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Lab-scale pyrolysis and hydrothermal carbonization of biomass digestate: Characterization of solid products

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DIEF Dipartimento di Ingegneria Industriale

Lab-scale pyrolysis and hydrothermal carbonization of biomass digestate: characterization of solid products

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Biochar: Production, Characterization and Applications
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Summary

- Feedstock: the digestate
- Experimental units: Slow Pyrolysis reactor and Micro-HTC
- Process conditions of thermochemical experiments
- Char analysis results
  - ✓ Comparison with EBC, IBI, Italian fertilization decree
- Complementary analyses: HTC liquid phase
- Conclusion

Feedstock: The digestate

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➢Origin:

- Anaerobic digestion plant in Grosseto, Italy
- Mesophilic conditions (~40˚C)
- Fed mainly with barley silage (60%), but also with wheat and herbaceous silage and poultry manure

➢Treatments:

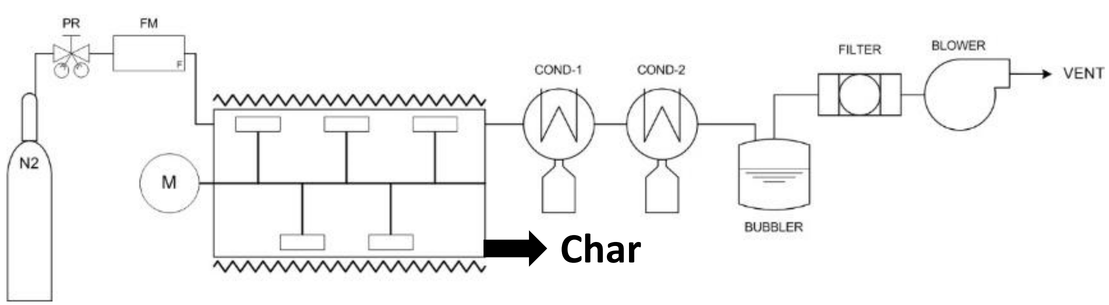
- Mechanical separation → 75% w/w water content

➢Analyses:

- CHN, S, ash, higher heating value, inorganics, BET, pH

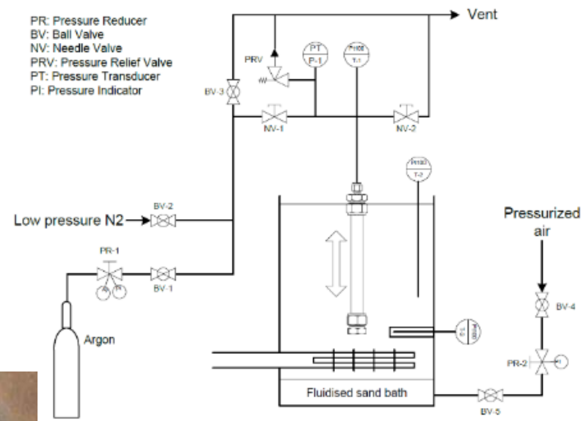
Experimental unit: Pyrolysis reactor

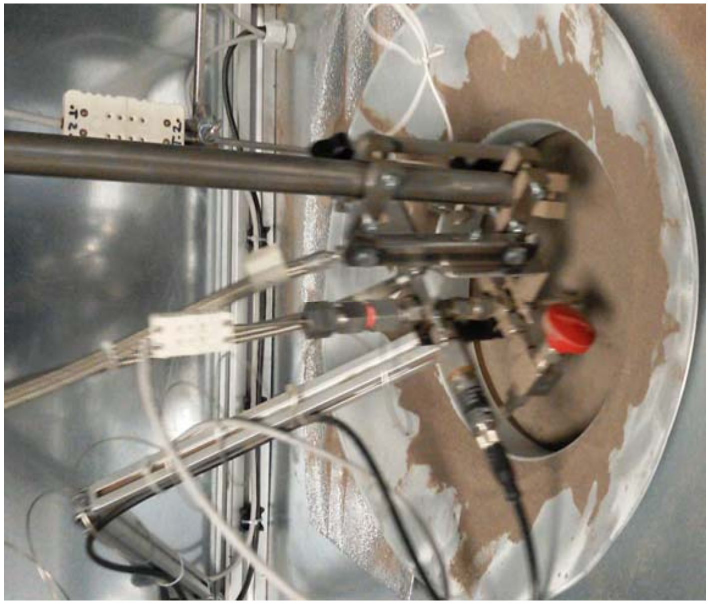
- Continuous reactor operated in batch mode
- Gross reactor volume: 31 l
- Electric heating system
- Inner stirring system
- Constant N_2 flow under suction



Experimental unit: Micro-reactor test-bench MRTB

- Custom-made test-bench
- Batch reactor: 27ml
- P and T sensors
- Fluidized sand bath
- Shaking device





Reactor

Thermochemical batch experiments

Operating conditions	Slow Pyrolysis	HTC
Pretreatment	Drying	Drying, milling
Digestate input	1 $kg_{\_DM}$	2 $g_{\_DM}$
Temperature	500°C	200-250°C
Time	1 h	0.5-3 h
Biomass/water ratio	-	10 wt%

Feedstock characterization

Parameter	Value	Norm
Moisture content [wt% w.b.]	76.2	UNI 13040
Ash content [wt%] d.b.	9.3	UNI 13039
Volatile matter [wt%] d.b.	68.9	UNI 15148
Fixed carbon [wt%] d.b.	21.8	Calculated
C [wt%] d.b.	46.71	UNI 15104
H [wt%] d.b.	5.50	UNI 15104
N [wt%] d.b.	1.15	UNI 15104
S [wt%] d.b.	0.46	Internal method
O [wt%] d.b.	36.88	Calculated
K [wt%] d.b.	0.97	UNI EN 15290
P [wt%] d.b.	0.28	UNI EN 15290
Higher Heating Value [MJ/kg] d.b.	19.24	UNI 14918
Lower Heating Value [MJ/kg] d.b.	17.95	UNI 14918
pH [-]	7.7	DIN ISO 10390
Surface area [m^2/g]	3.72	ASTM D 6556-10
Total pore volume [cm^3/g]	$1.10 \cdot 10^{-2}$	ASTM D 6556-10
Average pore diameter [nm]	11.61	Calculated

Results

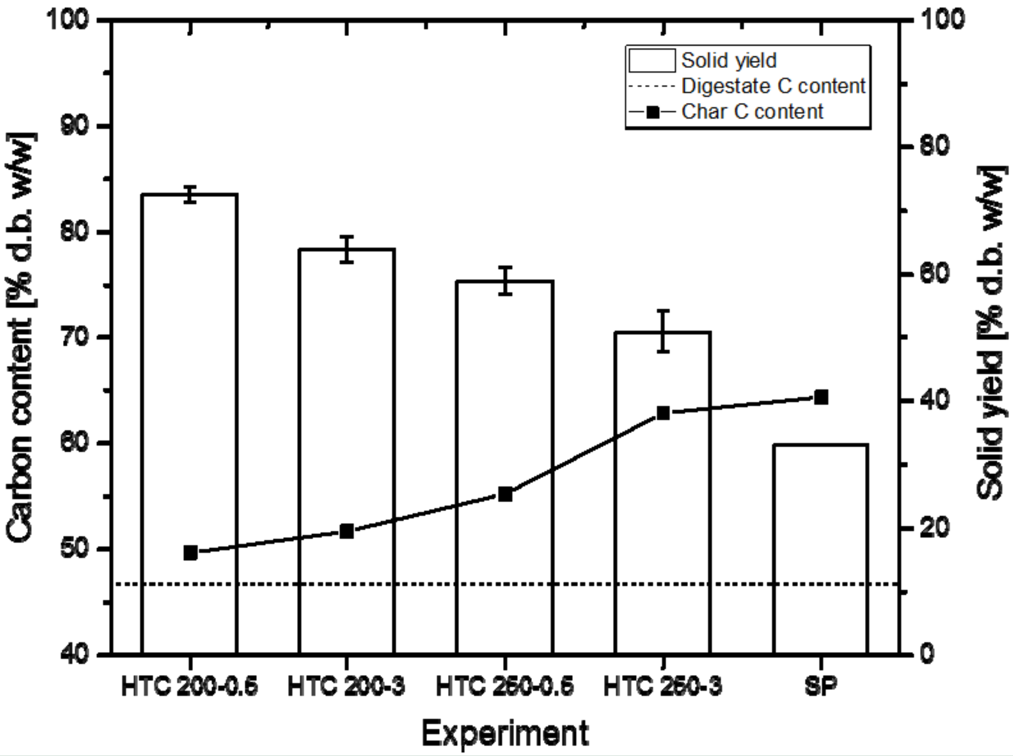
Char analysis results

➢Solid yield & C content

- Slow Pyrolysis: Solid yield 33.1 wt%; Carbon content 64.3 wt% db
- Hydrothermal Carbonization: Effect of reaction severity increase (T, t)
  - Decrease in solid yield from 72.6 to 51.0 wt% db
  - Increase in carbon content from 49.7 to 62.9 wt% db
  - Trade-off: Quantity VS Quality

Hydrochar

Pyrochar



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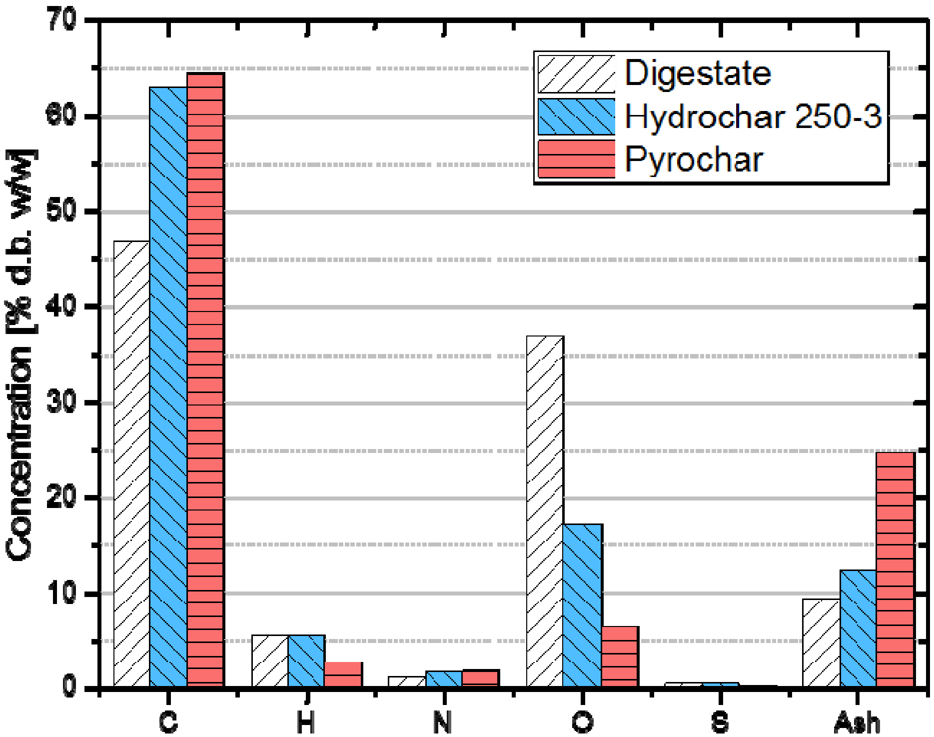
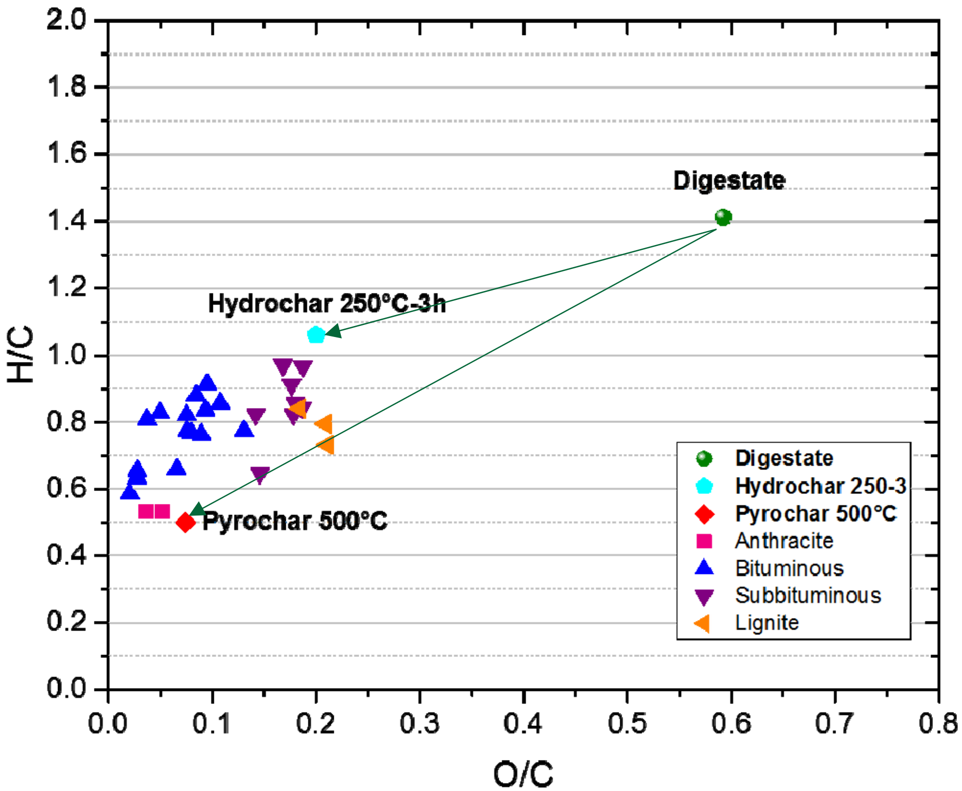
➢ Elemental analysis values are on dry basis

- Comparison between digestate, hydrochar with highest C% (250˚C-3h) and pyrochar





Different char quality: Pyrochar has lower O/C & H/C molar ratio

H. Huang, S. Wang, K. Wang, M.T. Klein, W.H. Calkins, A. Davis, Thermogravimetric and Rock-Eval studies of coal properties and coal rank, Energy and Fuels. 13 (1999) 396–400. doi:10.1021/ef980088q.

Char analysis results

Pyrochar: Polycyclic Aromatic Hydrocarbons

- **DIN CEN TS 16181:** Soxhlet-extraction with toluene and determination with HPLC

PAHs	ppm db
Acenaphthene	0.07
Acenaphthylene	0.00
Anthracene	0.04
Benz(a)anthracene	0.00
Benzo(a)pyrene	0.00
Benzo(b)fluoranthene	0.00
Benzo(ghi)perylene	0.00
Benzo(k)fluoranthene	0.06
Chrysene	0.53
Dibenz(a,h)anthracene	0.02
Fluoranthene	0.00
Fluorene	0.28
Indeno(1,2,3-cd)pyrene	0.17
Naphthalene	0.26
Phenanthrene	0.16
Pyrene	0.89
TOTAL PAHs	**2.47**

Pyrochar: pH-Value 9.4

BET analysis

Sample	Surface area	Average pore diameter	Total pore volume
	[m²/g]	*[nm]*	*[cm³/g]*
Digestate	3.72	11.61	$1.1 \cdot 10^{-2}$
Hydrochar 250-3	4.92	16.50	$2.0 \cdot 10^{-2}$
Pyrochar	23.10	14.80	$8.5 \cdot 10^{-2}$

Char analysis results

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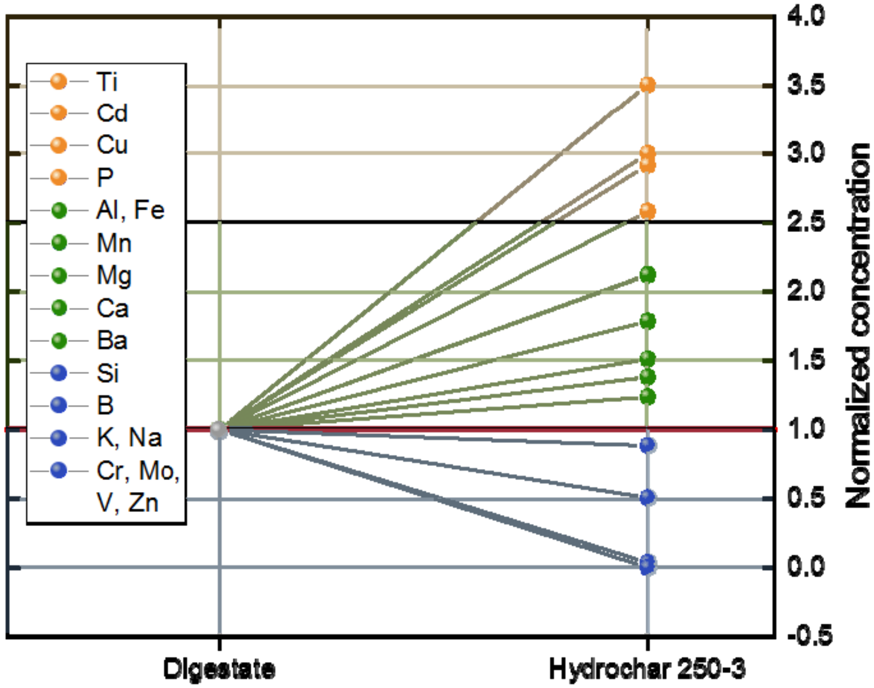
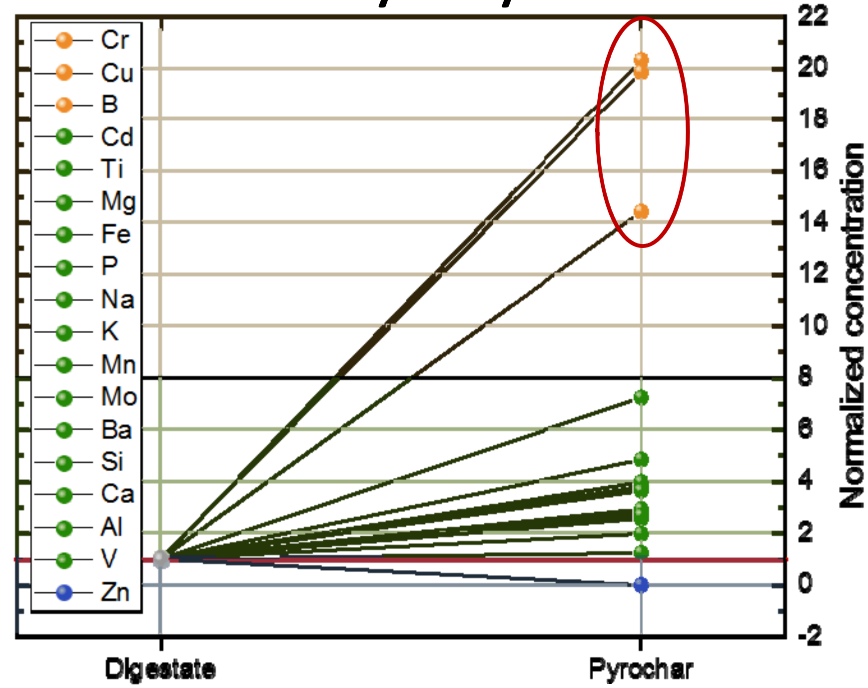
➢Inorganic elements

HTC



Slow Pyrolysis



Element [mg/kg]	Al	B	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	P	Si	Ti	V	Zn
Digestate	339	7.9	21	8315	2.9	3.1	7.2	387	9656	1224	70	7.6	1962	2751	812	9.7	2.9	41
Hydrochar 250-3	720	4	26	11480	8.7	bdl	21	820	364	1850	125	bdl	73	7100	718	34	bdl	bdl
Pyrochar	672	114	59	21397	21	63	143	1470	28170	4877	204	22	5752	10030	2179	47	3.6	bdl

bdl= below detection limit, 0.1 mg/kg

Char analysis results

➢Comparison with European and International biochar standards

Parameter	Hydrochar 250-3	Pyrochar	EBC	IBI
Carbon content [% w/w] d.b.	62.85	64.34	Not required	Class 1: >=60 Class 2: >=30 & <60 Class 3: >=10 & <30
Total organic carbon [% w/w] d.b.	n.m.	n.m.	>=50	Not required
Ash content [% w/w] d.b.	12.3	24.6	Declaration	Declaration
H/C_{org} O/C_{org}	1.06 0.2	0.5 0.07	<=0.7 <=0.4	<=0.7 Not required
pH - Value	n.m.	9.4	Not required	Not required
Granulometry through 0.5mm [% w/w] d.b.	n.m.	71.2	Declaration	Declaration
Surface area [m^2/g]	4.9	23.1	Declaration; better >150m^2/g	Declaration
PAHs [mg/kg] d.b.	n.m.	2.47	Premium: <4 Basic: >4 & <12	6-300

Calc. with C_{tot} not C_{org}

n.m.: not measured

International Biochar Initiative, Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, (2014); European Biochar Foundation (EBC), European Biochar Certificate - Guidelines for a Sustainable Production of Biochar, (2016); Decreto Legislativo 29 aprile 2010, n.75: “Riordino e revisione della disciplina in materia di fertilizzanti, a norma dell’artico-lo 13 della legge 7 luglio 2009, n. 88”, Gazzetta Ufficiale, 2010

➢Comparison with European and International biochar normative: Contaminants

Values in [mg/kg] d.b.

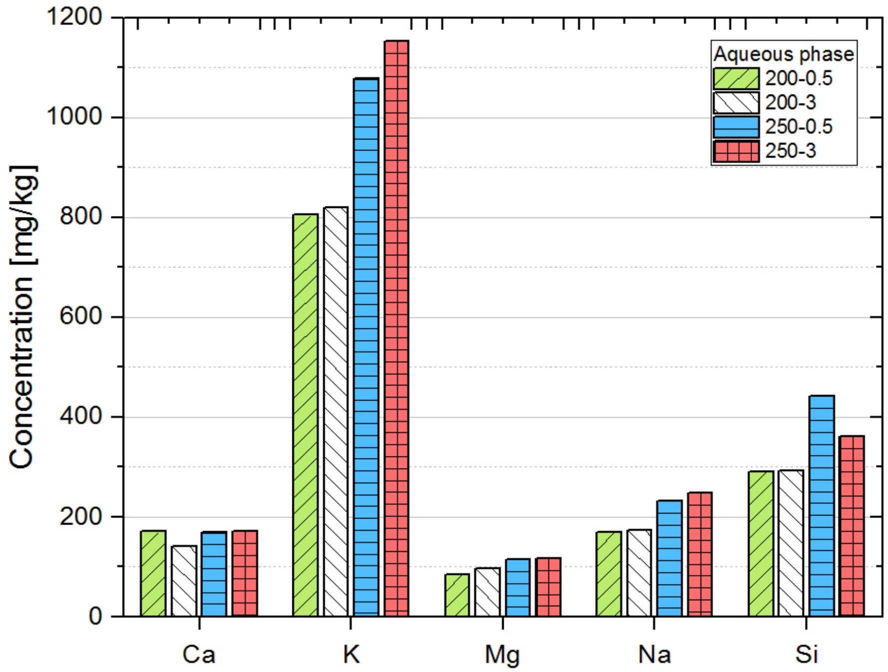
nm: not measured

Element	Digestate	Hydrochar 250-3	Pyrochar	EBC	IBI	D.L. 29 APRILE 2010, N. 75
Cd	2.9	8.7	21	Basic: <1.5 Premium: <1	1.4-39	<1.5
Cr	3.1	<0.1	63	Basic: <90 Premium: <80	64-1200	<0.5 (hexavalent)
Co	<0.1	<0.1	<0.1	Not required	40-150	Not required
Cu	7.2	21	143	Basic: <100 Premium: <100	63-1500	<230
Pb	<0.1	<0.1	<0.1	Basic: <150 Premium: <120	70-500	<140
Mo	7.6	<0.1	22	Not required	5-20	Not required
Zn	41	<0.1	<0.1	Basic: <400 Premium: <400	200-7000	<500

International Biochar Initiative, Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, (2014); European Biochar Foundation (EBC), European Biochar Certificate - Guidelines for a Sustainable Production of Biochar, (2016); Decreto Legislativo 29 aprile 2010, n.75: "Riordino e revisione della disciplina in materia di fertilizzanti, a norma dell'artico-lo 13 della legge 7 luglio 2009, n. 88", Gazzetta Ufficiale, 2010

HTC Aqueous phase

➢Inorganic elements



- Increase in reaction severity increases inorganic concentration
- Temperature impacts more than time
- Ca, Mg, P end up in hydrochar
- K in liquid

Element [mg/kg]	Al	B	Ba	Ca	Cd	Cu	Fe	K	Mg	Mn	Mo	Na	P	Si	Ti	Zn
Digestate	339	7.9	21	8315	2.9	7.2	387	9656	1224	70	7.6	1962	2751	812	9.7	41
Hydrochar 250-3	720	4	26	11480	8.7	21	820	364	1850	125	bdl	73	7100	718	34	bdl
Liquid phase 250-3	0.3	1.5	1.4	172	1.3	0.2	7.4	1153	117	1.7	0.2	249	bdl	362	1.6	1.9

bdl= below detection limit, 0.1 mg/kg

HTC Aqueous phase

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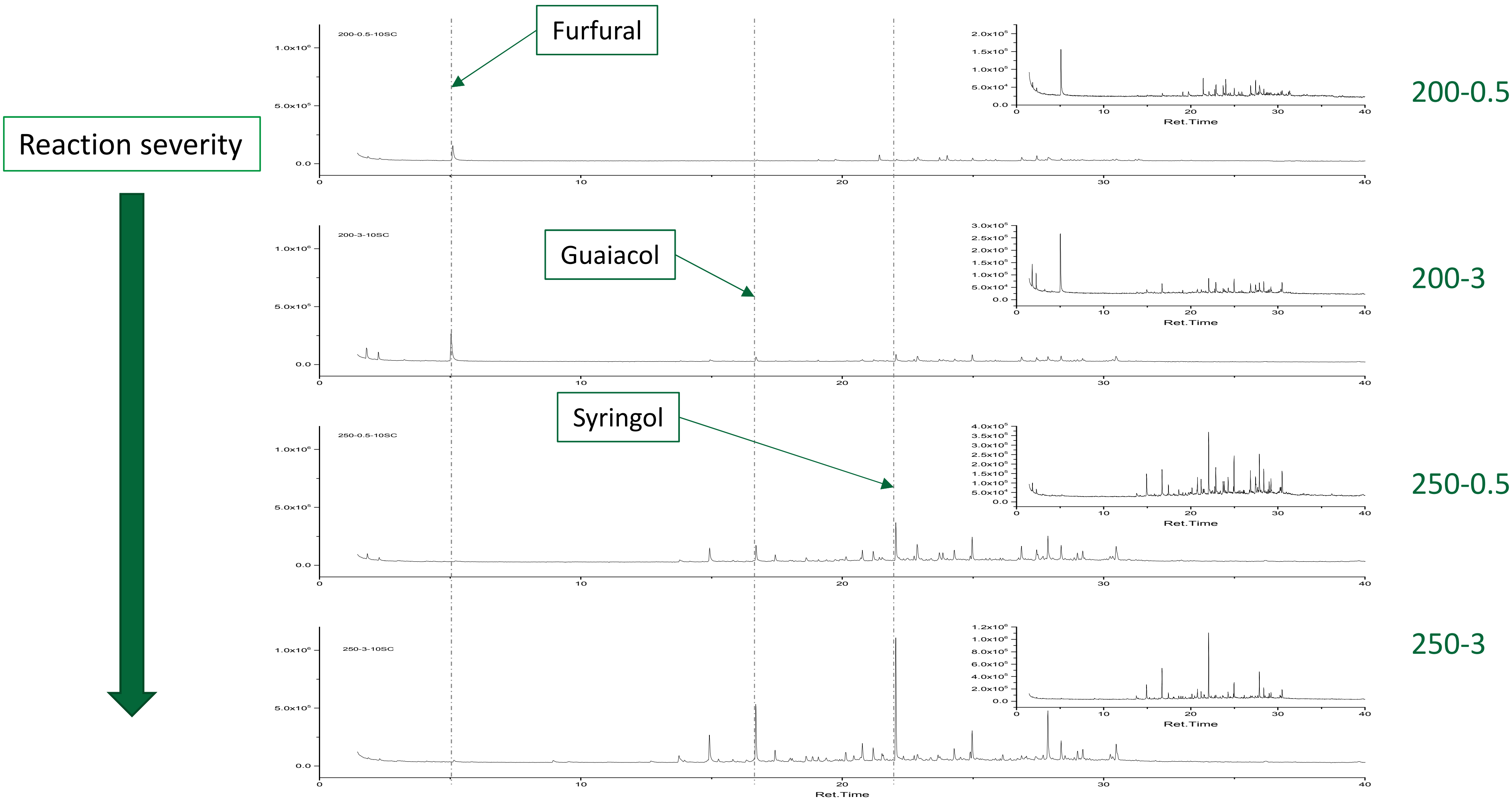
➢Gas chromatography - mass spectrometry (GC-MS) – DCM extract



HTC Aqueous phase

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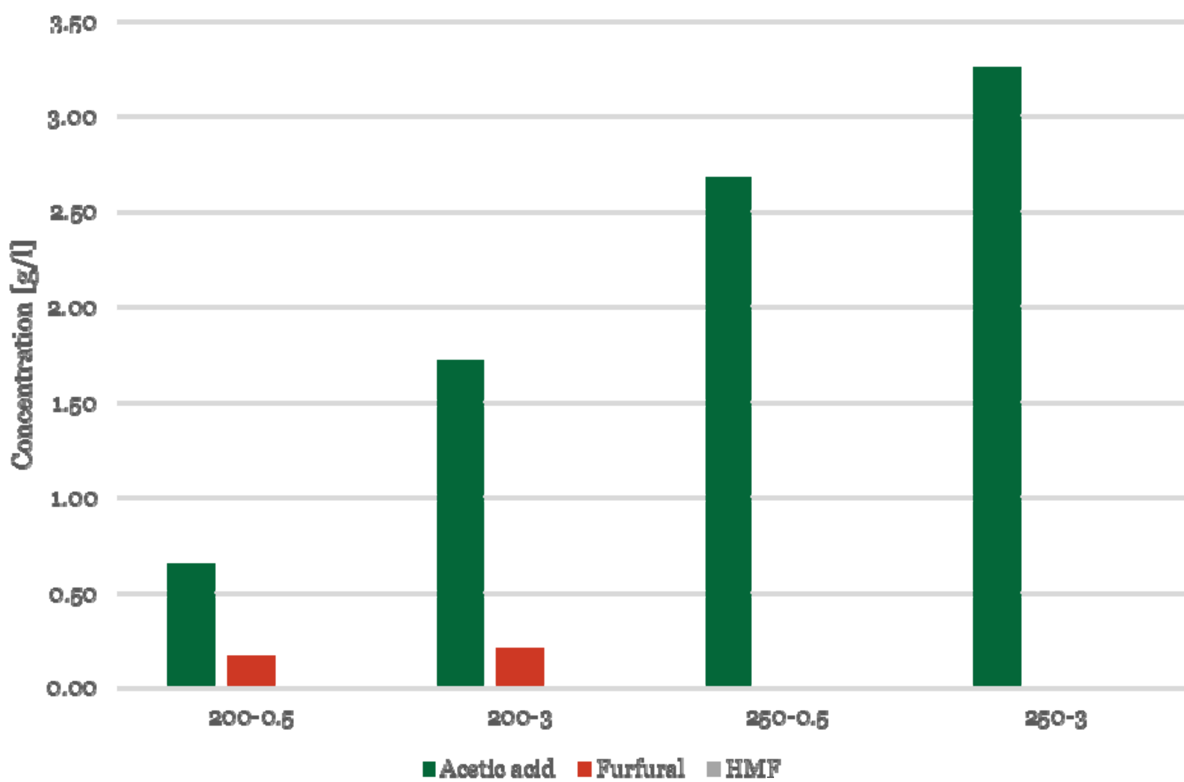
➢ HPLC (High Performance Liquid Chromatography) values are measured in g/l

Aqueous phase	Acetic acid	Furfural	HMF
200-0.5	0.65	0.16	<0.025
200-3	1.72	0.21	<0.025
250-0.5	2.68	<0.025	<0.025
250-3	3.26	<0.025	<0.025

- Acetic acid concentration increases with severity
- Furfural slightly increases with time only at 200˚C
- HMF always below detection limit



HTC Aqueous phase

➢ **Gas chromatography - Flame Ionization Detector (GC-FID) – DCM extract**

Conclusion

Conclusions and future works

➢ CONCLUSIONS

- Digestate was successfully converted into char by SP and HTC
- HTC: temperature has a greater effect on char yield & C content than time (quantity VS quality)
- Pyrochar: better quality than hydrochar due to more extended carbonization (similar C content, but lower O/C & H/C molar ratio)
- Very low surface area for both chars (pyrochar 1 OM higher)
- Pyrochar: almost all investigated inorganics increased in concentration; Hydrochar: lower increase and major dilution (K)
- Many hydrochar and pyrochar properties met most biochar standards
- By increasing reaction severity, the concentration of acetic acid, guaiacols, syringol, ketones and phenols increase in HTC aqueous phase

➢ FUTURE WORKS

- Anaerobic digestion of HTC aqueous phase
- Increase of pyrochar surface area through physical or chemical activation

➢ Acknowledgment

- Ministry for Agriculture (MIPAAF) – AGROCHAR Project

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Thank you for your attention!

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LAB-SCALE PYROLYSIS AND HYDROTHERMAL CARBONIZATION OF BIOMASS DIGESTATE: CHARACTERIZATION OF SOLID PRODUCTS

Chiaramonti David

Miliotti E., Casini D., Lotti G., Bettucci L., Pennazzi S., Rizzo A. M.

ECI

Biochar: Production, Characterization and Applications

August 20-25, 2017, Hotel Calissano, Alba, Italy

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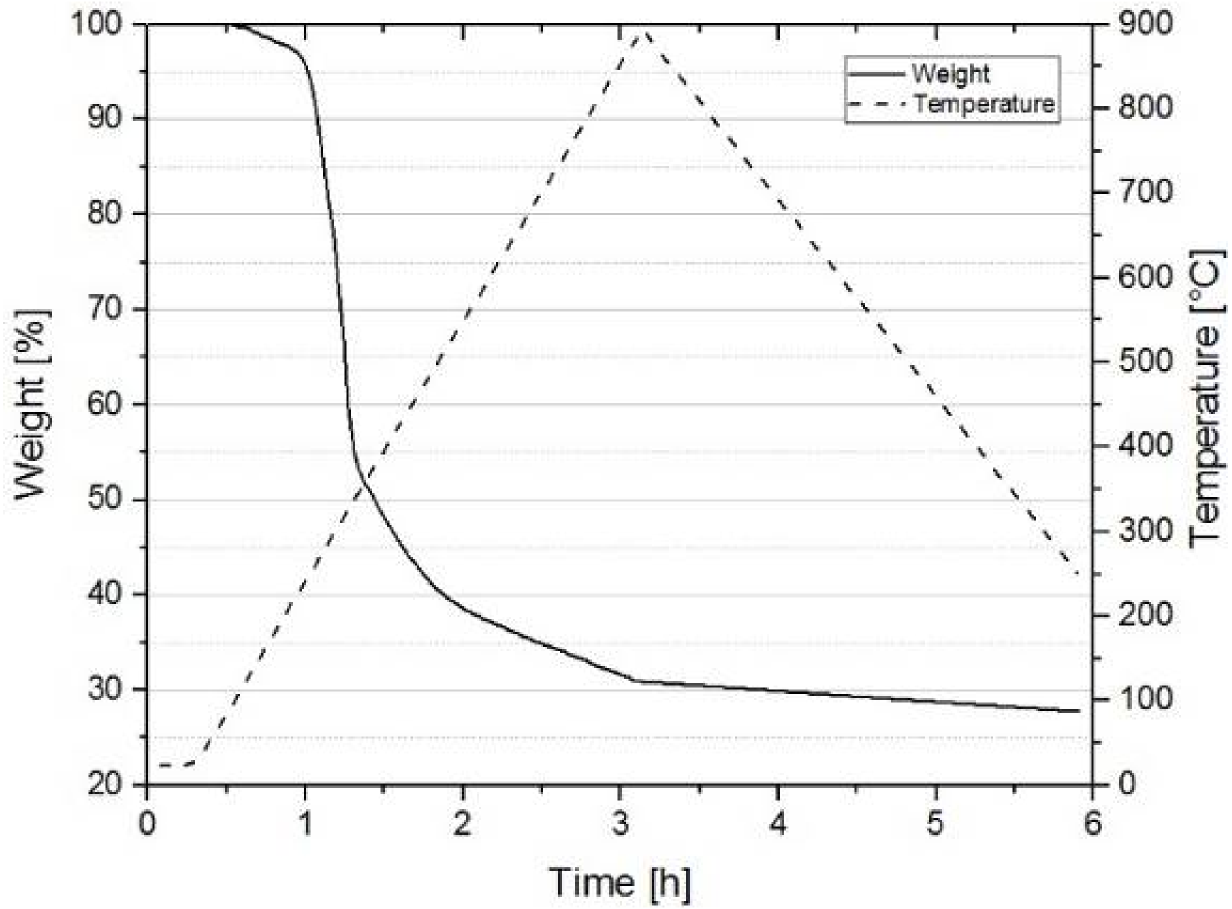
Slow Pyrolysis experiments

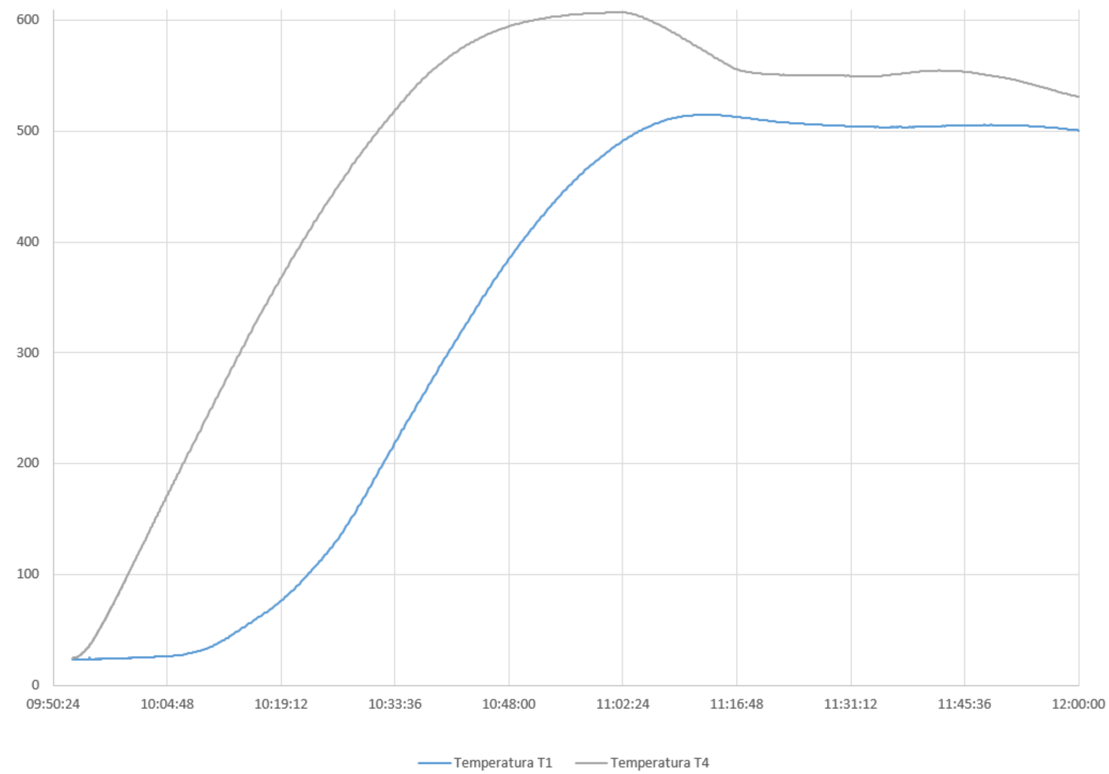
- Preliminary TGA → Minimum obtainable solid residue

  27.8% w/w d.b. at 900˚C

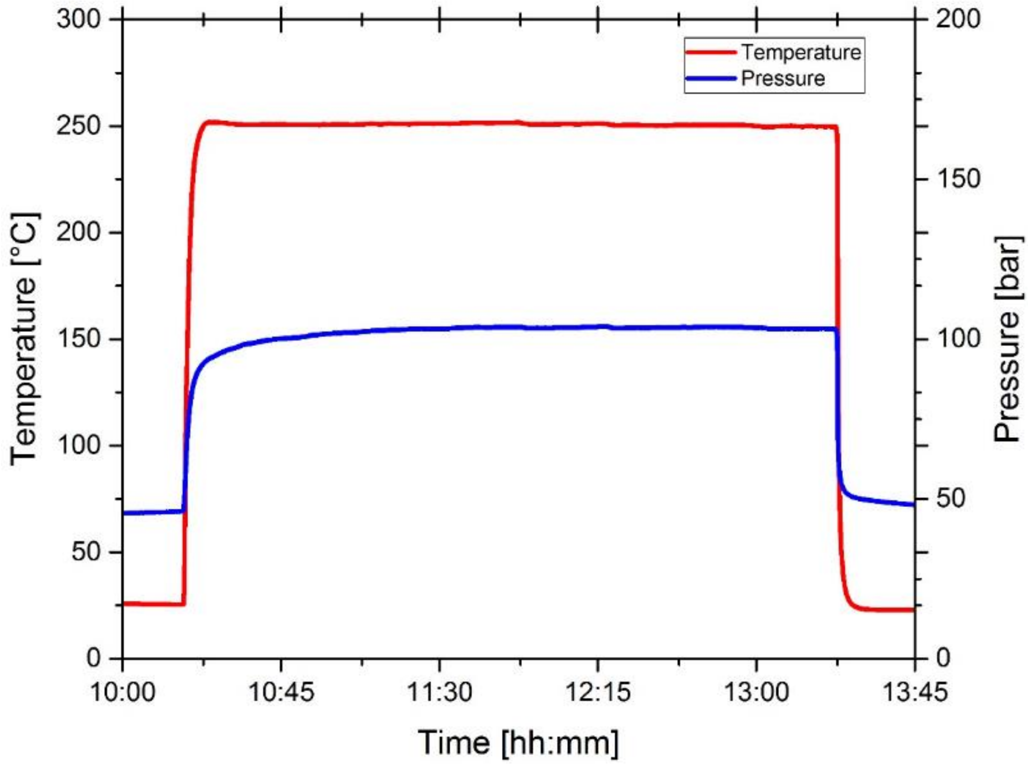


Slow Pyrolysis experiments

Experiment mode	Batch
Feedstock [g]	1074
Reactor heater temperature [°C]	600
Gas-line heater temperature [°C]	550
Mean reactor temperature [°C]	506
Holding time [h]	1
Nitrogen flow [l/min]	5.0
Stirring system	Active
Mean heating rate [° C/min]	7



Hydrothermal carbonization experiments



T [°C]	Time [h]	B/W db [w/w]	P0 [bar]	HR mean [°C/min]	T mean [°C]	Pfin-P0 [bar]
200	0.5	10%	20.15	33.96	201.27	0.99
200	3.0	10%	20.40	33.46	201.21	0.67
250	0.5	10%	45.23	42.97	251.49	1.41
250	3.0	10%	45.23	40.86	250.80	2.63

HTC Product recovery and GC analyses methodology