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Influence of feedstock and operational conditions on bio-chars derived from the pyrolysis of selected biomasses

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Influence of feedstock and operational conditions on bio-chars derived from the pyrolysis of selected biomasses

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University of Florence, Italy*

- **Main goals**

- ✓ *To investigate (lab.scale) biochar properties versus feedstocks and pyrolysis conditions*
- ✓ *To consider biochar porosity and CEC for use as soil amendment*

- **Feedstock**

- ✓ *Pinus nigra (softwood)*
- ✓ *Poplar (hardwood)*
- ✓ *Willow (hardwood)*

- **Methodology**

- ✓ *Slow pyrolysis in macro-TGA*

Pyrolysis PDU units at RECORD

(in-house developed technologies)

Rotary Kiln

Slow pyrolysis of biomass & waste to fuels and products

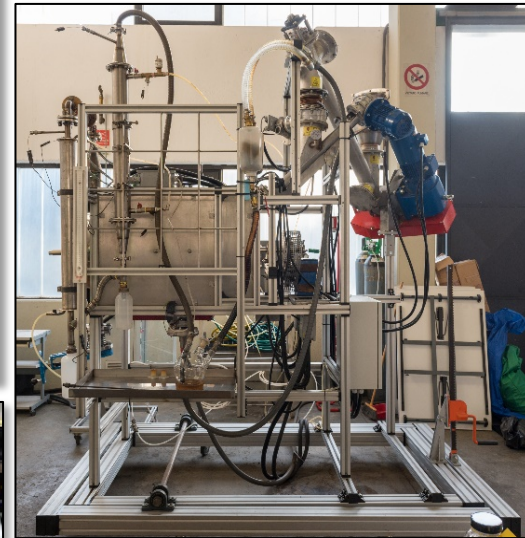
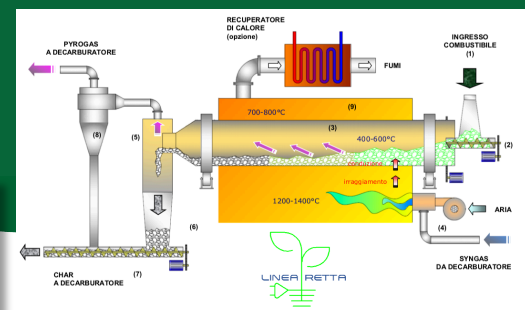
- Solid (as fuel or amendment) + high T heat
- Integration in large-scale Advanced Biofuel supply chain
- IN=100 kg/h



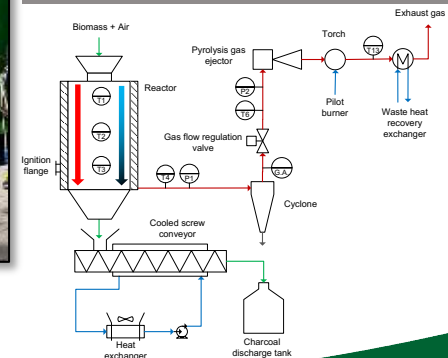
CARBON

Slow pyrolysis of biomass for charcoal and biochar making.

- Fixed bed, Open-top Oxidative Reactor (Autothermal)
- Designed and developed for small farmers
- Continuous operation.
- IN=50 kg/h. OUT=12kg/h ($\eta_c = 24 \text{ wt.}\%$)



Intermediate pyrolysis Pilot Unit



Feedstocks and process conditions



SOFTWOOD

Pine



Poplar



HARDWOOD

Willow



- *Drying*
- *Grinding to 2 mm*



TGA Leco 701

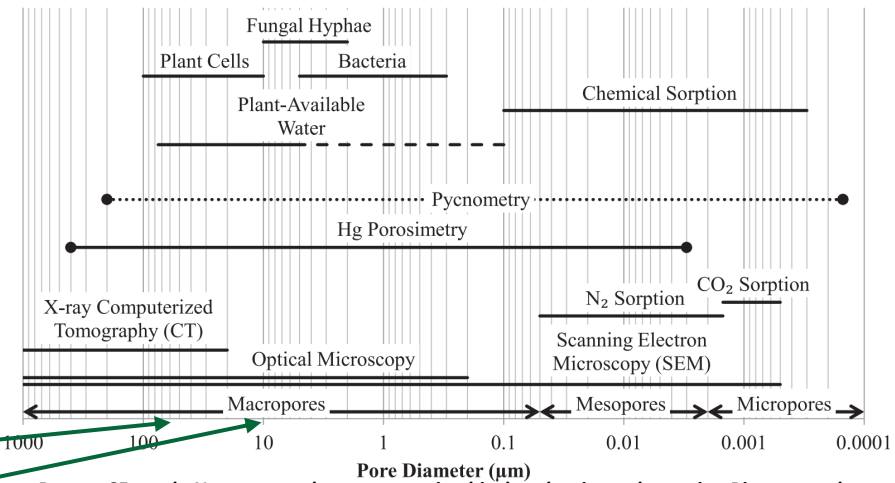
Temperature [°C]	Heating rate [°C/min]	Plateau [h]	N flowrate [l/min]
400	20	2	10
550	20	2	10
650	20	2	10



Specific surface, water retention....

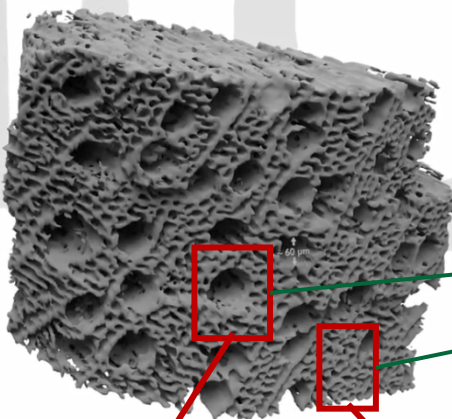


Source: Luke, Finland. X-ray tomographic reconstruction of a willow biochar sample pyrolysed at temperature 320 ° C. Image resolution is 1.14 μm. Camera moves through pores relevant for water retention (approx. 10 and 50 μm in diameter). <https://www.youtube.com/watch?v=xZeu8mNlxZQ>

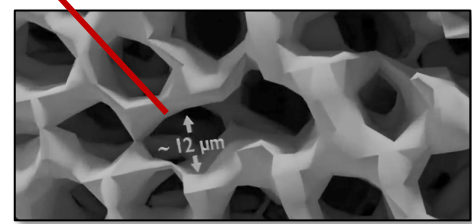
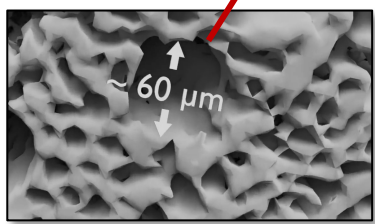


Brewer CE, et al., *New approaches to measuring biochar density and porosity, Biomass and Bioenergy* (2014), <http://dx.doi.org/10.1016/j.biombioe.2014.03.059>

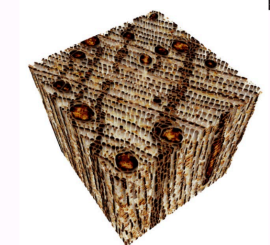
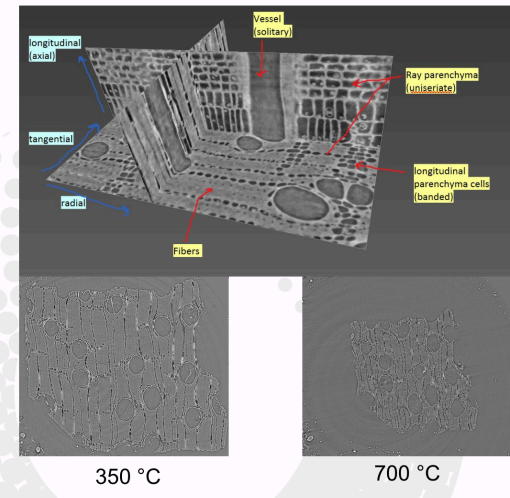
~ 615 μm



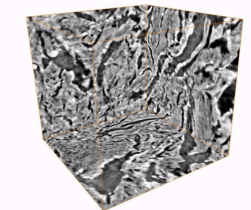
Willow
- Pyrolysis biochar
- T = 320 °C



Biochar structure engineering



Biochar from raw wood



Biochar from pelleted wood

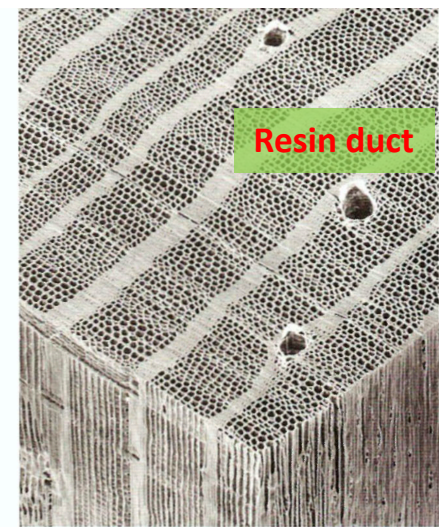
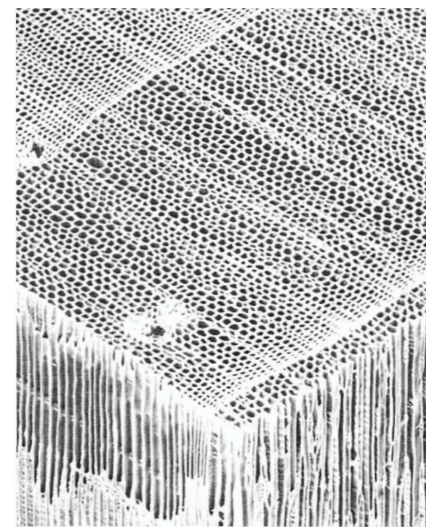
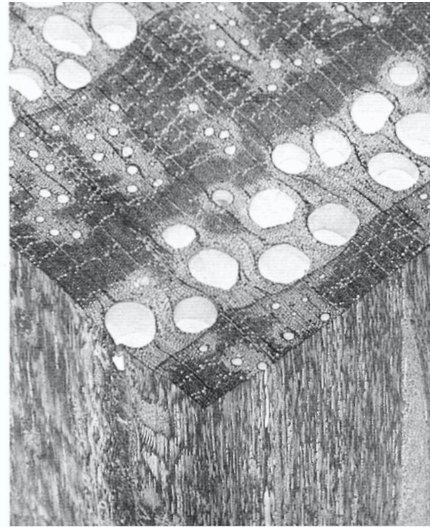
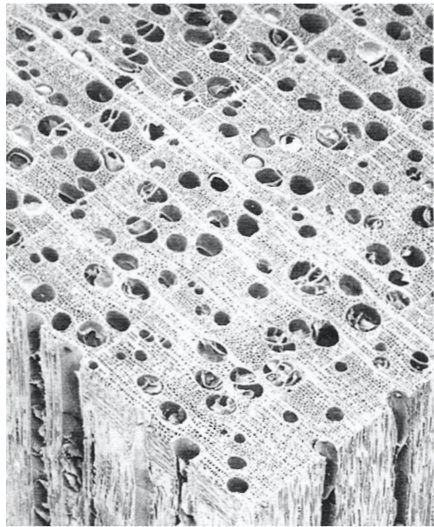
Wood structure: Hardwood/Softwood



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Hardwood *Angiosperms-Monocotyledons*

Softwood *Gymnosperm-Coniferous*

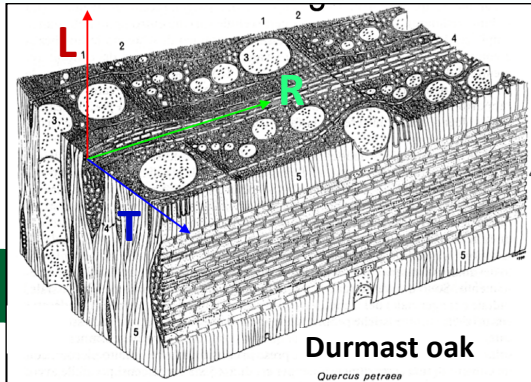


BLACK WALNUT

RED OAK

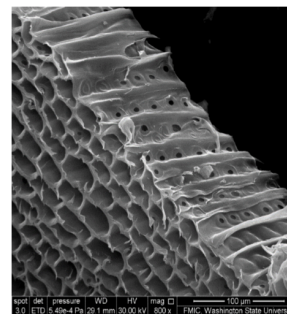
EASTERN WHITE PINE

SOUTHERN YELLOW PINE

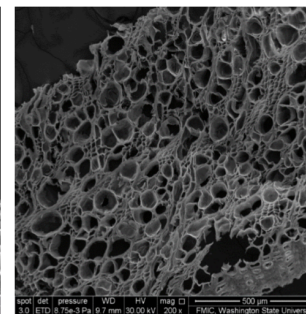


Durmast oak

Quercus petraea



Pine wood biochar
mag. 800X



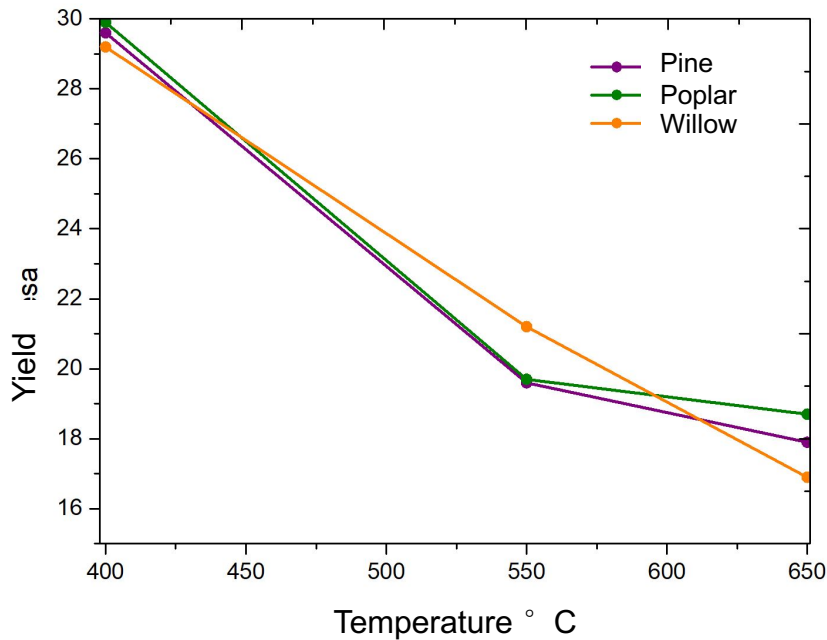
Pine bark biochar
mag. 200X



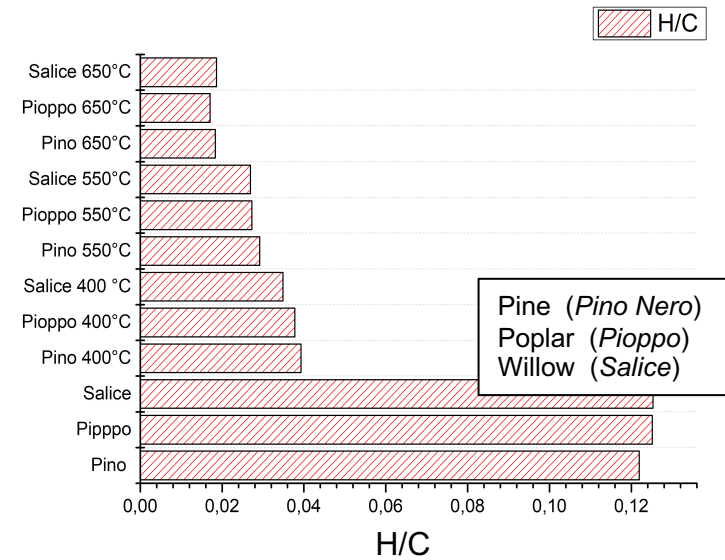
Poplar wood biochar
mag. 300X



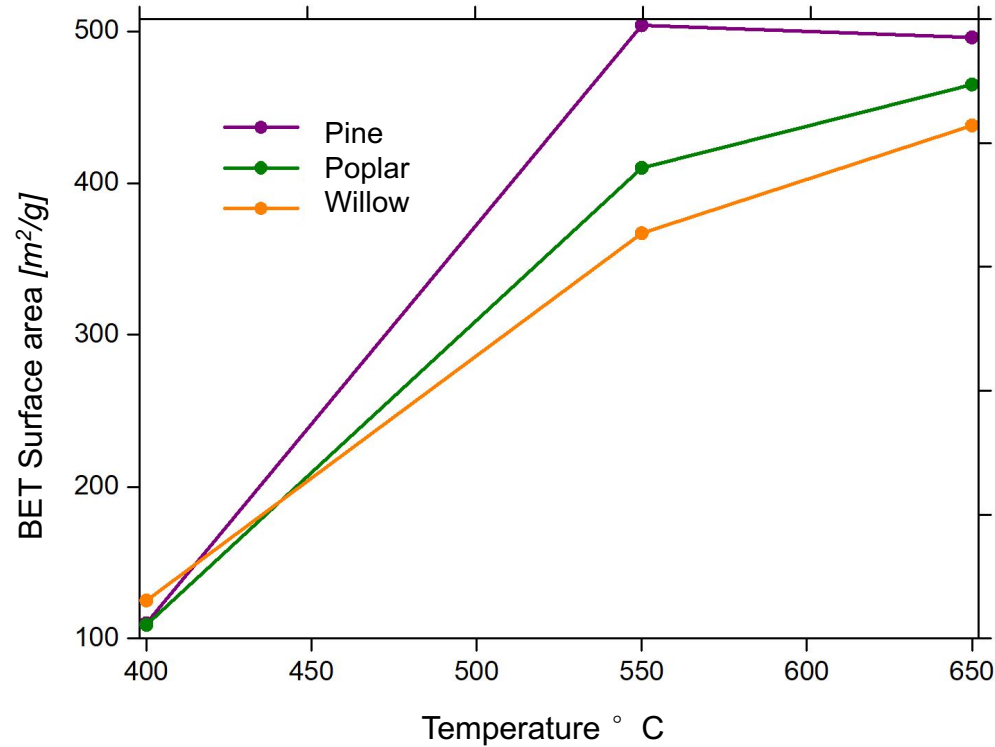
Yields and elemental composition



H/C ratio decreasing with carbonization T



	Biomass			Biochar								
	Pine	Poplar	Willow	Pine 400°C	Poplar 400°C	Willow 400°C	Pine 550°C	Poplar 550°C	Willow 550°C	Pine 650°C	Poplar 650°C	Willow 650°C
Moist. %	28,5	39,4	40,2	-	-	-	-	-	-	-	-	-
Yield % w/w	-	-	-	29,6	29,9	29,2	19,6	19,7	21,2	17,9	18,7	16,9

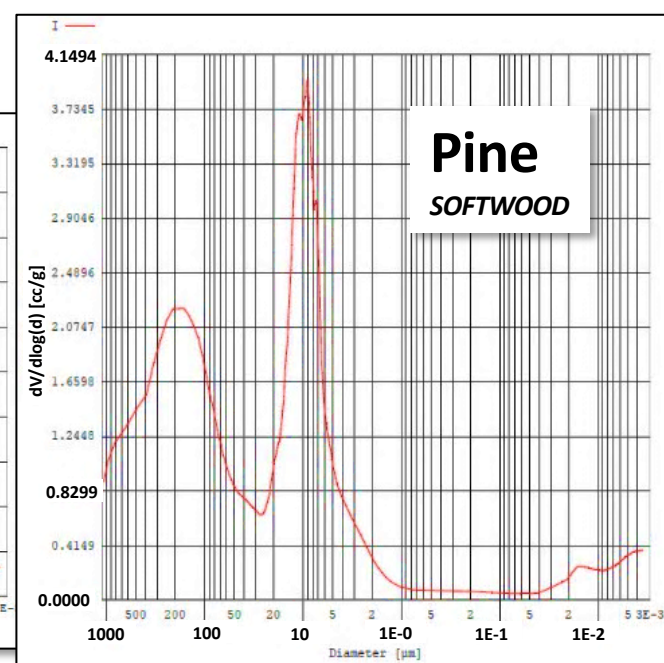
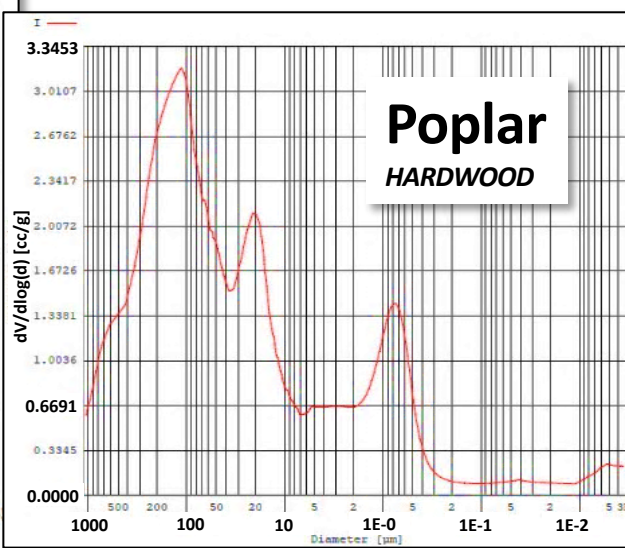
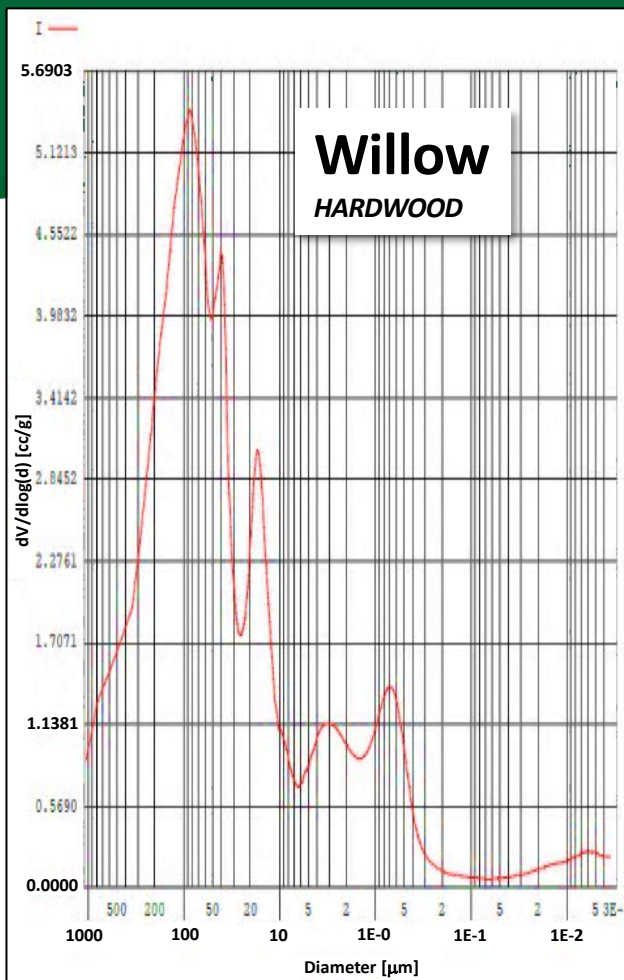


Softwood biochar (pine) shows higher BET values at 550 ° C and 650 ° C

Mercury porosimeter



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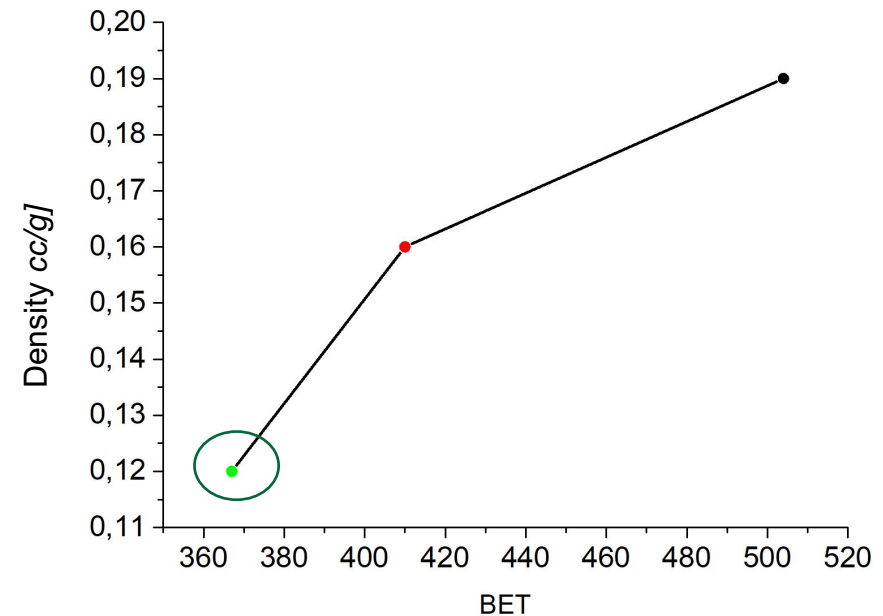


Wood	BET - Specific Surface (m2/g)	Mercury Porosimeter - Surface Area (m2/g)	Mercury Porosimeter - Total Intruded Volume (cc/g)
Willow	367	97.16	7.69
Poplar	410	78.85	5.33
Pine	504	126.86	4.53

Density vs superficial area - char produced at 550° C



Biochar 550° C	Total Porosity [%]	Density [g/cc]	Total intruded volume Hg [cc/g]
Pine	86	0,19	4,5
Poplar	86	0,16	5,3
Willow	91	0,12	7,6



I biochar a 550° C sono: Pino nero (●), Pioppo rosso (●), Salice verde (●).

SEM analysis



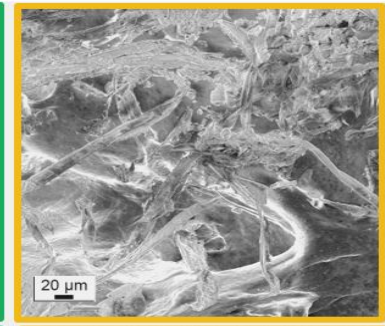
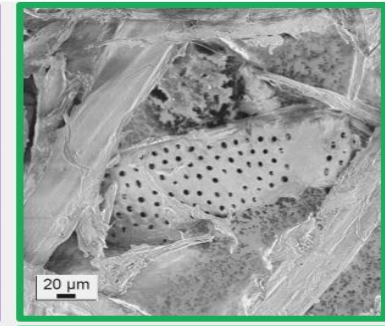
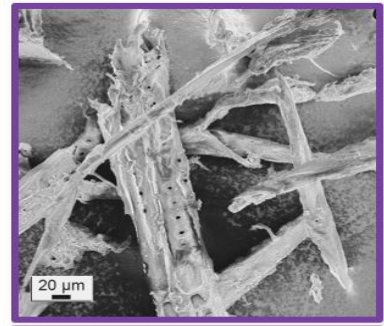
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Pine

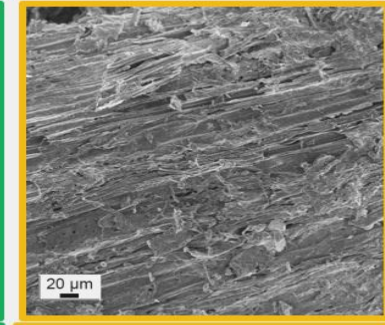
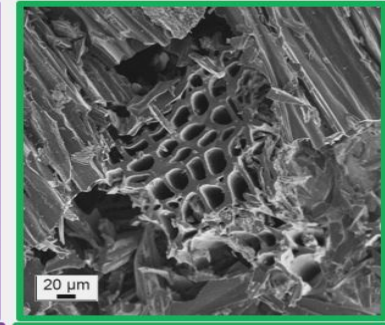
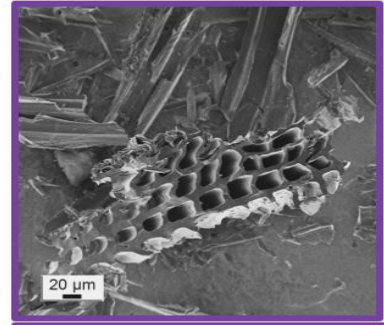
Poplar

Willow

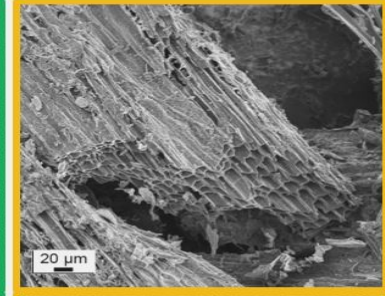
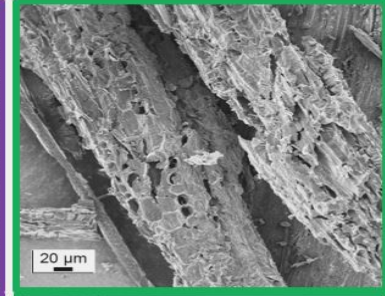
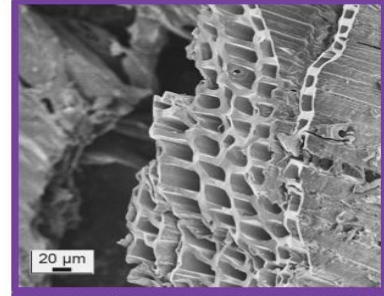
Biomass



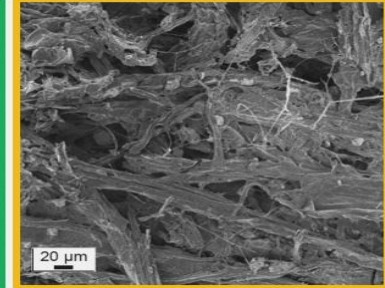
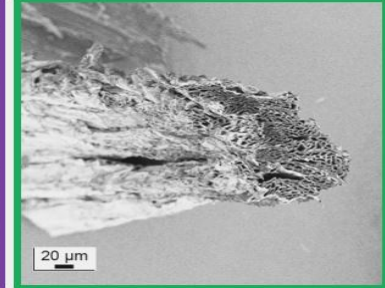
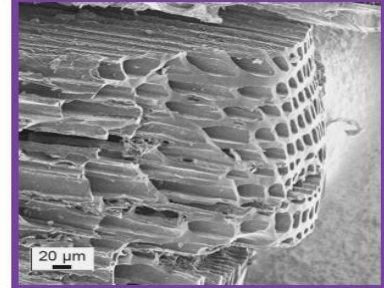
400°C

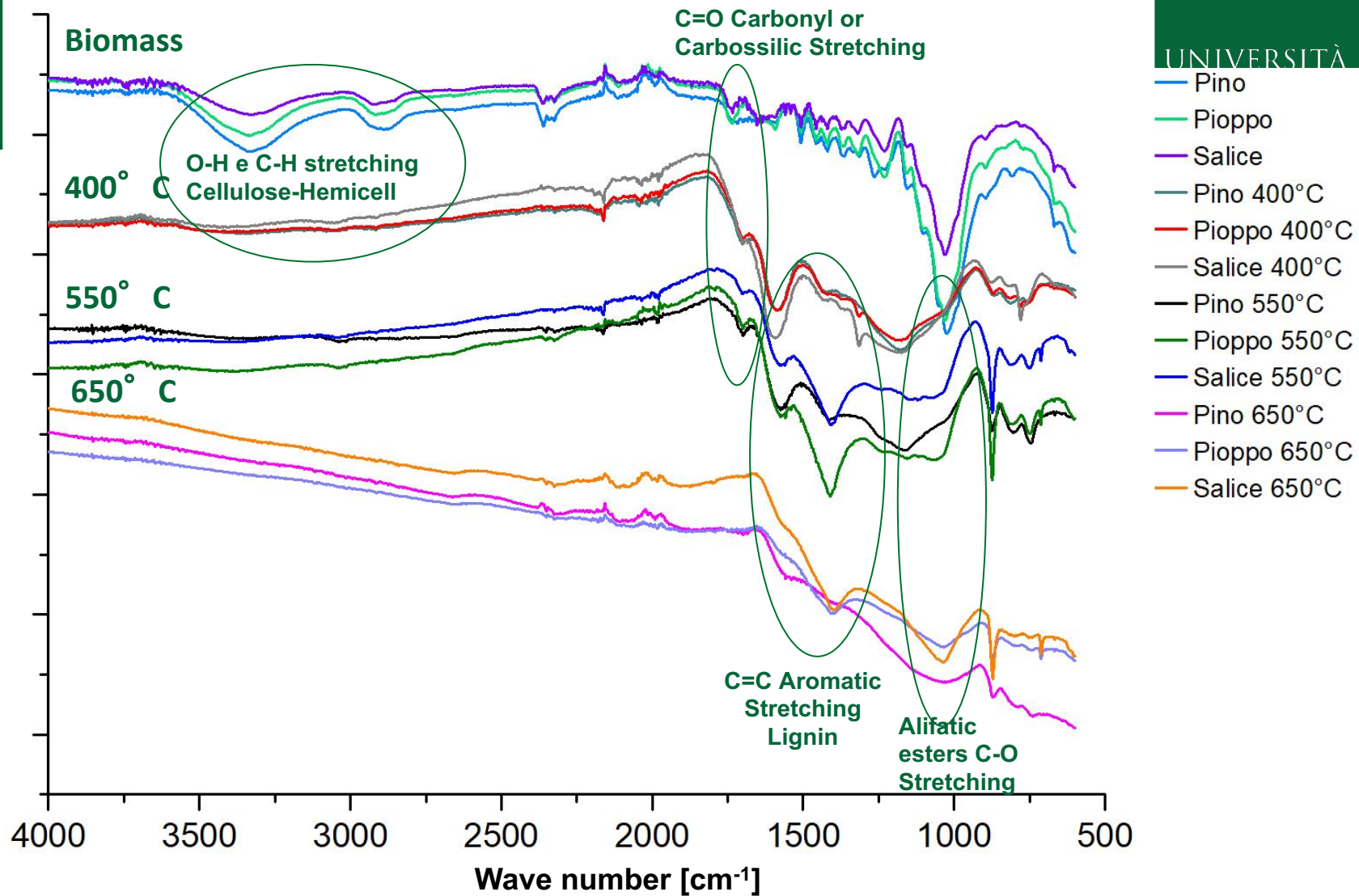


550°C



650°C





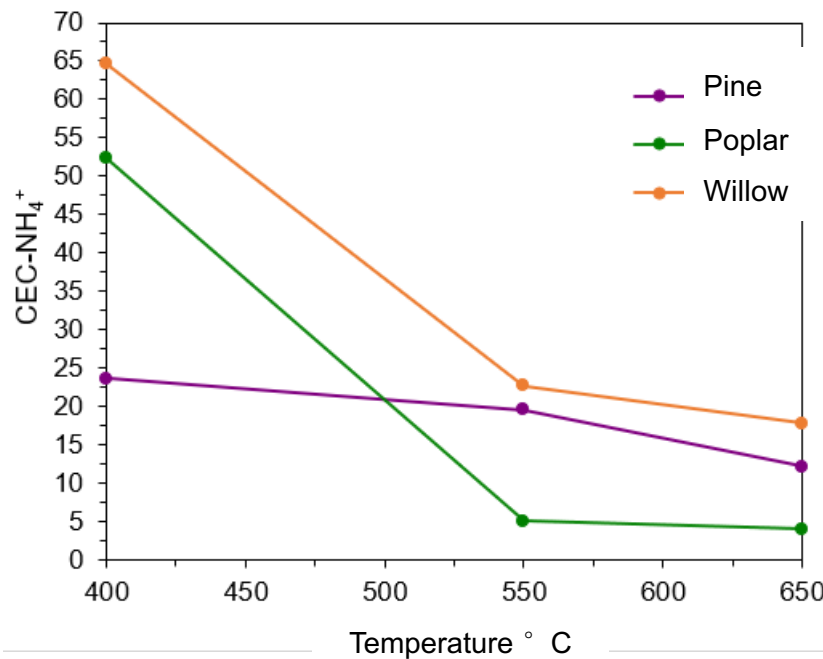
Broad bands at $\sim 3400 \text{ cm}^{-1}$ in the feedstock, together with bands at $\sim 2900\text{--}2800 \text{ cm}^{-1}$: they refer to cellulose and hemicellulose (due to the stretching $\nu\text{O-H}$ and νCH).

These signals disappear increasing pyrolysis T.

The signal at 1730 cm^{-1} , probably due to the hemicellulose ($\text{C} = \text{O}$), gradually disappear from 400 to 650° C .

Some bands at $\sim 1600\text{--}1500 \text{ cm}^{-1}$ attributed to aromatic group ($\text{C} = \text{C}$) both in biomass and in biochar; an increase in the intensity of aromatic CH at $870\text{--}850 \text{ cm}^{-1}$ probably due to graphitic structures

CEC – NH₄⁺



Sample	CEC-NH ₄ ⁺
Pine 400°C	23,7
Pine 550°C	19,6
Pine 650°C	12,2
Poplar 400°C	52,3
Poplar 550°C	5,1
Poplar 650°C	4,1
Willow 400°C	64,7
Willow 550°C	22,7
Willow 650°C	17,8

Criteria for assessment	CEC cmol(+)/Kg
High	> 20
Average	10-20
Low	< 10

Willow, 400 ° C: highest CEC-NH₄⁺. Trend in agreement with the reduction of oxygenated functional groups with temperature

Results in good agreement with literature and expectations:

- *Softwood* : higher BET surface (550° C).
- *Hardwood*: more macropores (consistent with wood structure). Better feedstock for plant water available water.
- CEC max at 400° C, decreasing with T (less oxygenated functional groups)

Ongoing R&D work

- Investigation of fresh and aged or partially oxidated biochar, both at lab and pilot scale
- Assessment of biochar characteristics vs plant and soil
- Final goal: framing process conditions and feedstock selection in the industrial scale of biochar production

Thanks for the attention



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