Bio-Char II: Production, Characterization and Applications
Proceedings

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Characteristic studies on the biochars produced by hydro-thermal and steam gasification of canola hull and canola meal fuel pellets

Franco Berruti

Sonil Nanda

Ajay K. Dalai

Janusz A. Kozinski

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Ramin Azargohar[1], Sonil Nanda[2], Ajay K. Dalai[1], <u>Franco Berruti[2]</u>, and Janusz A. Kozinski[3]

[1]Dept. of Chemical & Biological Engineering, University of Saskatchewan, Canada
[2] Department of Chemical & Biochemical Engineering, Western University, ON, Canada
[3] Department of Chemical Engineering, University of Waterloo, ON, Canada

Introduction

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- In 2018, nearly **20.3 and 10.9 million tonnes of canola** were produced in Canada and Saskatchewan, respectively.
- **Co-firing of fuel pellets** (in the range of 10-30 wt%) with coal is a promising method to drastically decrease GHG emissions.
- These pellets also can be **exported to Asia and Europe** to produce revenue from agricultural residues.

Objective

Comparative investigation on the physico-chemical structure and properties of biochars produced using steam and hydro-thermal gasification of canola-based fuel pellets

Pelletization

<u>Production of fuel pellets</u>

Precursors:

- Canola hull
- Canola meal

<u>Bio-additives</u>

- Alkali Lignin
- Glycerol
- Amino acid

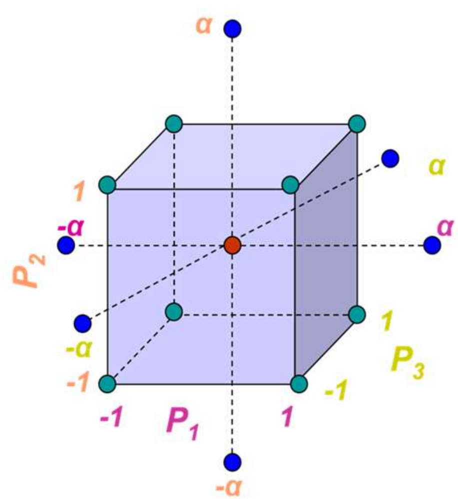
and: Water

Optimization of pellet formulation

(Concentrations of bio-additives and water)

Effects of pelletization operating conditions

- Temp.: 80-120 °C
- Applied force: 3,500-4,500 N
- Relaxation time: 15-55 s

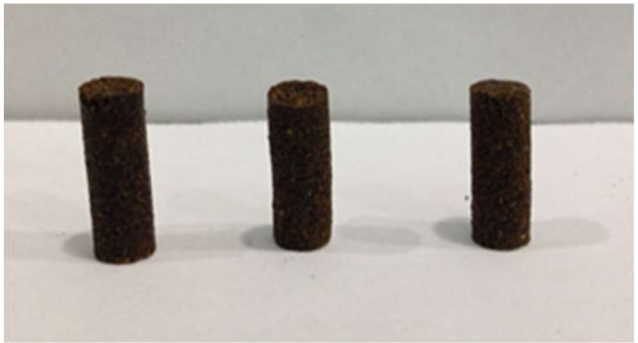


Central Composite Design

Single Unit Pelletizer (Instron 5966)

Steam and hydro-thermal gasification

Fuel pellets
- Canola hull
- Canola meal



Steam gasification
- Temp. : 650-850 ^{o}C
- Steam/biomass (SBR) : 0.31-0.62 wt/wt

Hydro-thermal gasification
- Temp. : 350-650 ^{o}C
- Pellet/water mass ratio : 10-25 wt%
- Reaction time: 15-60 min
- Pressure: ~24 MPa

Precursors characterization

Canola Hull

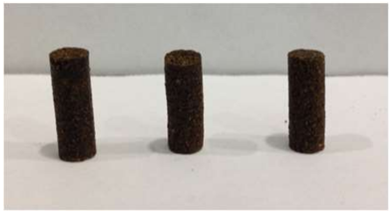
C = 43% H = 6% N = 2% S = 1% O = 39%
Ash = 9% Moisture = 8% Volatiles = 70%
Fixed C = 13% HHV = 17%

Canola Meal

C = 48% H = 6% N = 6% S = 0.6% O = 32%
Ash = 7% Moisture = 8% Volatiles = 72%
Fixed C = 13% HHV = 20.5% Oil = 11%

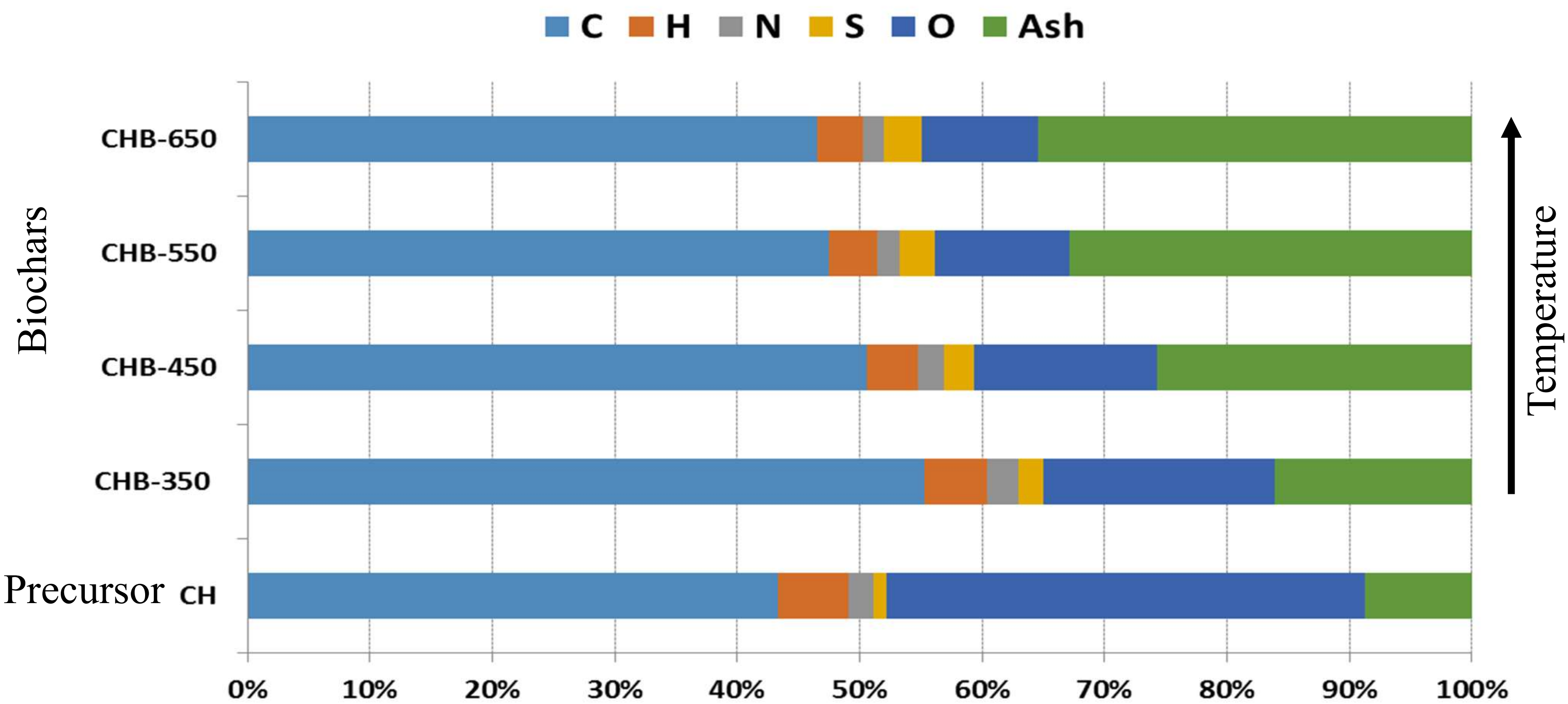
Pellet properties

	Canola hull pellet	Canola meal pellet
Optimized formulation	L6/G4/A6/W17	L8/G8/A2/W4
Relaxed density (kg/m^3)	1,110	1,015
Temperature (°C)	100	100
Pressure (N)	3,500	3,500
Higher heating value (MJ/kg)	17	21
Mechanical durability (%)	99	99
Moisture adsorption at 30 °C and 90% humidity (wt%)	19.1	21.1



Elemental analysis of CH hydro-thermal biochar

(similar to all others)



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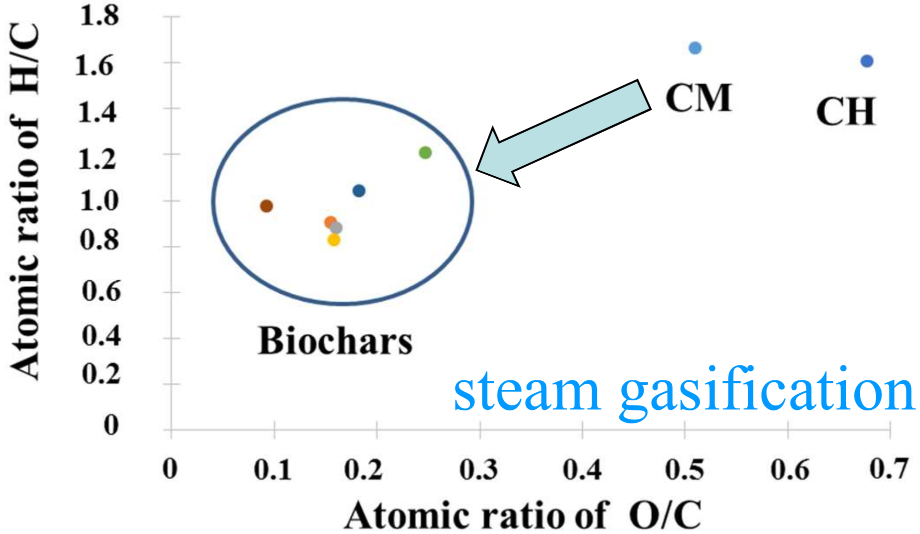
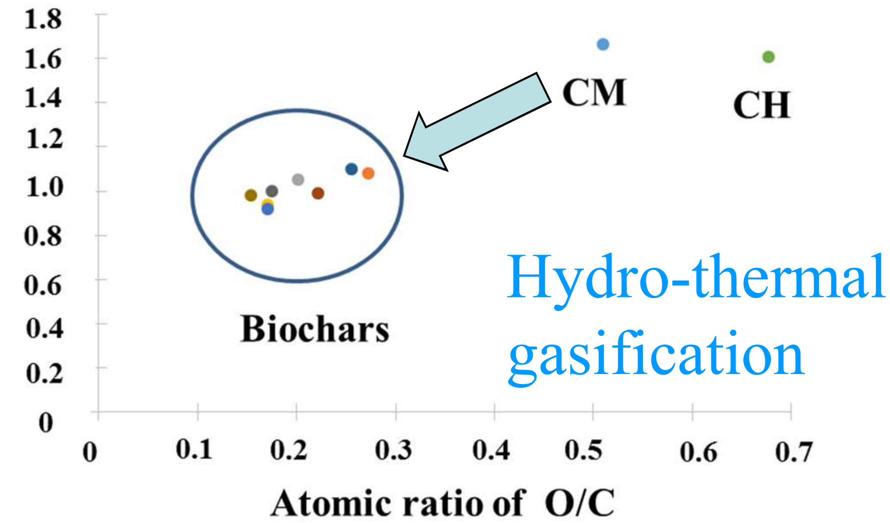
Elemental analysis highlights

- **Oxygen content** for both precursors decreased and **ash** sharply increased with increased severity
- **Carbon content** slightly decreased due to conversion to gaseous compounds.

Van Krevelen plots for biochars and precursors





Thermogravimetric spectra (hydro-thermal gasification)

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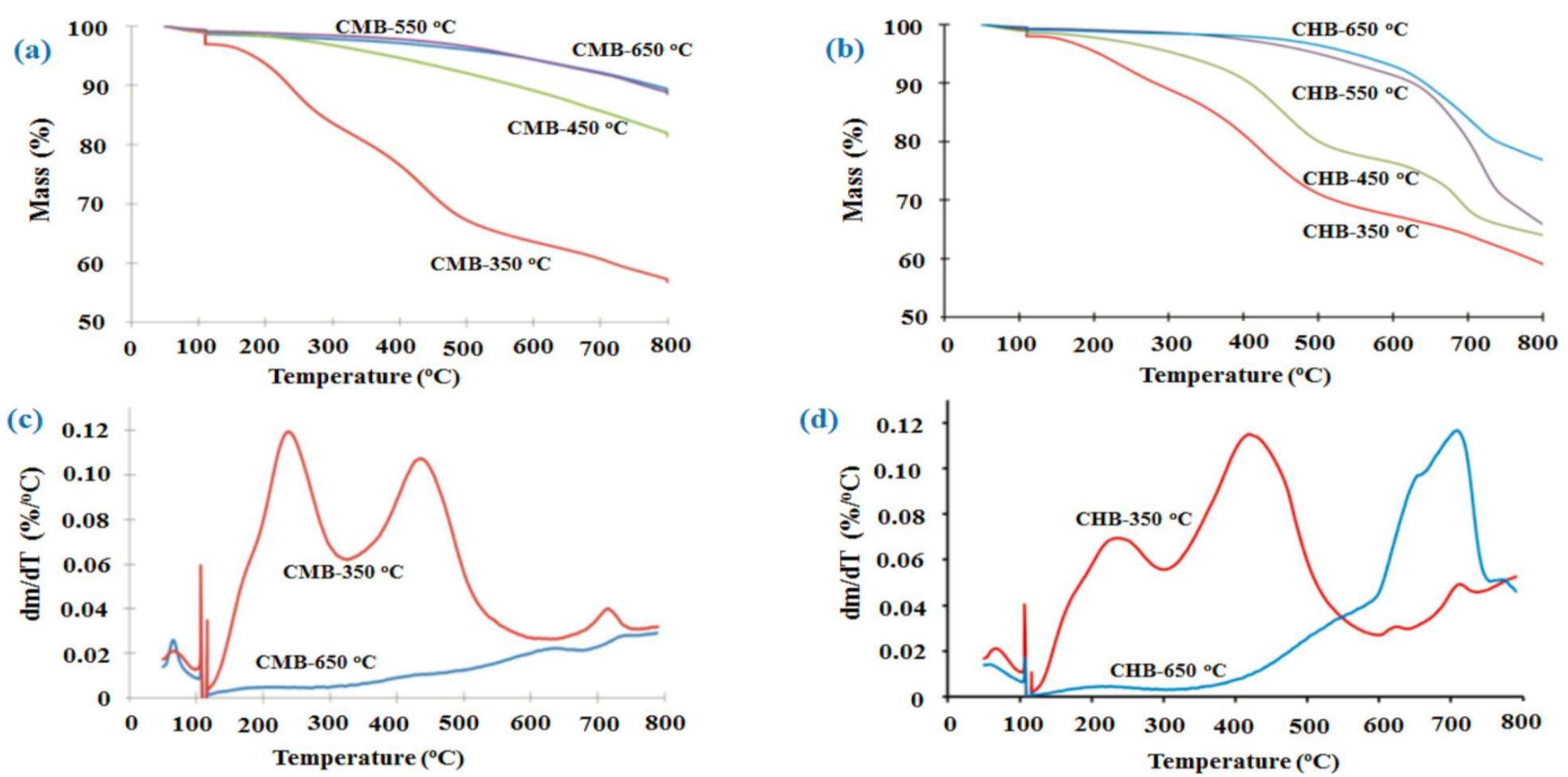
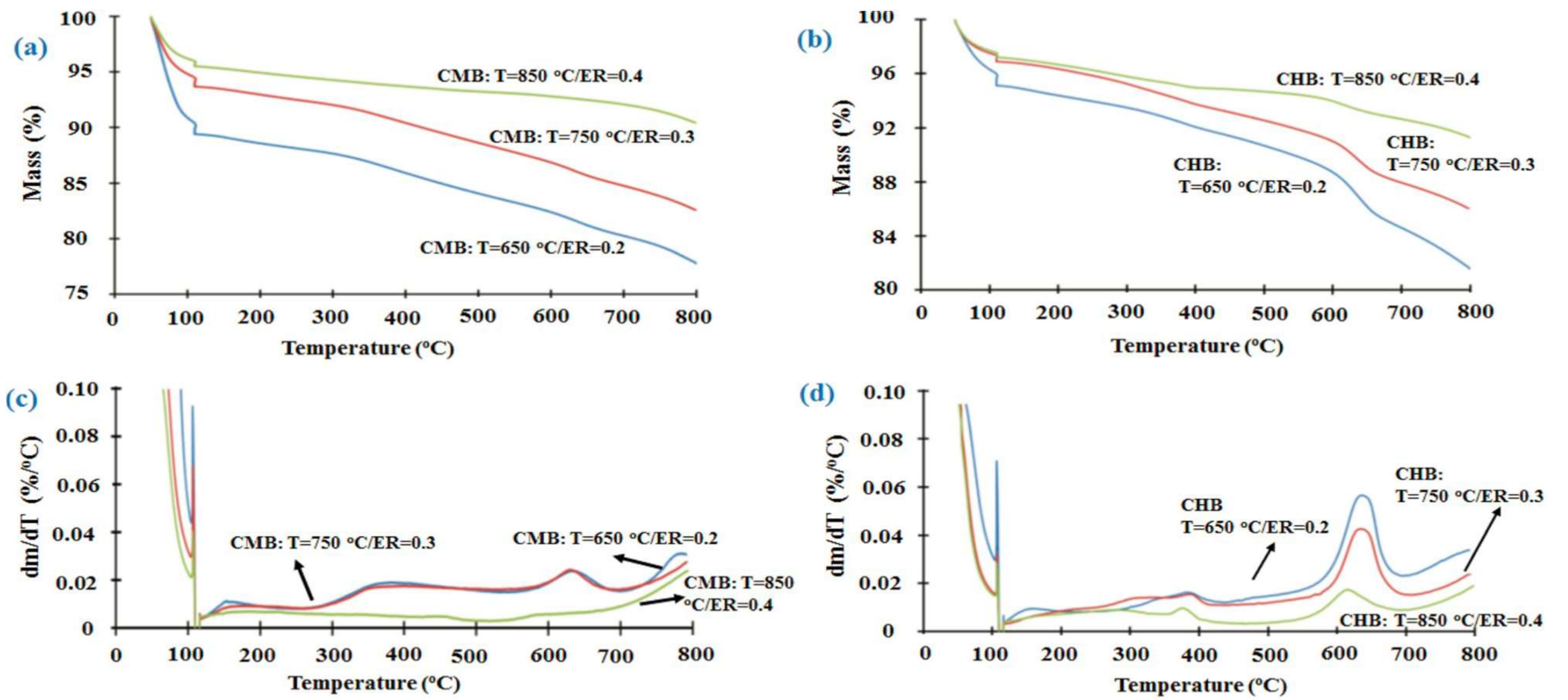


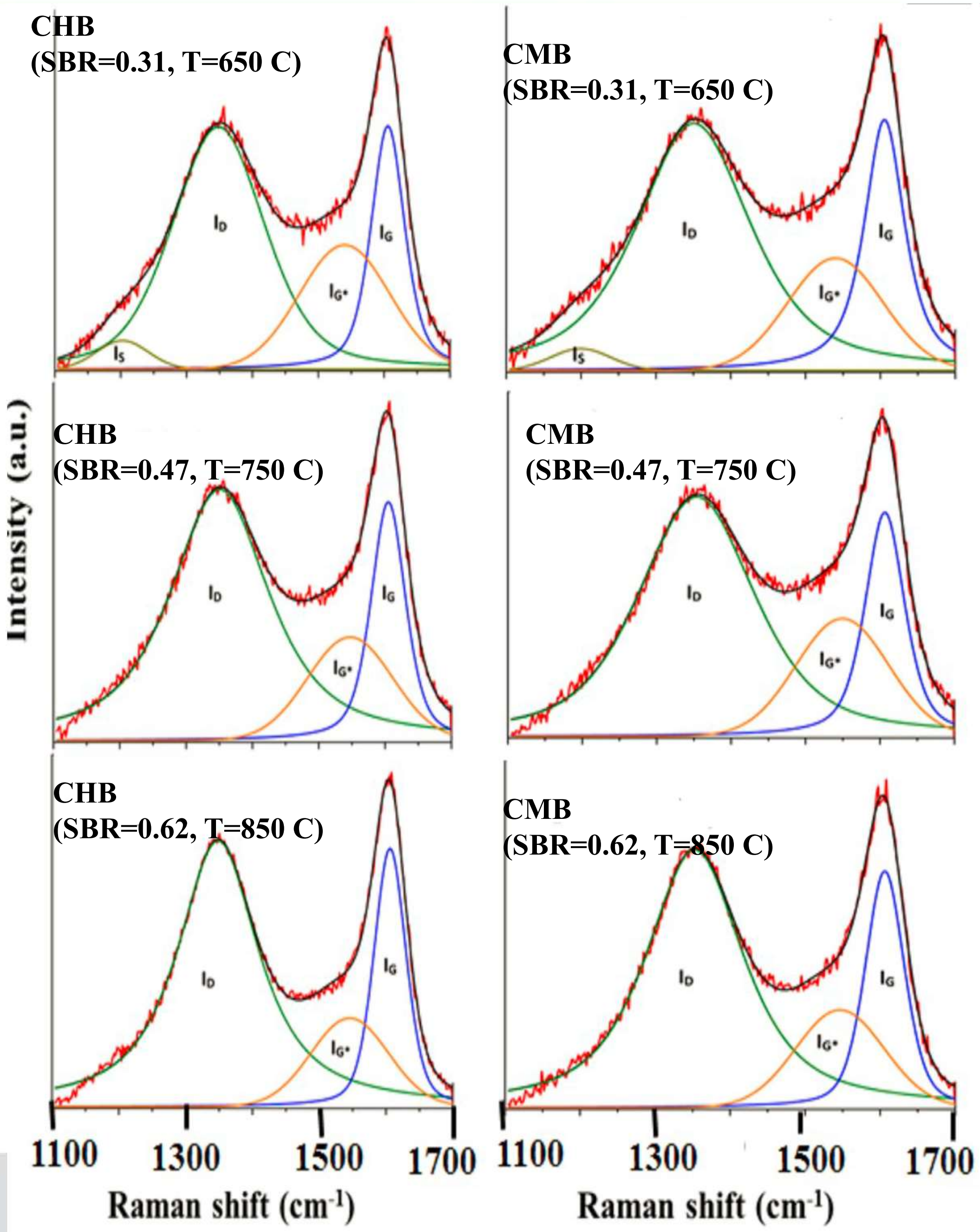
Thermogravimetric spectra (steam gasification)



Thermogravimetric spectra

- Biochars produced at more severe operating conditions showed higher stability
- The mass change at higher temperatures is related to the development of aromatic structure of biochars and/or decomposition of carbonate compounds (inorganic carbon) in the ash

Raman spectroscopy (steam gasification)



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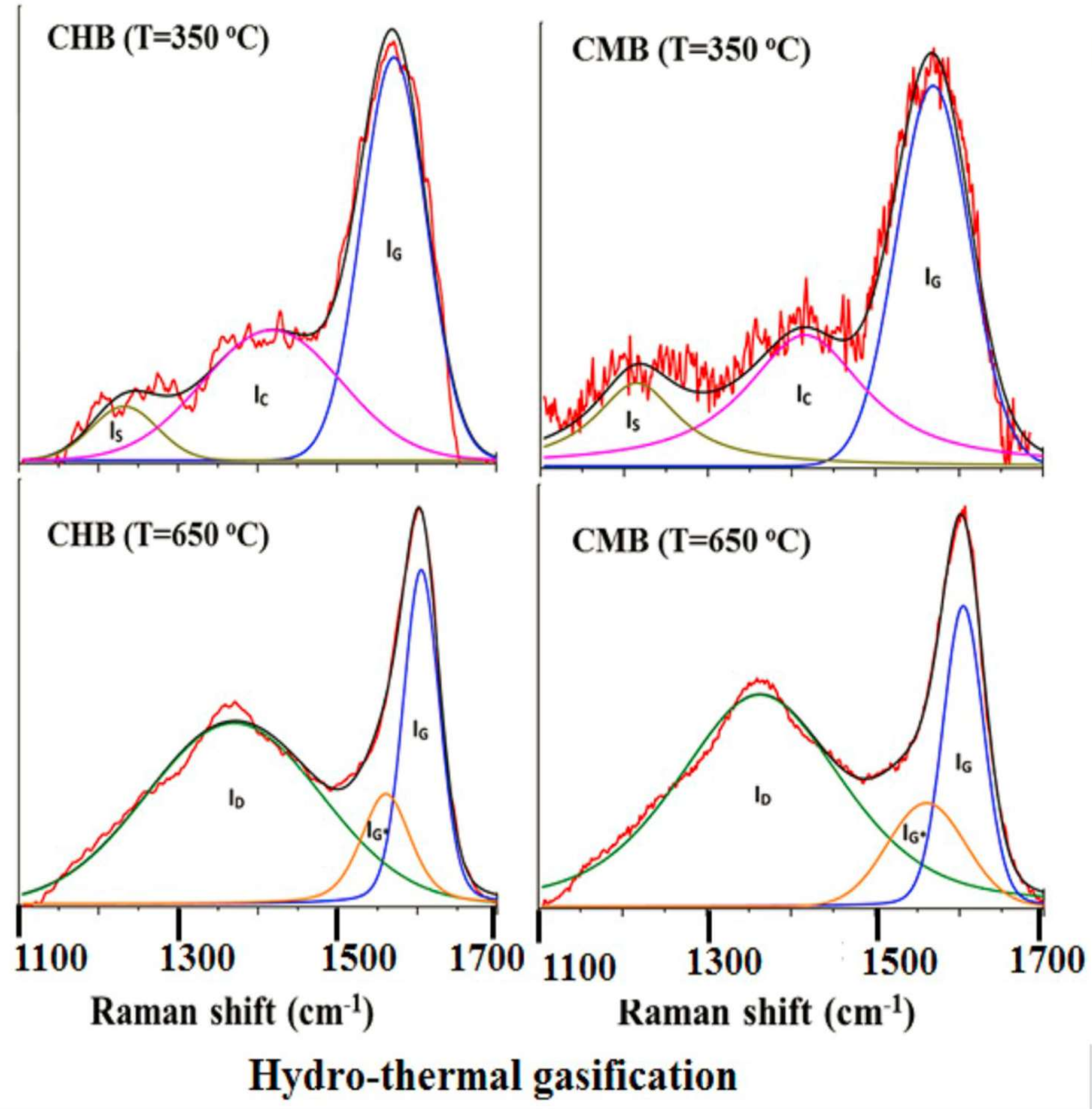
Raman spectroscopy (hydro-thermal gasification)



Raman spectroscopy

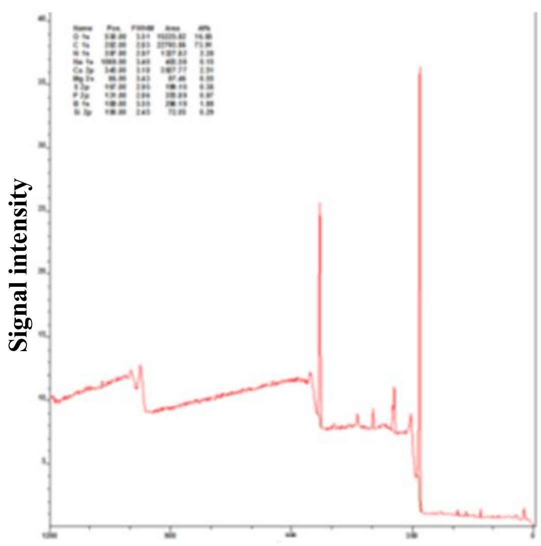
	Gasification operating conditions	I_D/I_G	Atomic ratio O/C	Atomic ratio H/C
Steam gasification				
CHB	SBR=0.31/T=650 °C	2.6	0.25	1.21
	SBR=0.47/T=750 °C	3.0	0.18	1.04
	SBR=0.62/T=850 °C	2.9	0.09	0.97
CMB	SBR=0.31/T=650 °C	2.5	0.16	0.90
	SBR=0.47/T=750 °C	3.0	0.16	0.88
	SBR=0.62/T=850 °C	2.9	0.16	0.83
Hydro-thermal gasification				
CHB	T=350 °C	0.0	0.26	1.10
	T=650 °C	2.4	0.15	0.98
CMB	T=350 °C	0.0	0.27	1.08
	T=650 °C	2.9	0.17	0.92

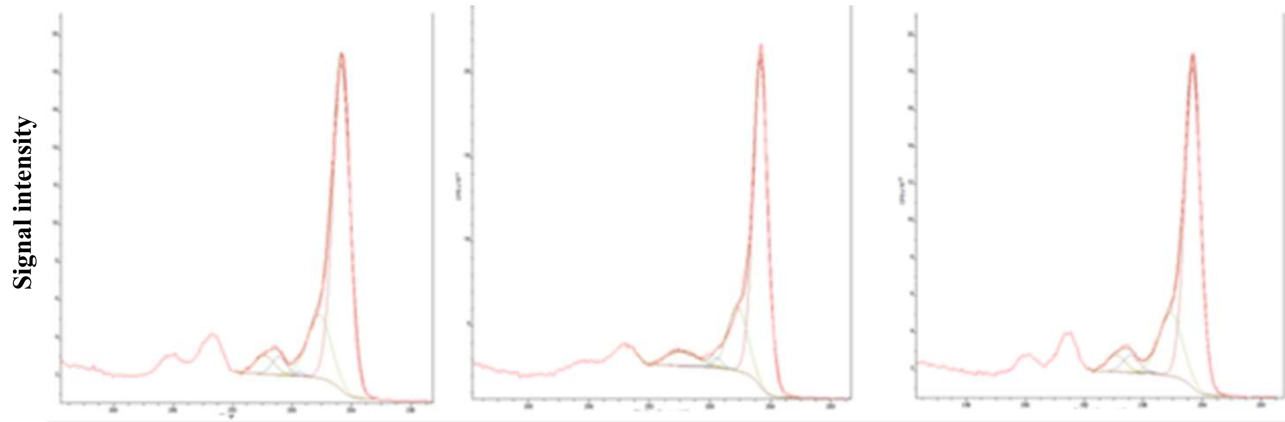
Raman spectroscopy

- **For hydro-thermal gasification**, biochars prepared at the highest temperature (650 ^{o}C) showed a **large change in I_D/I_G ratio** confirming a drastic structural change in biochar structure, which can be related to the development of **aromatic structures**.
- **For steam gasification**, there was no significant difference in the values of I_D/I_G of biochars prepared from CH and CM at the same gasification operating conditions.

X-ray photoelectron spectroscopy (XPS)

identify and quantify basic elements and functional groups on the bio-chars





Typical XPS survey scan (for CHB-650 C)

- **Peak deconvolutions of high resolution C1s spectra were accomplished using the CasaXPS software (version 2.3.16 PR 1.6).**

X-ray photoelectron spectroscopy (XPS)

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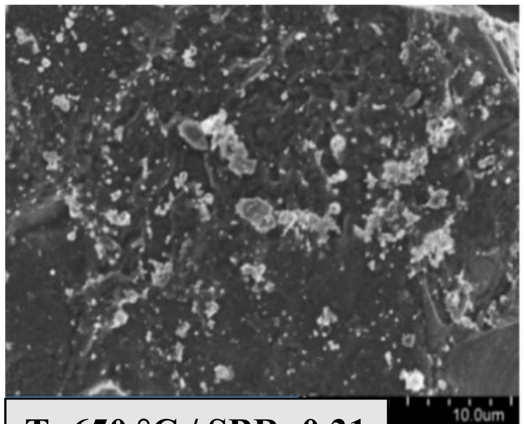
- For both classes of biochars, a decrease in O content and increase in C content with severity was observed corresponding to **aromatization**.
- Survey scan showed the presence of **mineral elements** in the produced biochars.

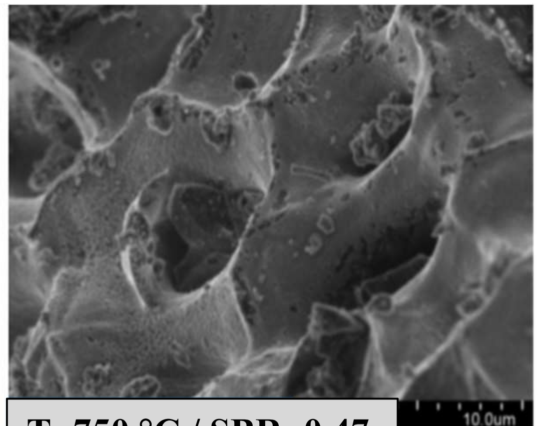
X-ray photoelectron spectroscopy (XPS)

- The **aromatic/aliphatic carbon contents of biochars were larger than 69%** for all conditions, which confirm the aromatization in biochars
- No significant change in aromatic/aliphatic carbon content for canola hull biochars produced using **steam gasification**
- For biochars from canola hull through **hydro-thermal gasification**, an increase in temperature showed a positive effect on aromatic/aliphatic carbon content

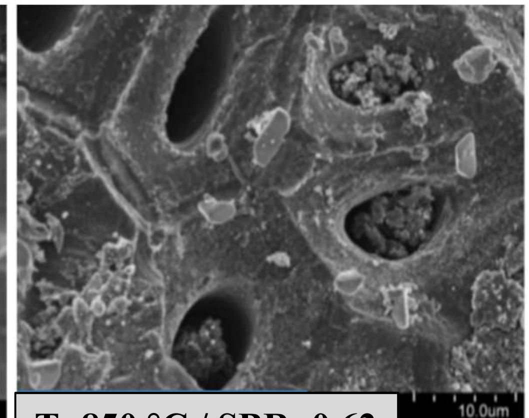
Porosity (steam gasification of CM)



T=650 °C / SBR=0.31



T=750 °C / SBR=0.47



T=850 °C / SBR=0.62

BET (m^2/g)	226	397	440
Pore volume (cm^3/g)	0.09	0.24	0.28

The same trend was observed for CH-based biochars

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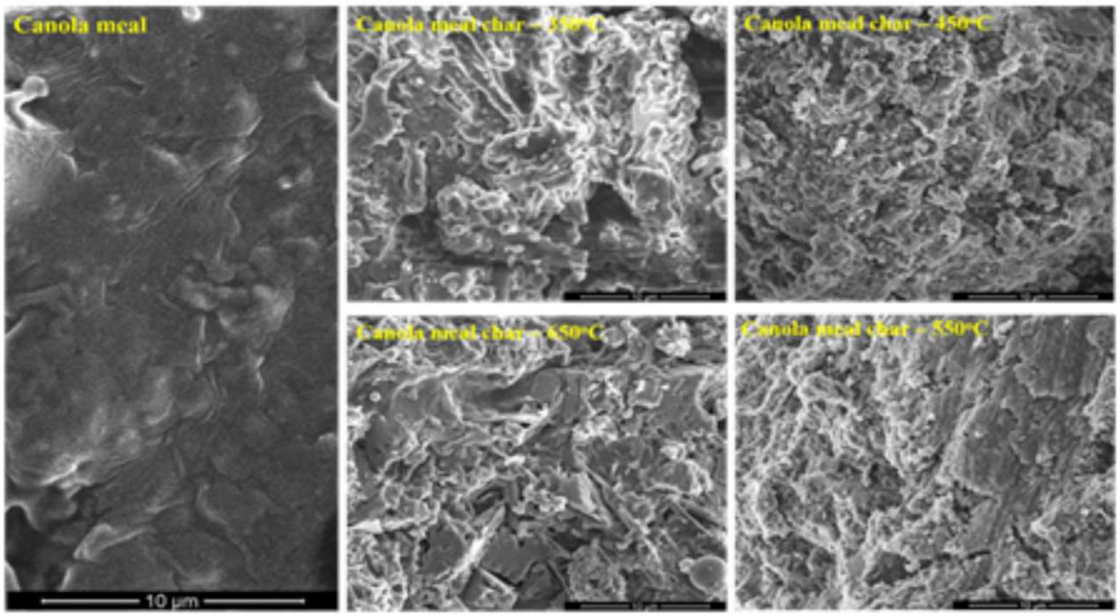
Porosity
(hydro-thermal gasification of CM)



BET surface area of hydro-thermally produced biochars were <10 m^2/g

The same trend was observed for CH-based biochars

Inductively coupled plasma mass spectrometry (ICP-MS) – CM biochars

Elements	Biochar (T=650 °C / SBR=0.31)[1]	Biochar (T=750 °C / SBR=0.47)	Biochar (T=850 °C / SBR=0.62)	Biochar (SCW-650 °C)
Essential elements (mg/g of biochar)				
Na	21	12	21	25
K	50	51	61	70
Mg	34	41	46	<1
Ca	20	20	24	27
P	63	61	75	99
Fe	13	14	14	4
Total (essential elements)	201	199	242	225
Heavy/toxic elements (mg/g of biochar)				
Al	<1	<1	1	1
Cr	3	3	3	1
Cu	<1	<1	<1	<1
Mn	<1	<1	<1	<1
Mo	<1	<1	<1	<1
Ni	1	2	1	1
Zn	<1	<1	<1	<1
Total (heavy elements)	6	7	6	5

The concentration of essential elements is much larger than that for heavy metals.

Low level of heavy metals ⟹ no potential risk for soil amendment.

The same trend was observed for CH-based biochars

Key outcomes

- **Hydro-thermal biochars** have "transition char" characteristics when produced at low temperature, and "amorphous char" properties at high temperatures (≥550 ^{o}C)
- Based on the higher BET surface area and other characterization results, **steam-gasified biochars** have a "composite char" structure
- An increase in aromaticity and inherent mineral compounds are known to increase stability (oxidation resistance) of biochar
- Hydro-thermal biochars are suitable for soil amendment.
- The higher BET surface area for steam-gasified biochars shows their potential as adsorbents or for catalytic applications.

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