Transforming Low Value Agri-food Processing Wastes to High Value Chemicals and Materials

Animesh Dutta, Professor and Director
Bio-Renewable Innovation Lab (BRIL)
School of Engineering, University of Guelph, Canada

Biomass Canada Cluster Webinar Series
"De-risking and commoditizing underutilized biomass resources: Facilitating the evolving Canadian bioeconomy"
December 2020 – March 2021

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

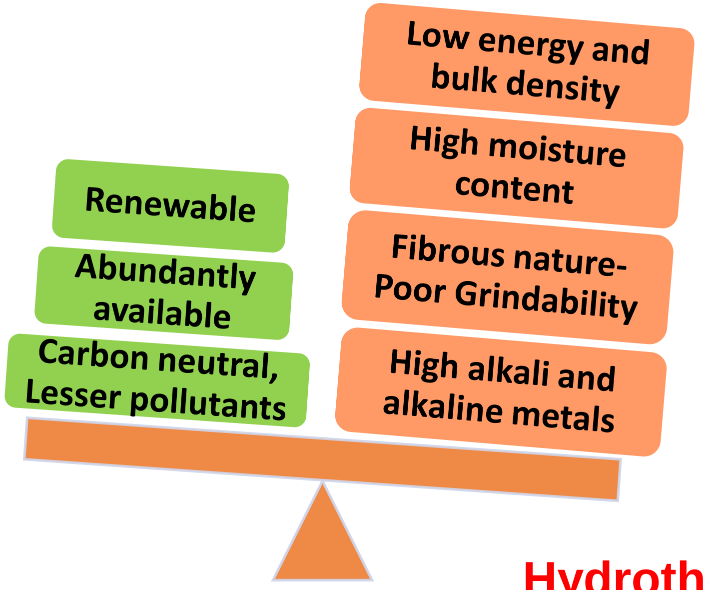
Our Ultimate Goal is to Develop

"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."

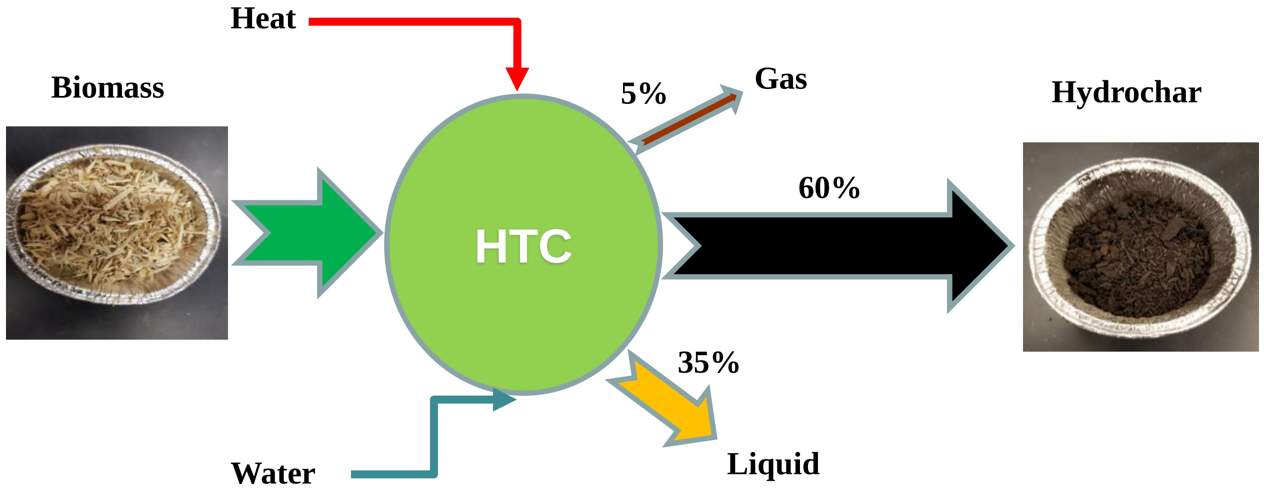
Meeting Biomass Canada Cluster's Goal by

- 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

Theme of the research:
"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) is a technique where biomass is treated with hot compressed water instead of drying

	Conventional pre-treatment: Drying, torrefaction, pyrolysis	**Alternative Pre-treatment:** Hydrothermal conversion
❑ Moisture	✗	✓
❑ Ash	✗	✓
❑ Processing time	?	✓
❑ Energy intensity	✗	?
❑ Operation	✓	?

Project Overview

Theme: “Waste is a resource - waiting for an opportunity”

- Biocarbon (hydrochar) produced through hydrothermal carbonization (HTC) of low quality agri-food residue, exhibits unique physicochemical properties while it produced HTC process water as co-products
- HTC products 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)?
- Can we produce activated carbon/biocatalyst from this hydrochar
- Will there be any industrial grade biochemical as a co-product from HTC Process Water (HTCPW)?

Approach

Hypothesis:

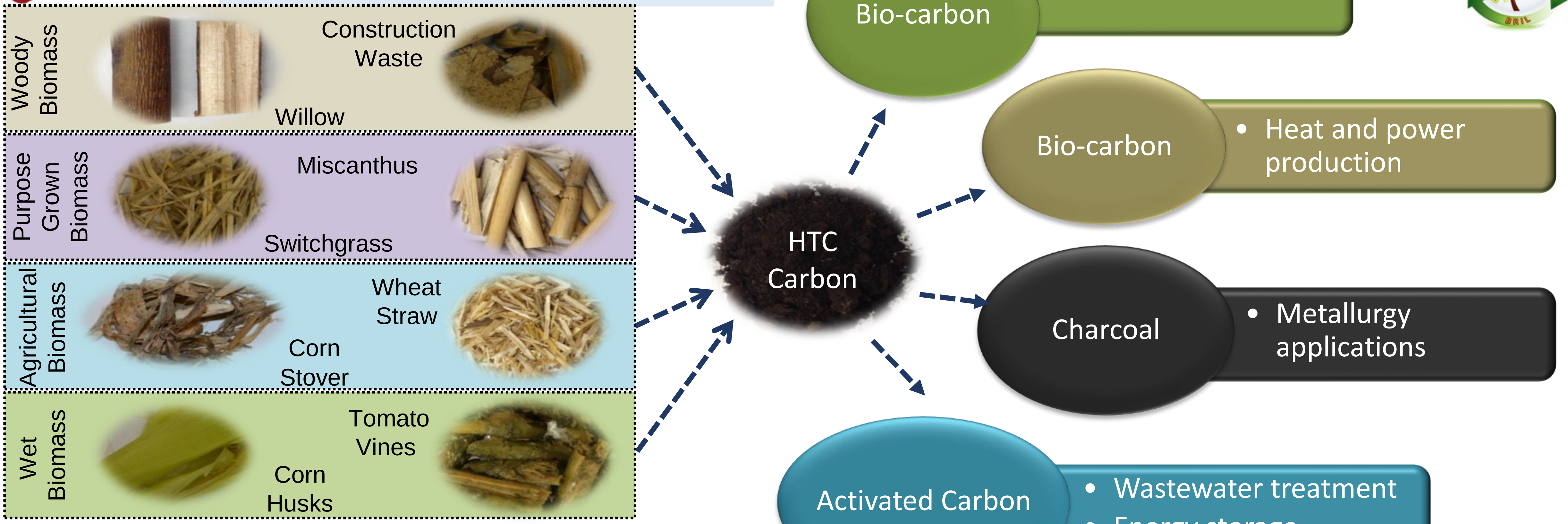
1. Changing HTC processing conditions (time, temperature, feedstocks sizing, etc.) will generate recipes for biocarbon (hydrochar) of required morphological properties for various applications. **(help eliminate some of the key barriers to Agri-food waste stream)**
2. Hydrochar can be further processed to produce activated carbon/biocatalyst
3. By applying this HTC process water into AD (Anaerobic Digestion) system, the hydrolysis process would be accelerated, which is the main limiting factor for AD system (**help eliminate some limiting factors for AD system**)

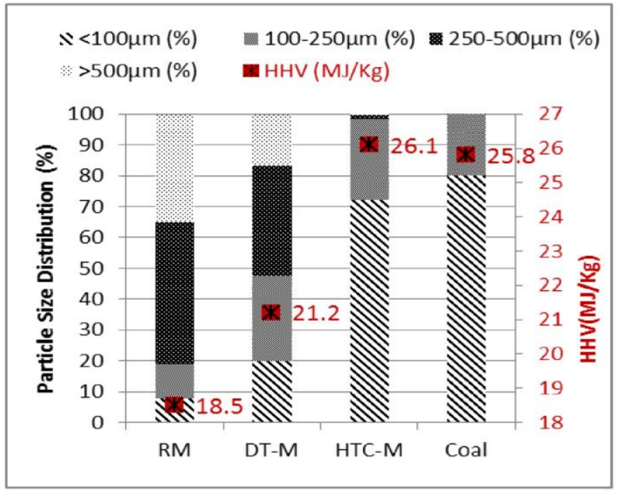
Approach to establish of these hypothesis includes:

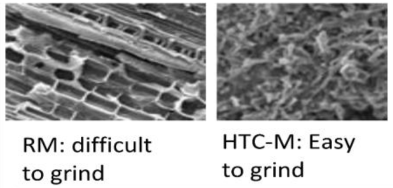
1. We defined milestones with
   - HTC Process design and development
   - Feedstock processing and characterizations (HTC & AD)
   - Process design for end products and characterizations
2. Identified critical deliverable
   - Life cycle assessment (LCA) and life cycle costing (LCC)

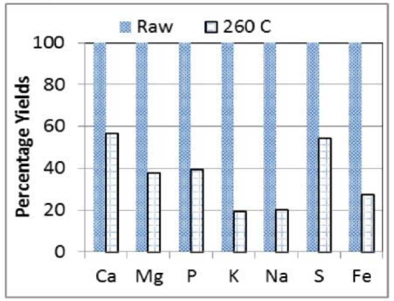
UNIVERSITY of GUELPH

Biocarbon development research







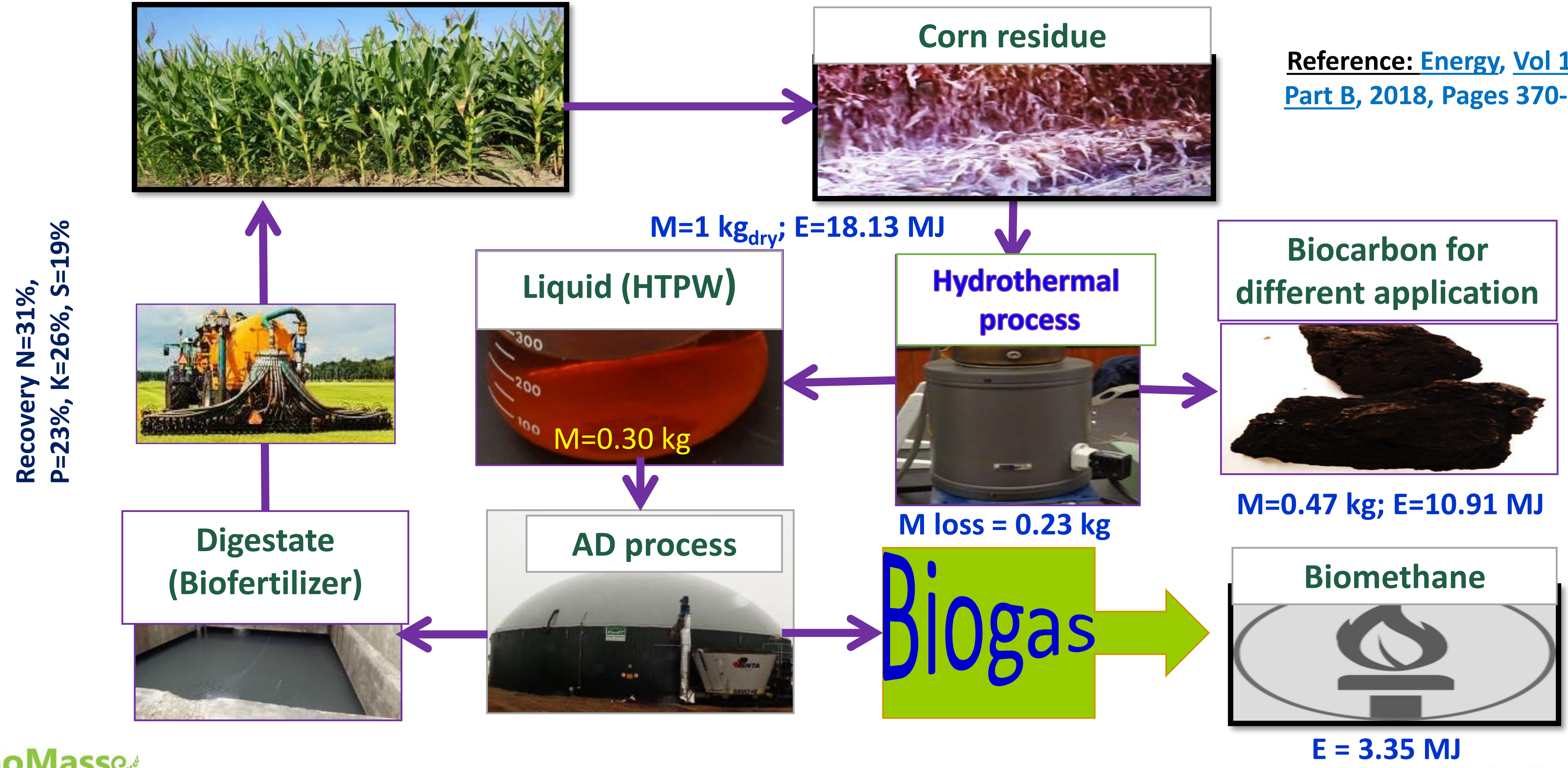


- **HTC can be an ideal pre-treatment method to remove some of the barriers.**
- **Depending upon applications, it may require further processing**

RÉSEAU BIOFUELNET CANADA

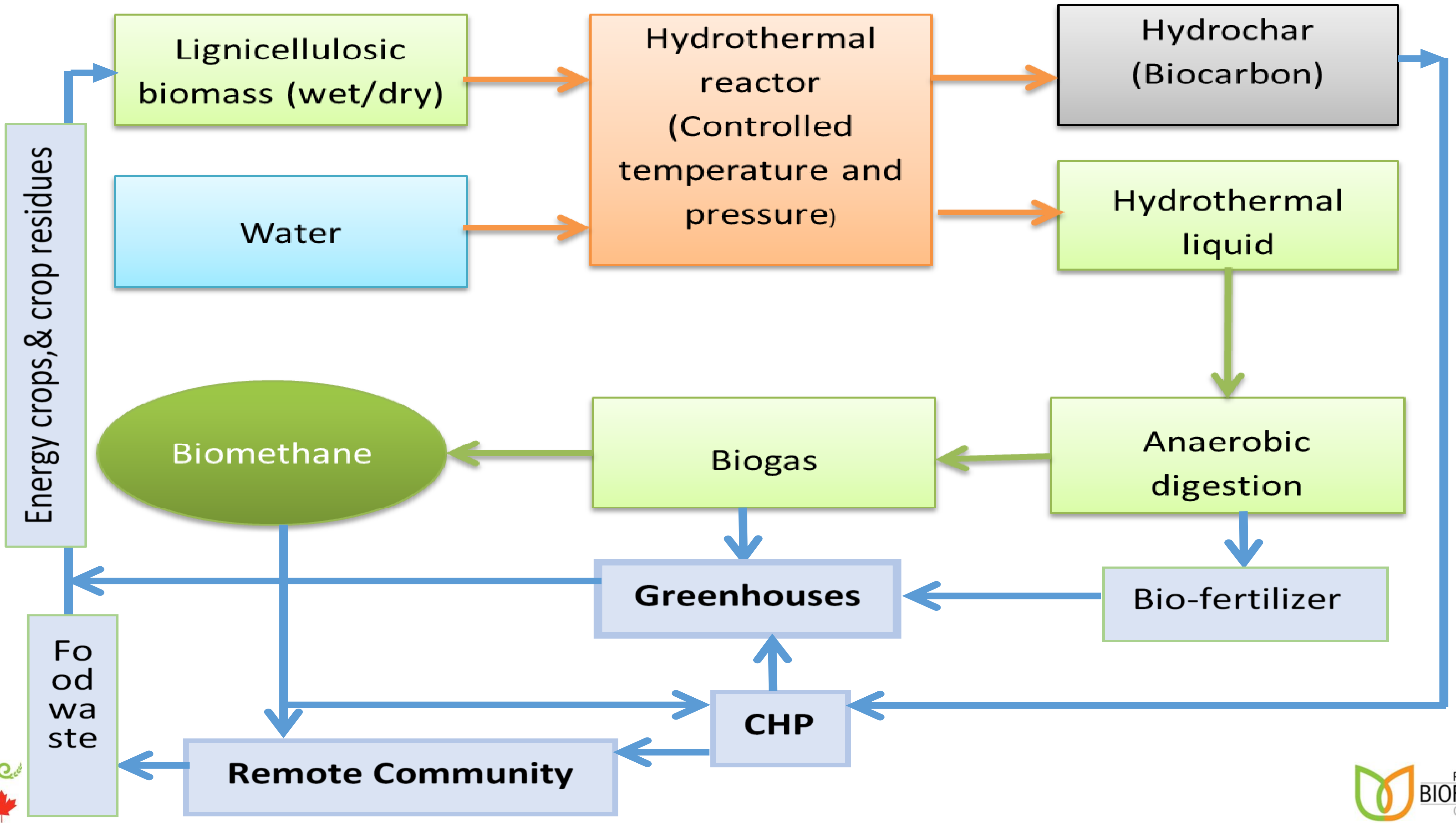
Case Study 1: Bioenergy and biofertilizer from hydrothermal treated corn residue: a circular economy concept

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



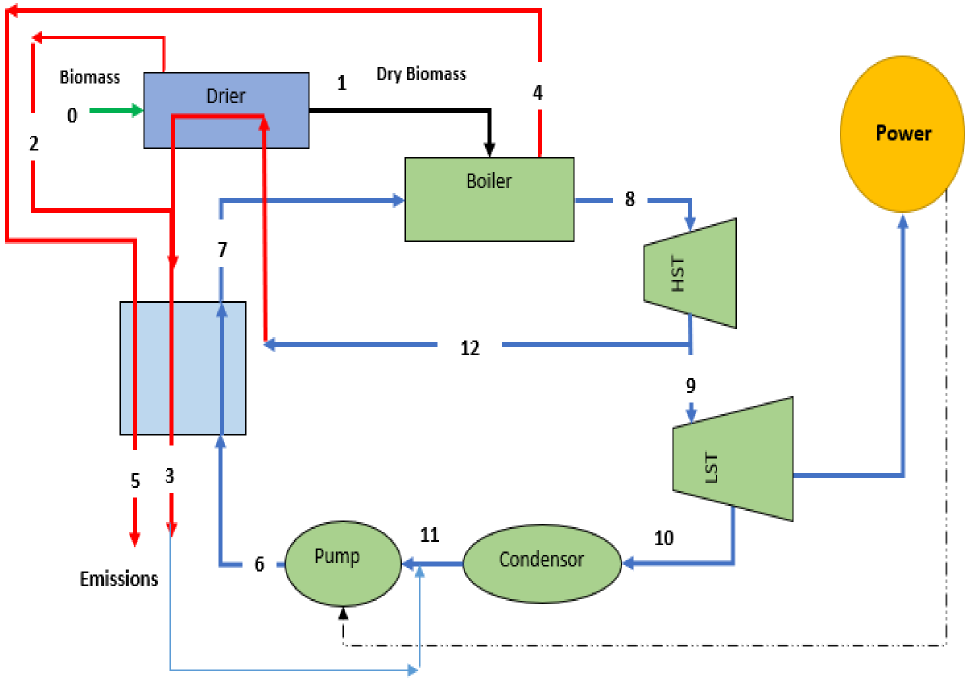
Overall energy recovery efficiency=79%

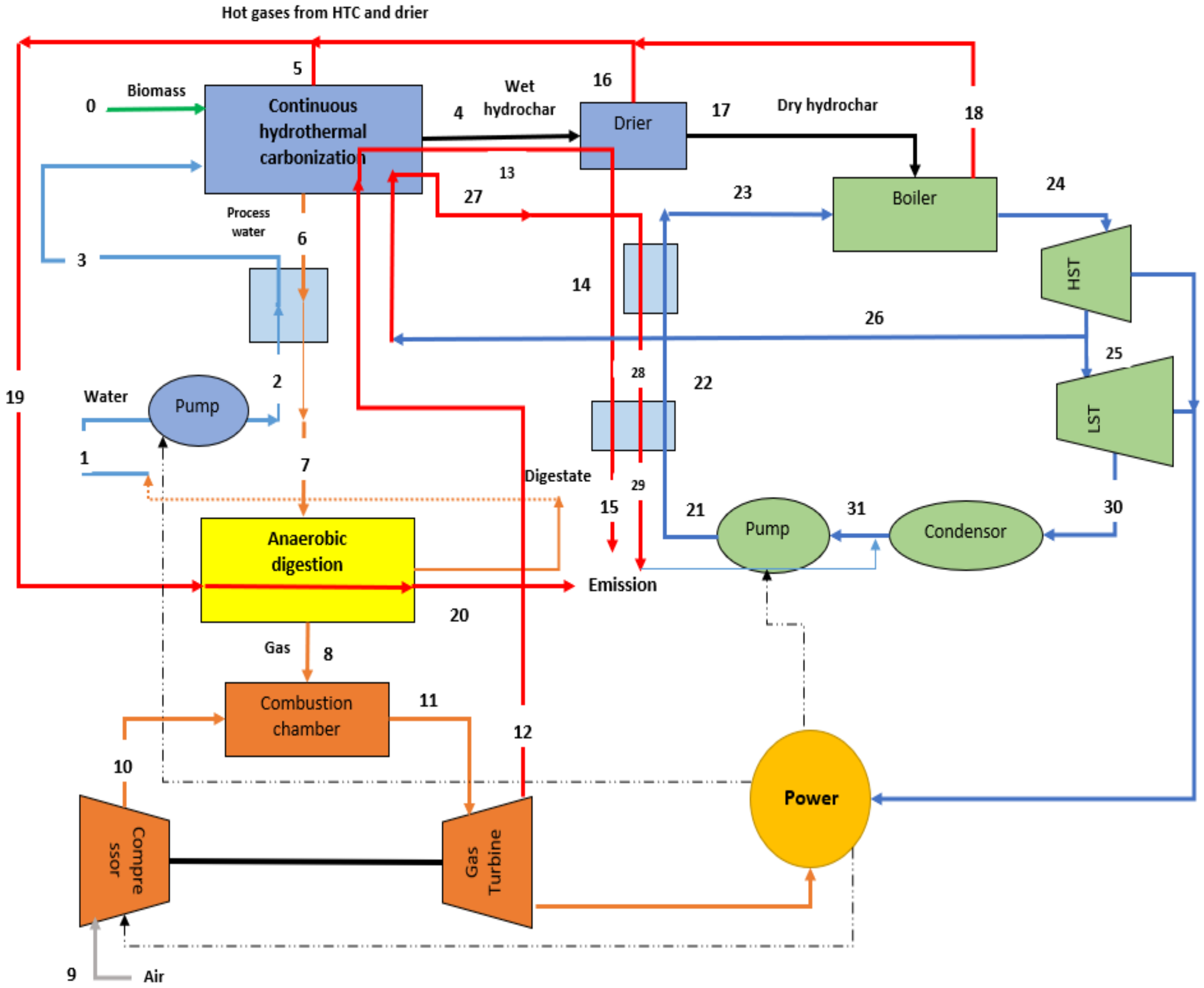
Case Study 1: Waste to Wealth: A Circular Economy Based Approach

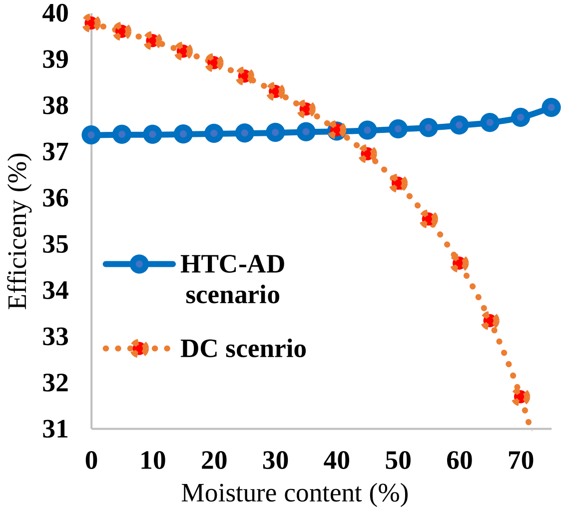


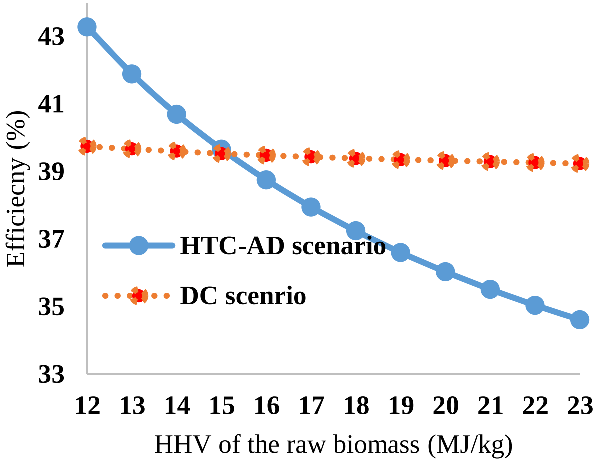
Case Study 1: Numerical analysis of an integrated HTC-AD system for power generation

Ref: Processes 2020, 8(1), 43







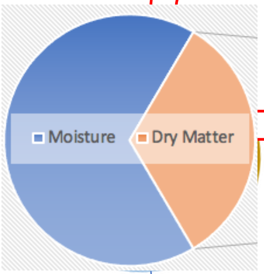


HTC-AD scenario shows a better performance compared to DC one when the moisture content of the biomass is over 40%

Case Study 2– Biorefinery Approach

Establishment of Biorefinery Product Stream for Process Wastes

Non-lignocellulosic Agri-food process wastes

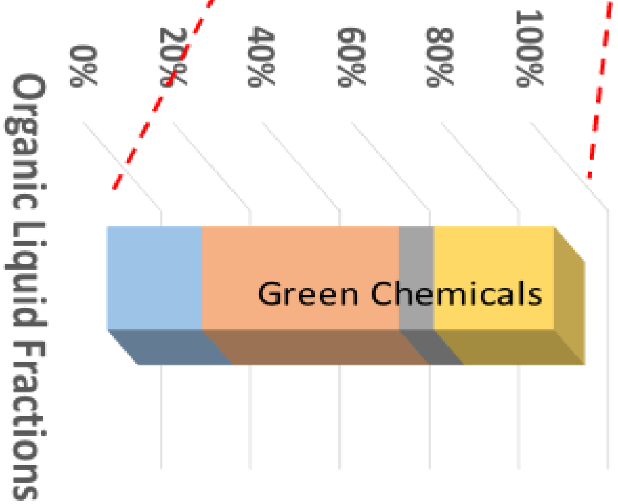


Toxic residue / organic extracts

Hydrothermal Carbonization

Proteins

Extractive Biochemicals



Adopted

and

Established

Biorefinery

Approach

Protein Concentrate

Functional Peptides for Feed

Amino acids

Bio carbon

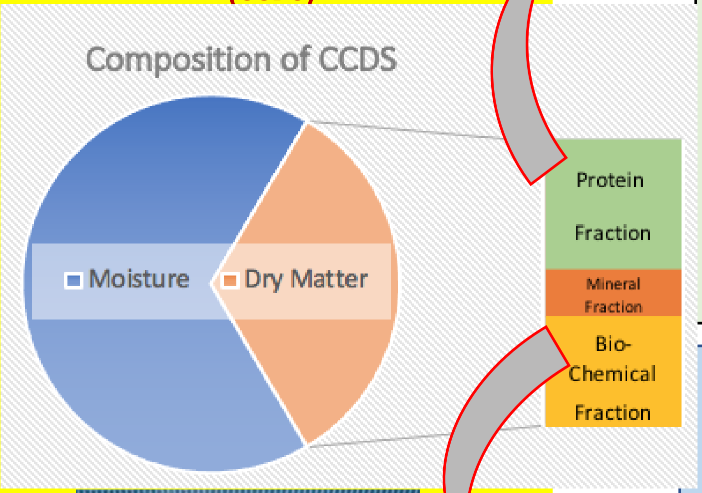
Adsorbent / Fertilizer

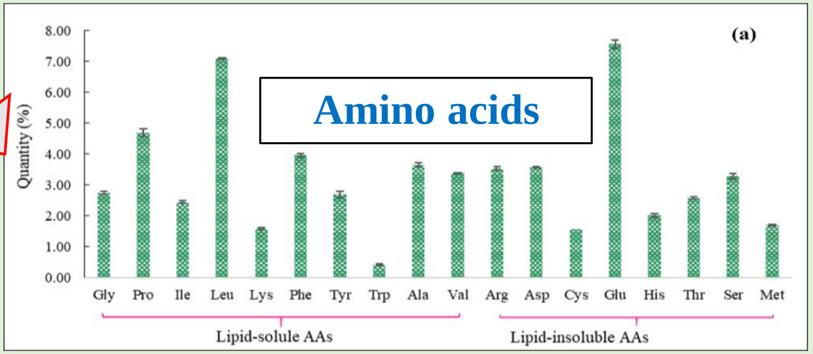
Case 2: Technical Progress/Results – Potentials Identified

Valorization of low-grade Condensed Corn Distillers Solubles - CCDS (aflatoxin contamination)

Biorefinery

Condensed Corn Distillers Soluble (CCDS)





Glu, Leu and Pro were the most abundant

Trypsin hydrolyzed peptides

- VFVDHPLFLER
- TGGLGDVLGGLPPAMAANGHR
- NPESFLSSFSK
- ILHTISVPGEFQFFFGPGGR
- FAFSDYPELNLPER

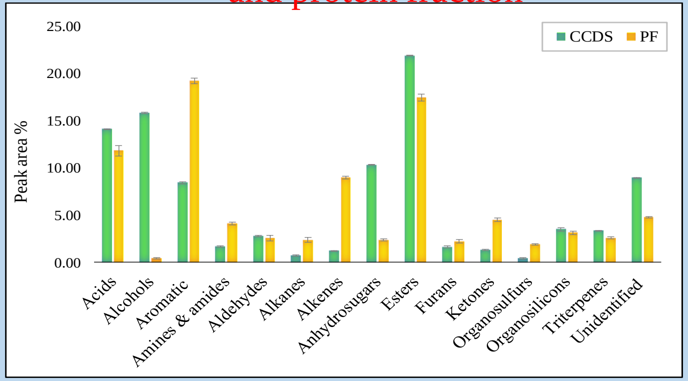
Bioactivities ⇒

- Antiamnestic
- ACE Inhibitor
- Antithrombotic
- Stimulating
- Regulating
- **Antioxidative***
- Hypolipidemic
- DPP IV Inhibitor
- DPP III Inhibitor
- Campde Inhibitor
- Renin Inhibitor

Major compounds in solvent extracted fraction from CCDS during GC/MS analysis (BCF Fraction contents)

Compound	Molecular formula	%Area	Molecular weight
2,3-Butanediol, [R-(R*, R*)]-	$C_4H_{10}O_2$	34.65±0.96	90.07
Benzene ethanol, 4-hydroxy-	$C_8H_{10}O_2$	10.42±0.60	161.08
Pentanedioic acid, 3-(1,2-diphenylpropylidene)-, monomethyl ester	$C_6H_{10}O_4$	5.24±0.54	338.15
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	3.90±0.21	256.24
9,12-Octadecadienoic acid (z, z)-	$C_{18}H_{32}O_2$	10.43±0.76	280.24

Distribution of pyrolysate compounds in CDS and protein fraction

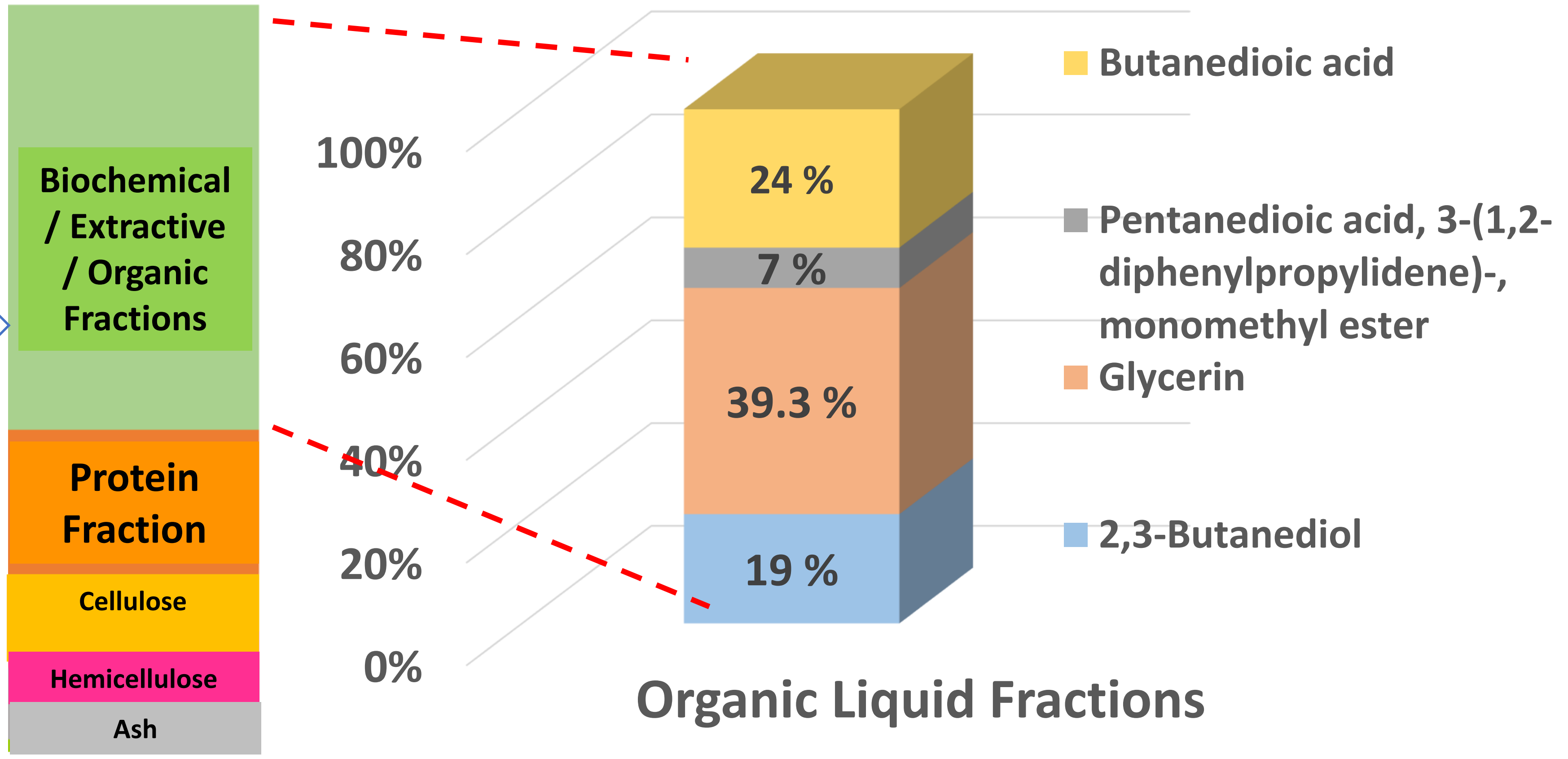


Case 2: Technical Progress/Results - Green Chemicals

Valorization of CCDS Liquid Components to Green Chemicals

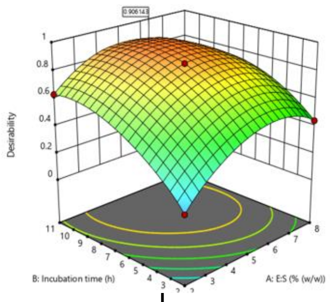
Agri-food waste-based Bio-resources

Condensed Corn Distillers Solubles - CCDS



Green Industrial Chemicals For Paint & Plastics

Case 2: Technical Progress/Results– Peptides for Feed

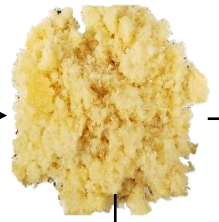


Response surface optimization

Incubation time = 9.3 h
Enzyme: substrate = 5.2% (w/w)

Alcalase hydrolysis

Protein fraction

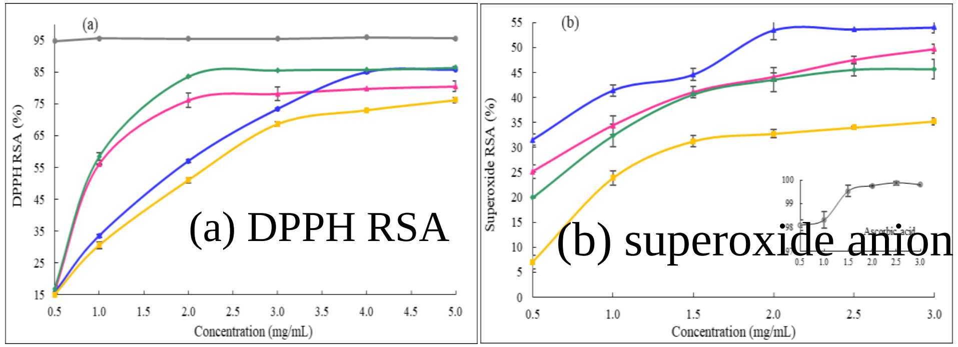


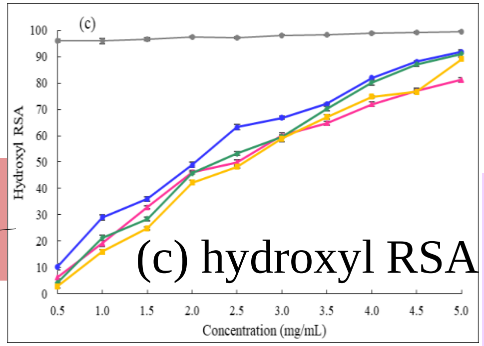
Protein hydrolysate

Molecular weight distribution (kilo Dalton)

< 3 kDa ~ 70%
3 -10 kDa ~ 15%
> 10 kDa ~ 15%

Antioxidant evaluation





Antioxidant activities of the three purified fractions with molecular weights of < 3 kDa, 3 – 10kDa and > 10 kDa

Three fractions tested demonstrated +ve antioxidant activities

Ascorbic used as a positive control. (RSA: radical scavenging activity)

Most abundant amino acids

Glutamic acid (Q)
Leucine (L)
Proline (P)

Potential peptides in < 3 kDa fraction

FLPF, VALPL, LLPF, SNIPLSPL, NPILQPY, QQPIIGGA, LPPYLSPA, NIIPSPI

Antioxidant sequences by BIOPAP-UWM

GP, LPM, LLPF, WY, PWV, PW, TY, AY PWT, WPL, VKV

Physico-chemical characterization by PepDraw

Hydrophobicity = +2.58 to +13.19 kcal/mol
Net charge = -1 to +1
Isoelectric point = 3.21 to 10.21

UNIVERSITY of GUELPH

Case 2: Technical Progress/Results–

PUBLICATIONS: Biorefinery of Corn CDS

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

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 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]

COMMUNICATED :

Journal: **Food Chemistry**
Title: Evaluation of peptides in enzymatic hydrolysates of corn distillers solubles from selective milling technology

BioMasse Canada

RÉSEAU BIOFUELNET CANADA

Case 2: Technical Progress/Results - Biocarbon

Valorization of Condensed Corn distillers Solubles - CDS and Corn Pericarp Fiber

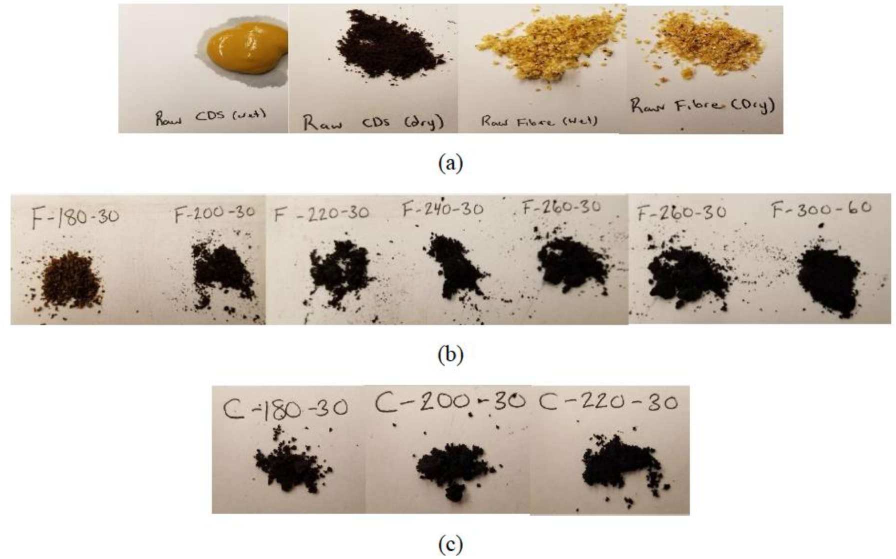
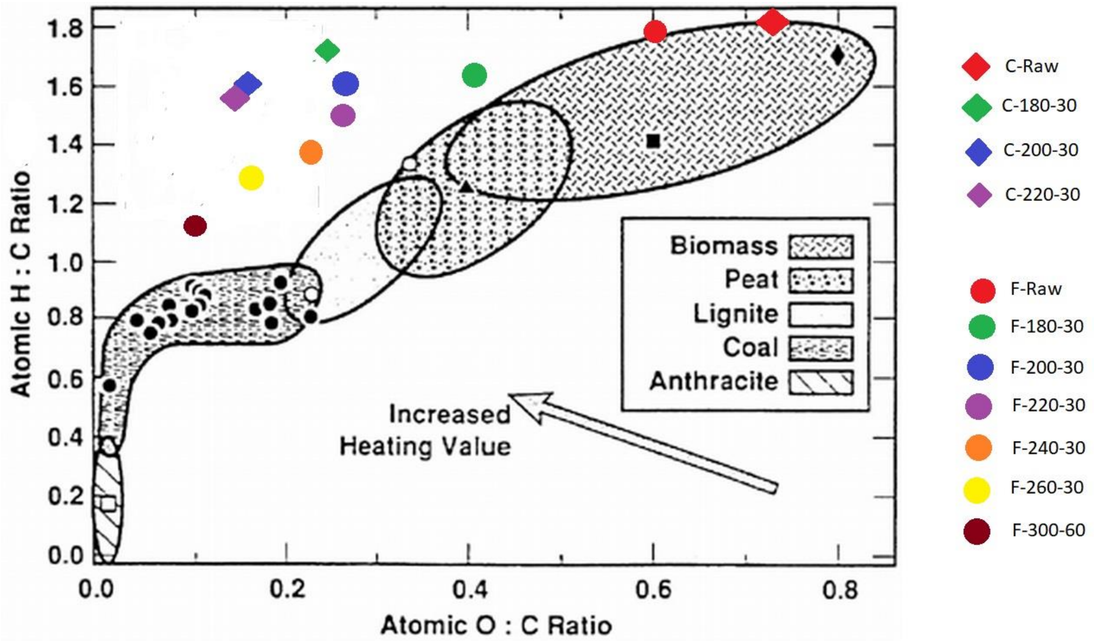
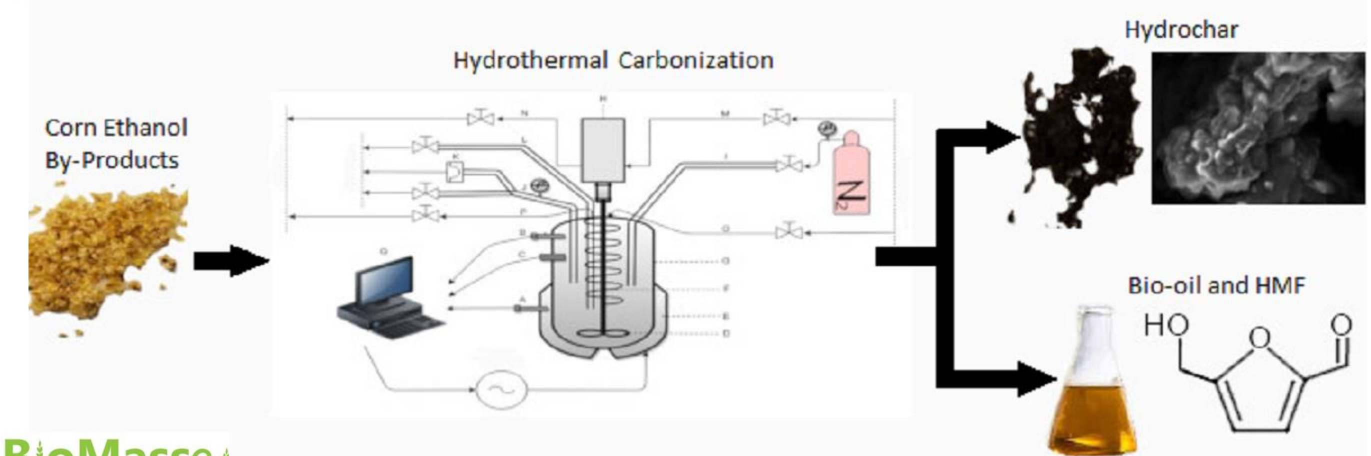


Figure 1: Physical appearance of (a) raw materials, wet and dry (b) Corn Fibre hydrochars, and (c) CDS hydrochars.



The H/C and O/C atomic ratios have been plotted on a Van Krevelen Diagram to show how the products compare with typical carbon-based materials.

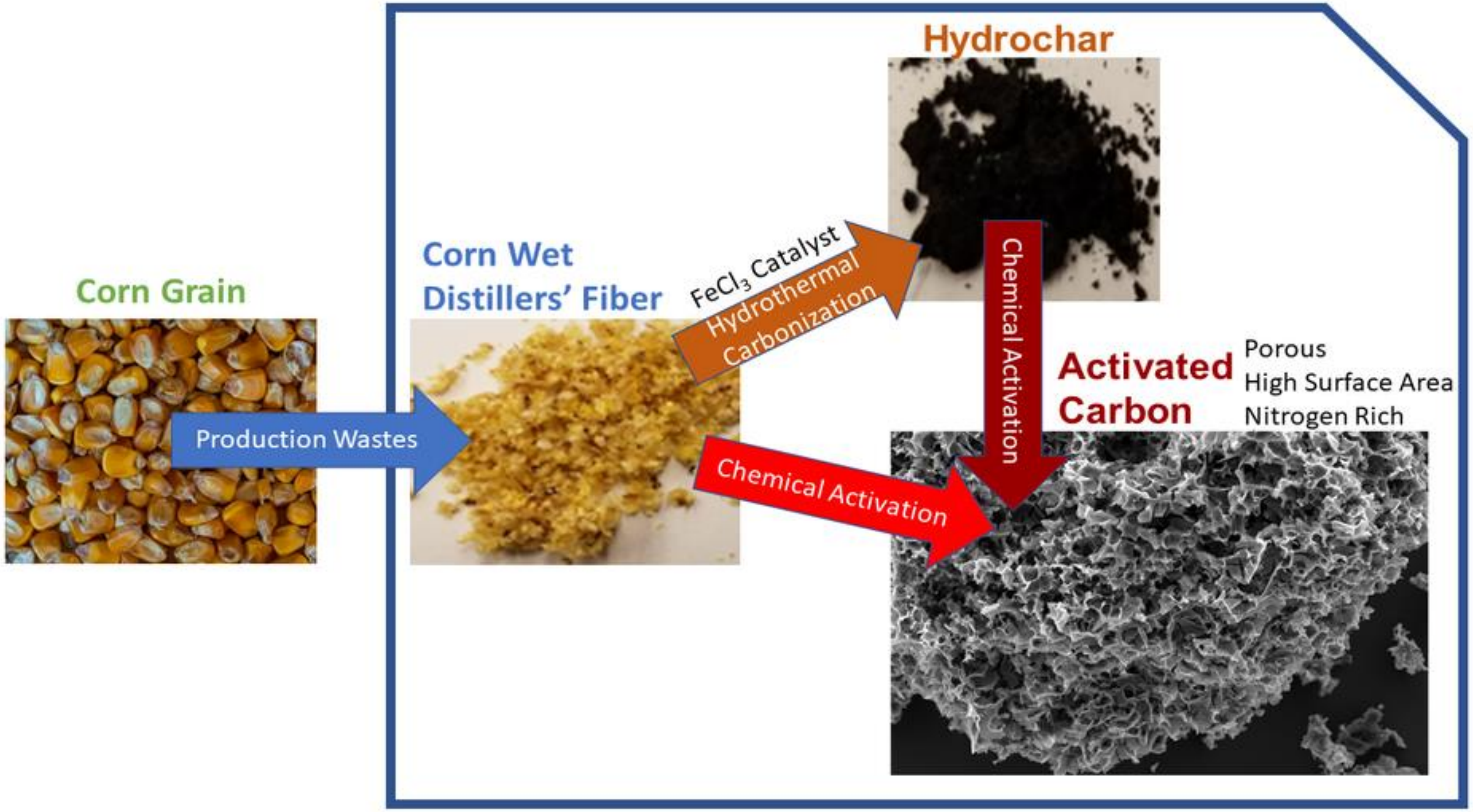
A high H/C ratio and low O/C ratio indicate a high HHV.



Communicated in Journal of Environmental Chemical Engineering

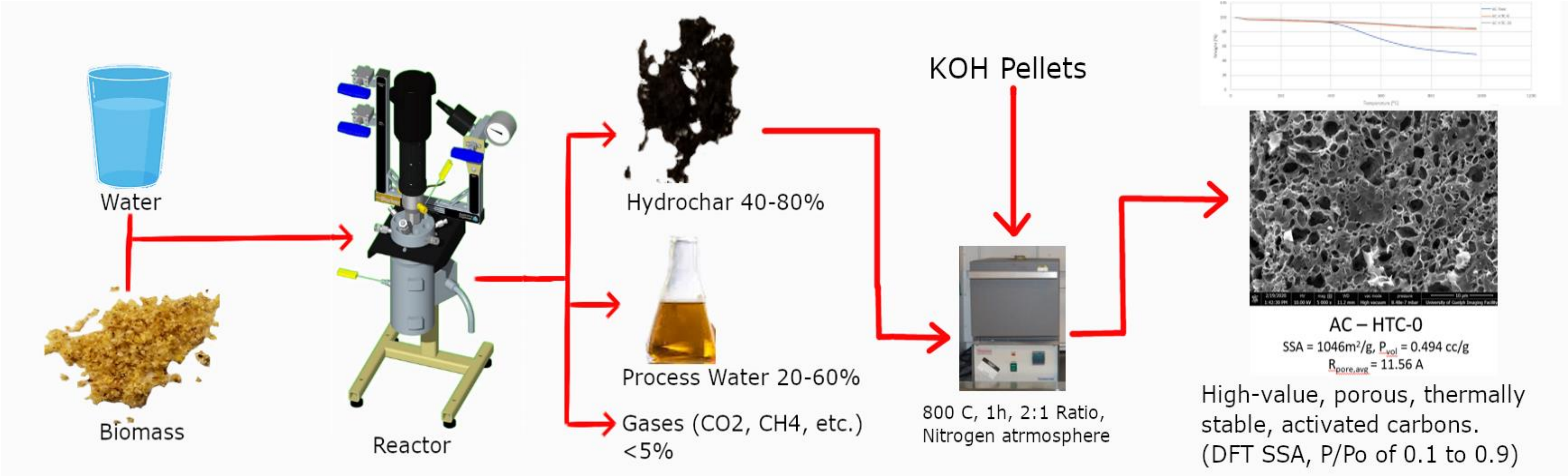
Title: Hydrothermal Carbonization Valorization as an Alternative Application for Corn Bio-Ethanol By-Products

Case Study 3: A Tunable Approach for Activated Carbon Production from Low Value Biomass



Case Study 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.



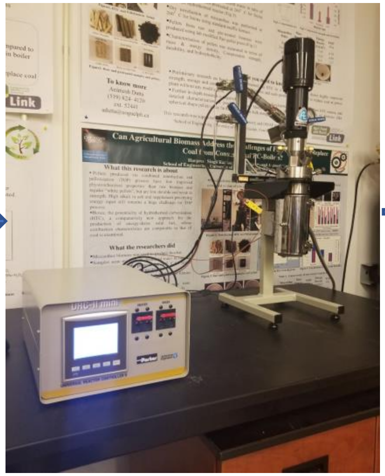
Communicated in ACS Omega Journal

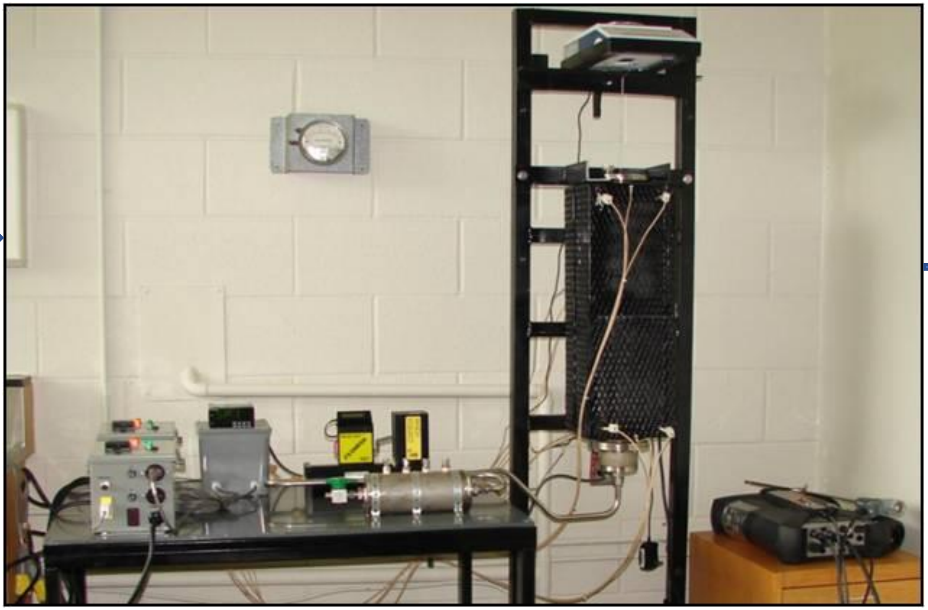
Title: Effects of $FeCl_3$ Catalytic Hydrothermal Carbonization on Chemical Activation of Corn Wet Distillers' Fibre

UNIVERSITY of GUELPH

Case Study 3: Miscunthus/Switchgrass to Biocabon for Iron and Steel Industries: A Tunable Approach

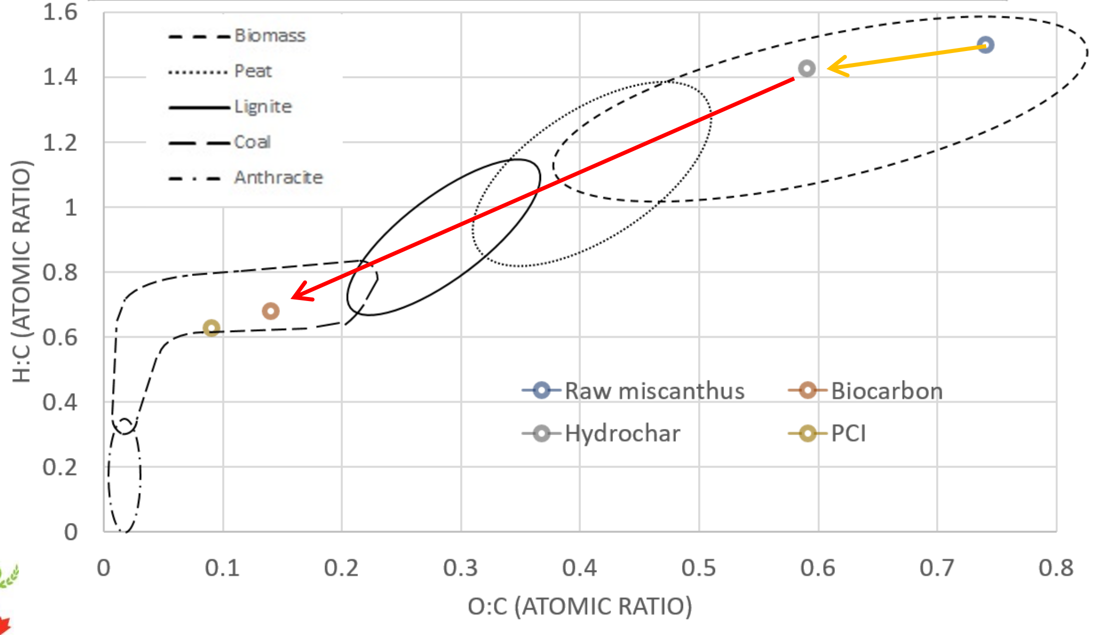
Bio-renewable Innovation Lab BRIL





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**



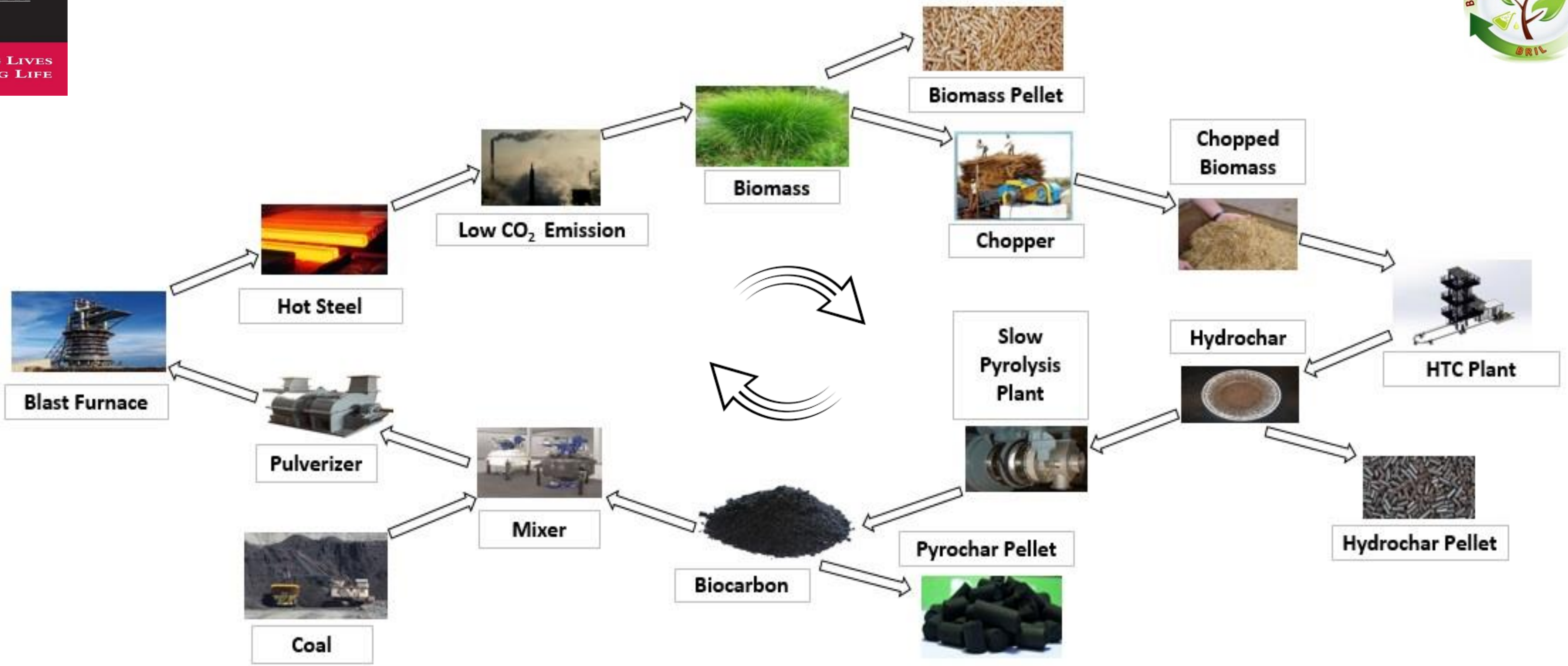
Biocarbon	
C(%)	**79.67**
H(%)	4.5
N(%)	0.35
S(%)	0
O(%)	**14.69**
Ash(%)	**0.79**
FC(%)	63.71
VM(%)	35.5
HHV (MJ/Kg)	**32.59**

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**

BioMasse Canada

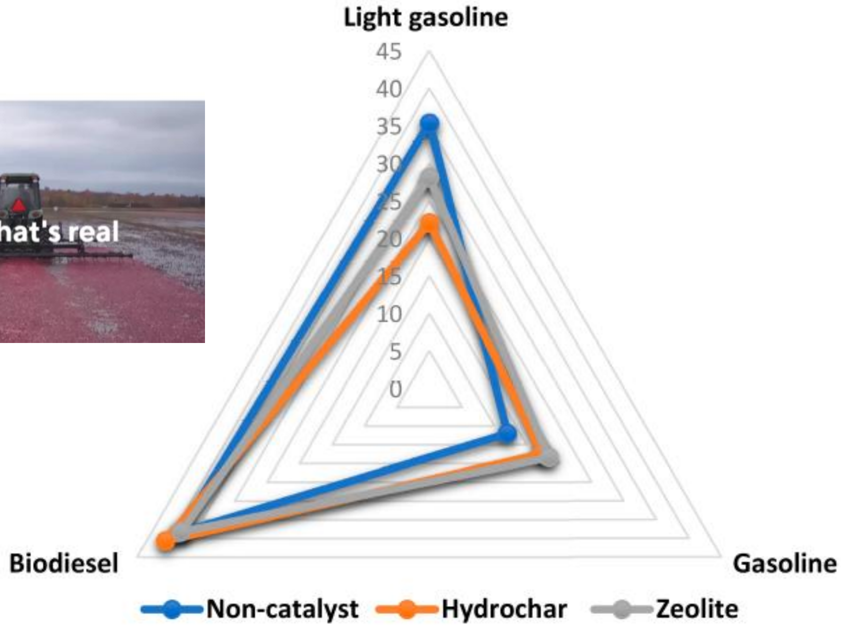
RÉSEAU BIOFUELNET CANADA

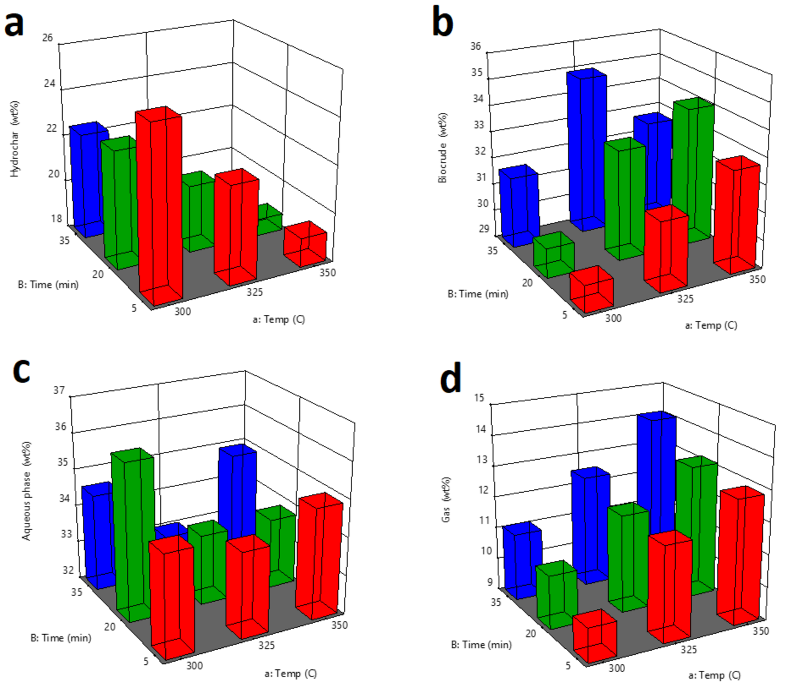
Case Study 3: Overall Approach



- 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 ironmaking process
- Reduction of GHGs emission

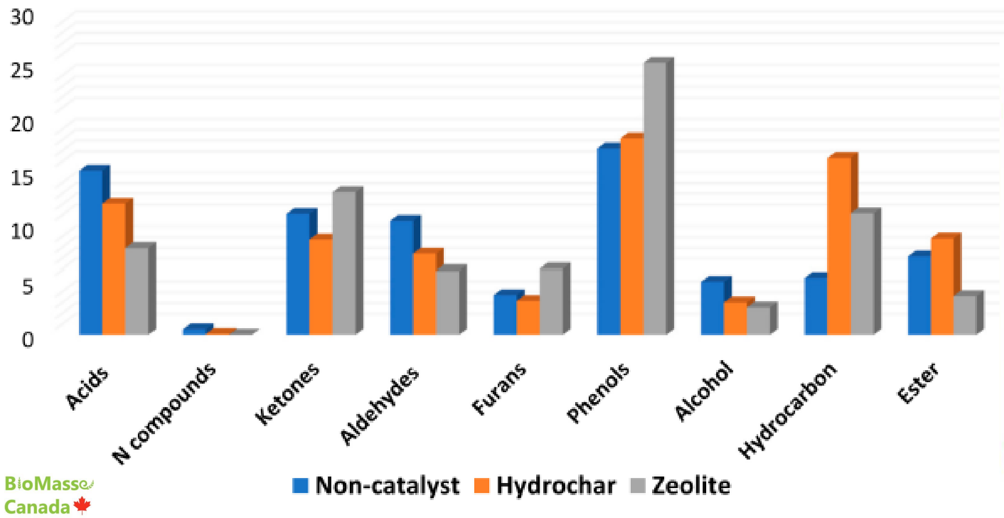
Case Study 4: New Insights for the Future Design of Composites Composed of Hydrochar and Zeolite from Cranberry Pomace. Ref: Energies 13 (24), 6600, 2020

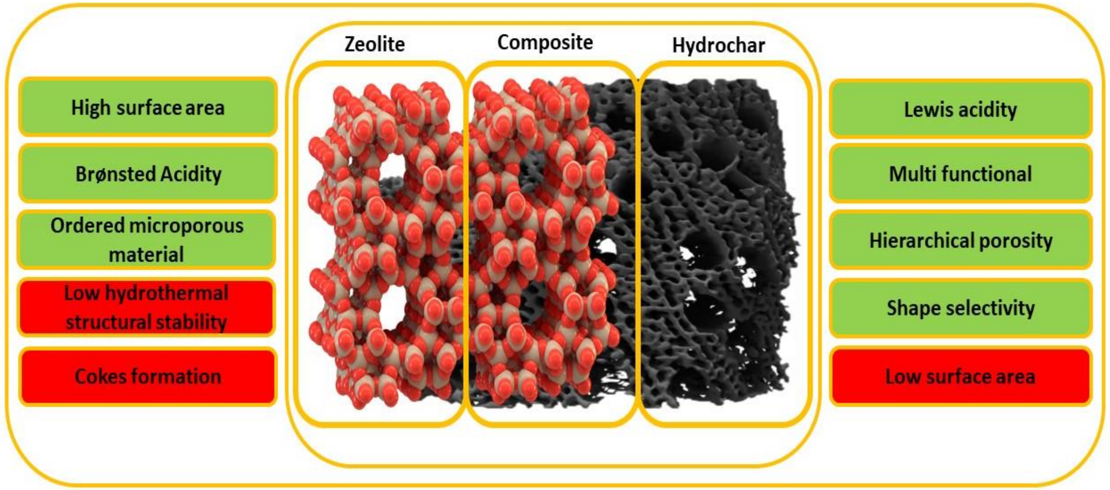




A catalyst based on hydrochar and zeolite (hydrochar/zeolite composite) can resolve present limitations and challenges by:

- 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

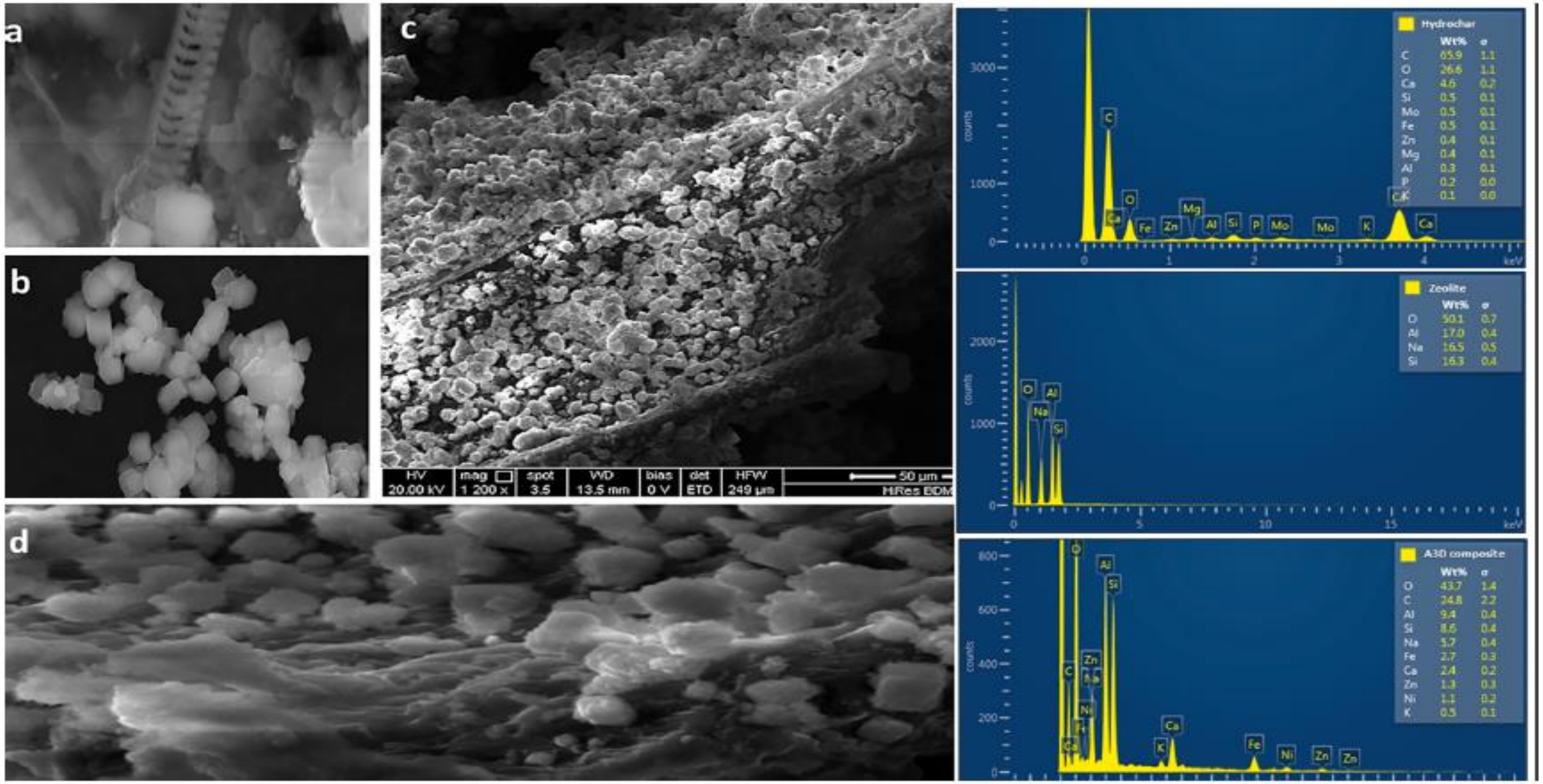




BioMasse Canada

UNIVERSITY of GUELPH

Case Study 4: Design of a ternary 3D composite from hydrochar, zeolite and magnetite powder for direct conversion of biomass to gasoline

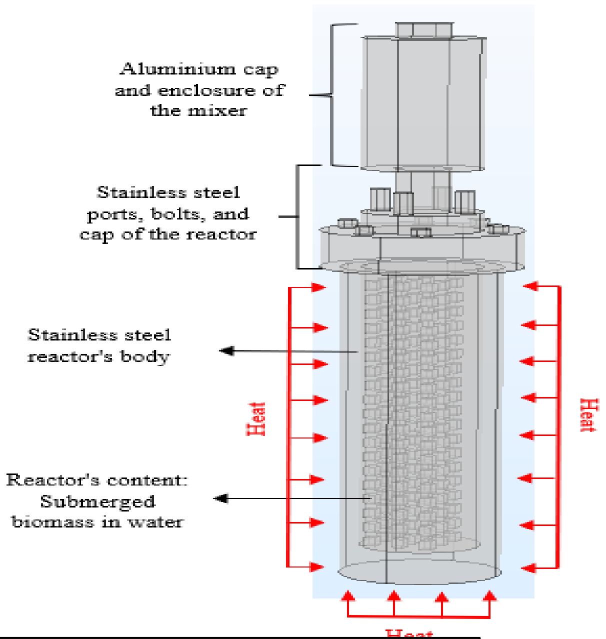


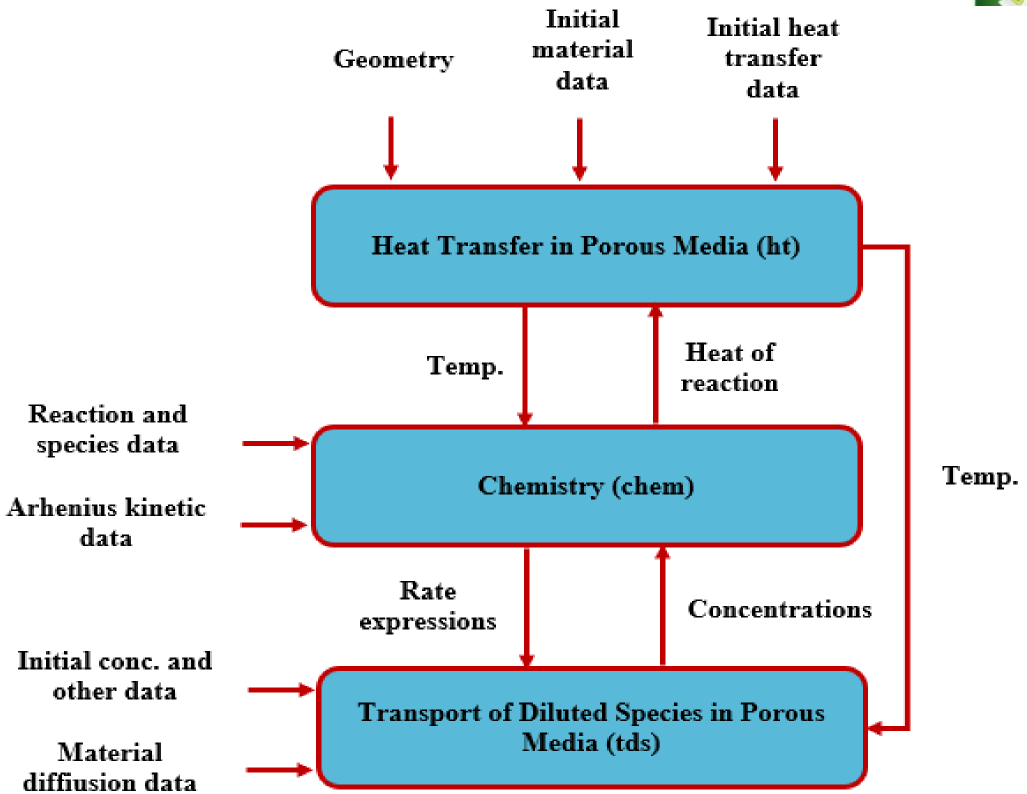
- We have synthesized a zeolite-hydrochar composite using a simple one-step hydrothermal liquefaction (HTL) process.
- hierarchically structured porosity of the composite facilitates diffusion of macromolecules and their derivatives inside the composite and improves the accessibility to lewis acid sites.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

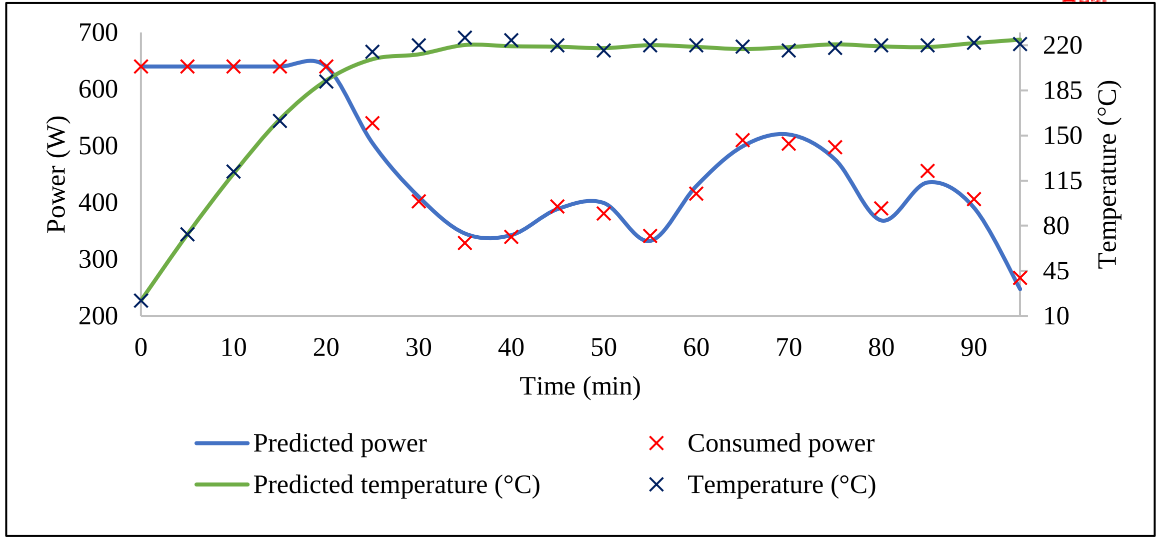
BioMasse Canada

RÉSEAU BIOFUELNET CANADA

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.

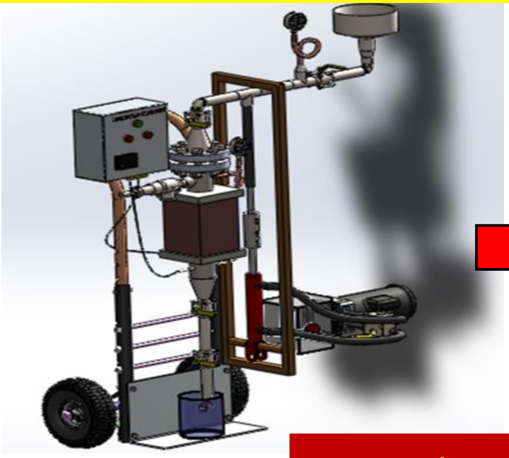
Ref: Energy, Vol 214, 2021, 119020

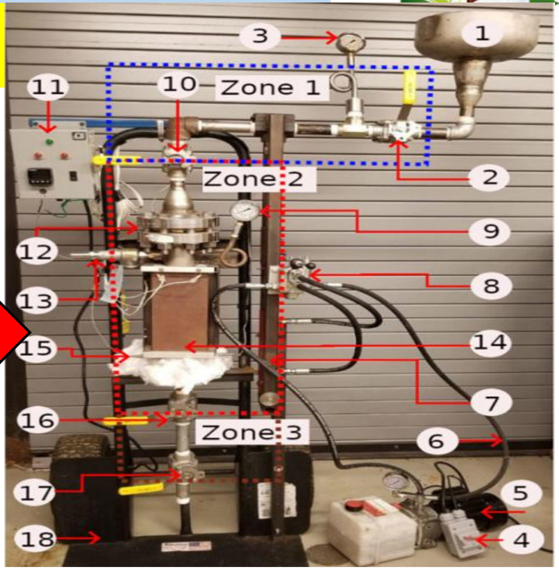
Technical Progress

Lab scale continuous hydrothermal carbonization (HTC) reactor

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

Conceptual Design





Complete

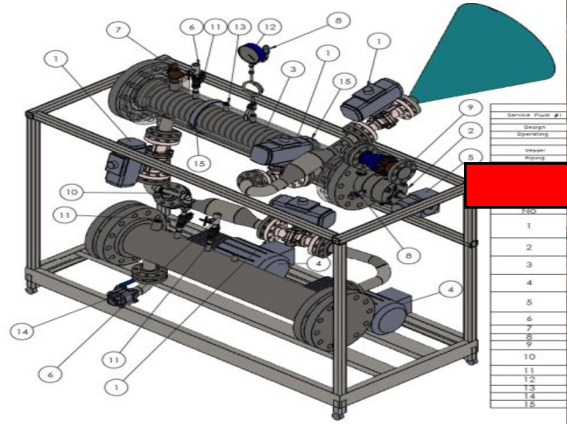
[Ref: Biomass Conversion and Biorefinery]() **(2020)**

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 being developed. The process was validated with laboratory scale trials.

Conceptual Design

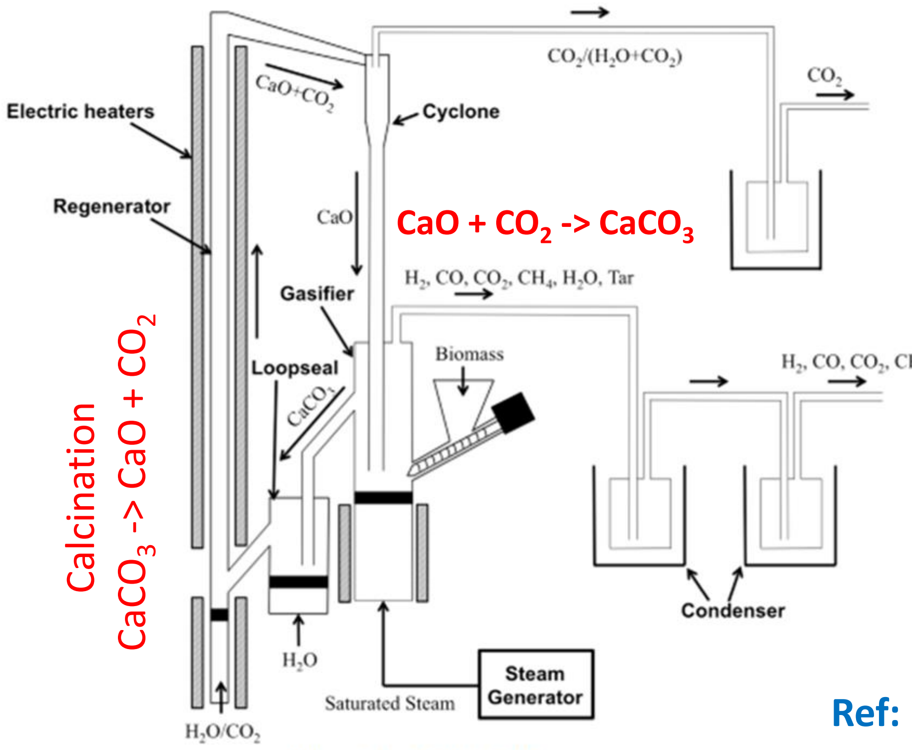


Under Commissioning

BioMasse Canada

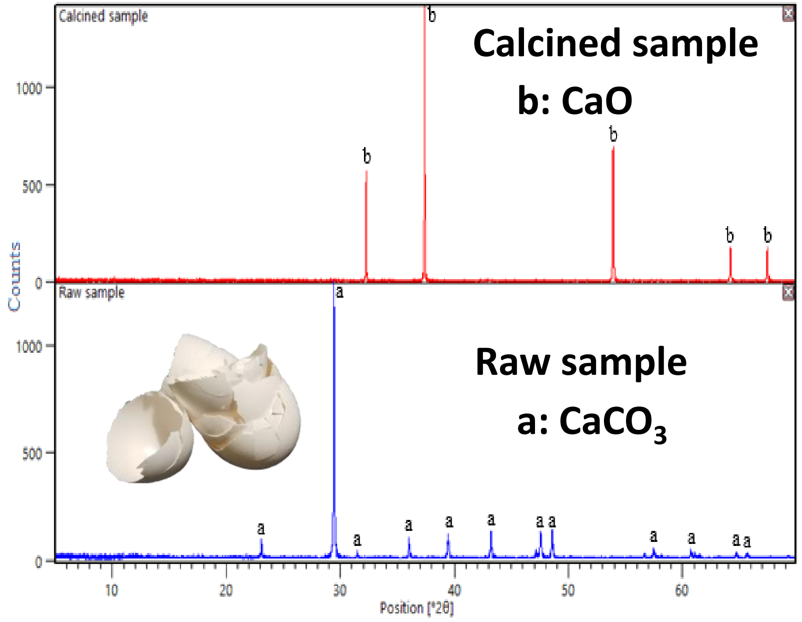
RÉSEAU BIOFUELNET CANADA

Hydrogen-rich gas stream from steam gasification of biomass: Eggshell as a CO_2 sorbent



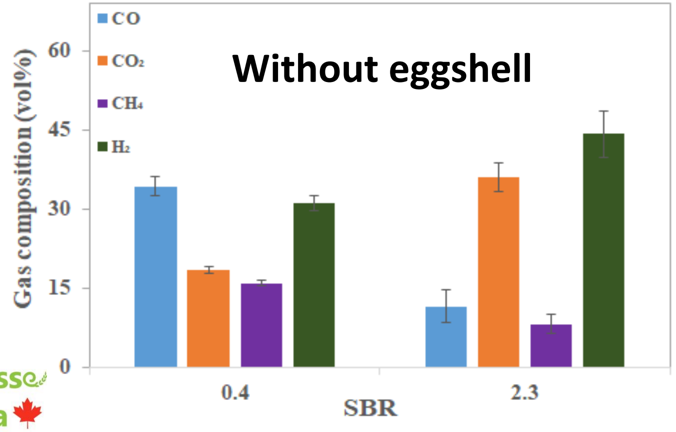
Schematic of CFB-CLG

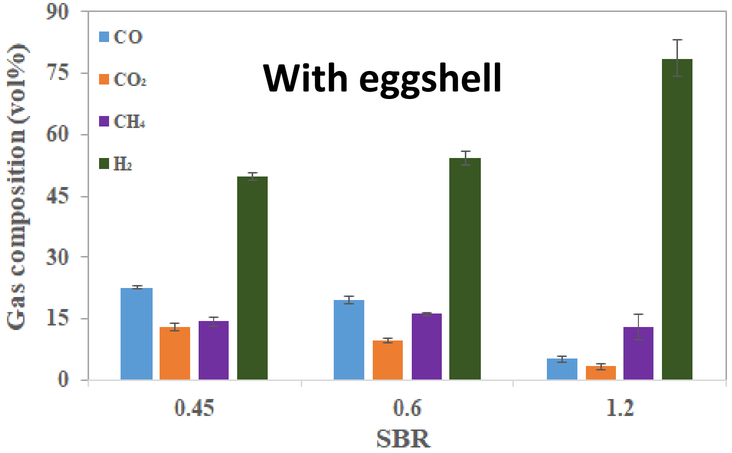
Ref: Energy Fuels 2020, 34, 4, 4828–4836



XRD results show that eggshell is mainly $CaCO_3$

Eggshell has been converted from $CaCO_3$ to CaO

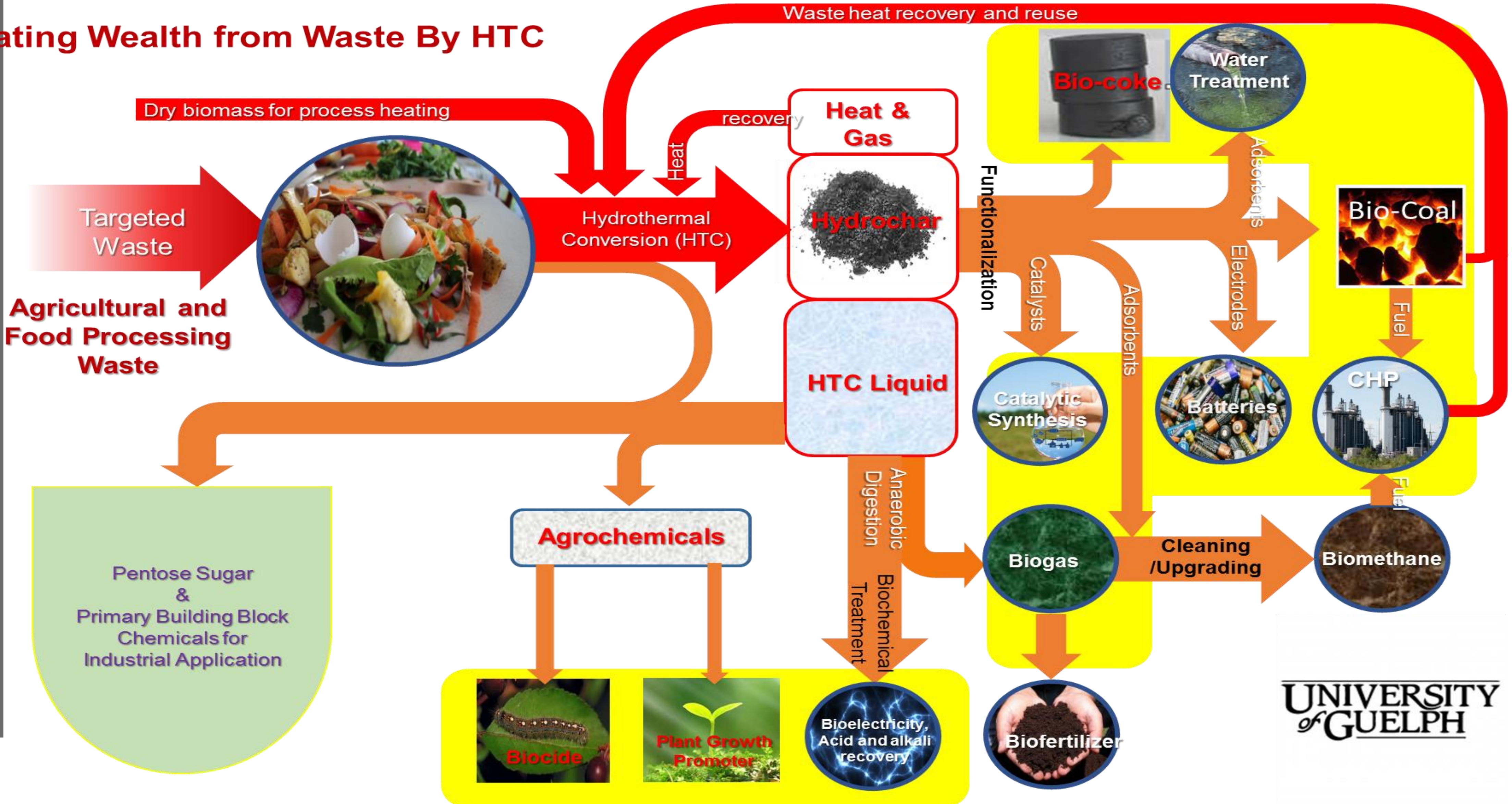




- The utilization of eggshell in gasification has been experimentally investigated.
- The inclusion of calcined eggshell in the process reduced CO_2 concentration and increased hydrogen concentration

Conclusion: Preprocess greenhouse residues, energy crops, crop residues, municipal green bin fruit processing wastes through HTC processing.

Approach Under Evaluation



Leading to zero-waste solutions

HTC products from low quality agri-food residue can be a potential newer value chain

UNIVERSITY of GUELPH

BRIL TEAM

Bio-renewable Innovation Lab BRIL

Thank You for Your Time

Acknowledgement

BioMasse Canada

RÉSEAU BIOFUELNET CANADA

Canada Foundation for Innovation
Fondation canadienne pour l'innovation

CINDAR POWER DEVELOPMENTS INC.

Customized Steam Solutions
Your Steam System Integrators

CCRA
Canadian Carbonization Research Association

igpc ETHANOL

NSERC CRSNG

Ministry of Agriculture, Food & Rural Affairs

Ontario
Ministry of the Environment and Climate Change

Shrimp Canada

Ontario
Ministry of Research and Innovation