insoluble Fraction ~8%
- Soluble Fraction ~14% w/w
- Ultrafiltration
- <3 kDa Peptide mix (ACE inhibitory)
- ~10% w/w
- >3 kDa (~4% w/w) Peptides mix

Corn Distillers Solubles (CDS) 100 gm

Protein (~20%)

- Crude Protein 24 gm 54.7% ±1.3%
- Defatted Protein 22.83 g (81.75% ± 0.7%)

Insoluble Fraction 7.89 g

Soluble Fraction 13.94 g (71.34 ± 0.96%)

Hydrolyzed Protein

- Extensive hydrolysis
- Partial hydrolysis
- Mild hydrolysis

Ultrafiltration

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
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 attract investors and policy makers for commercialization of technology.
Lab scale continuous hydrothermal carbonization (HTC) reactor

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

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.
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:**

  - **1st Stage**
    - Carbonaceous Organic Material → Carbonization (pyrolysis, 600-900°C) → Char/Biochar
  - **2nd Step**
    - Activation and Oxidation (500-1000°C) → Activated Carbon

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

  - **1st Stage**
    - Corn Fiber → Hydrothermal Carbonization (180-240°C, 1hr) → GO-Assisted Hydrochar
  - **2nd Step**
    - Chemical Activation (700°C, 1-3hr) → Activated Carbon for Hydrogen Storage/Various Applications

**Advantages:**

- Corn fiber is high in moisture and nitrogen content:
  - Low-value by-product of corn ethanol industry
  - Suitable for HTC, enhancement of H₂ storage properties from N₂ functionality

- Addition of GO ($C_{140}H_{42}O_{20}$):
  - Act as catalyst during HTC, enhance morphology of hydrochar
  - Promote HTC reactions and facilitate carbonization

- HTC for carbonization step:
  - Enhances pore formation and degree of carbonization
  - Reduction in ash content and impurities

- Chemical Activation with KOH:
  - Promote formation of micropores
  - Higher surface area
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 $\sim$1500m$^2$/g$^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**
Thank You for Your Time