Study of the carbonization and activation of different lignocellulosic precursors for the elaboration of activated carbons with controlled porosity

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Exploring lignocellulosic biomass!
23 & 24 June 2016 in Reims - France

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Context

Valorization of Lignocellulosic Biomass

→ **Energy** —— **Solid Fuels**

→ **Materials** —— **Activated Carbons**

PYROLYSIS	GASIFICATION	COMBUSTION
gas, liquid	$CO + H_2$	*Heat,* $CO_2 + H_2O$

PHYSICAL ACTIVATION

Carbonization — *Ar or* N_2 — *500-800°C* + *Activation* — H_2O *or* CO_2 *or* O_2 — *up to 800°C*

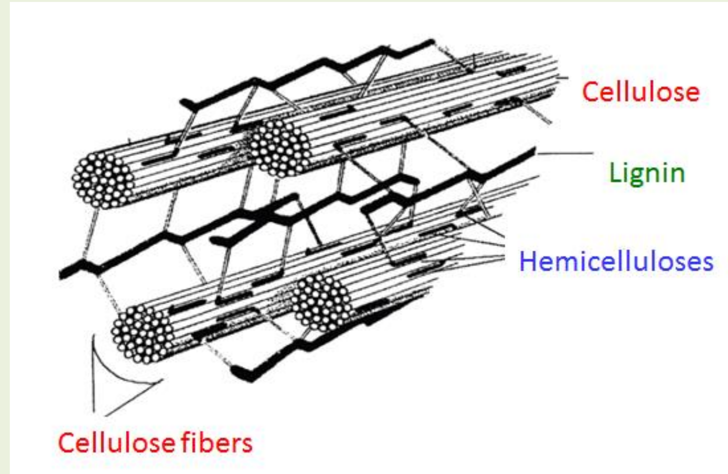
CHEMICAL ACTIVATION

Activating Agent — H_3PO_4 *or* HNO_3 + *Carbonization* — *Ar or* N_2 — *500-800°C*

OPTIMIZATION via the the study of the CARBONIZATION/PYROLYSIS

COMPLEX *for a* ***lignocellulosic precursor*** *due to:*
-differences in reactivity between hemicellulose, cellulose and lignin
-the competition of the reactions accompanying their decomposition

KNOWLEDGE OT THE RAW MATERIAL MANDATORY: *Elementary analysis, biochemical composition, FTIR, XRD, Thermal decompositions by thermogravimetry (TGA-DTA)*



Thermal behavior of Raw Material and lignocellulosic compounds

TGA-DTA carried out on all the lignocellulosic precursors and on the three compounds (H., C., L.) => estimation of their respective contribution in the final mass of the solid phase (chars and activated carbons)

Lignocellulosic compounds (commercial)

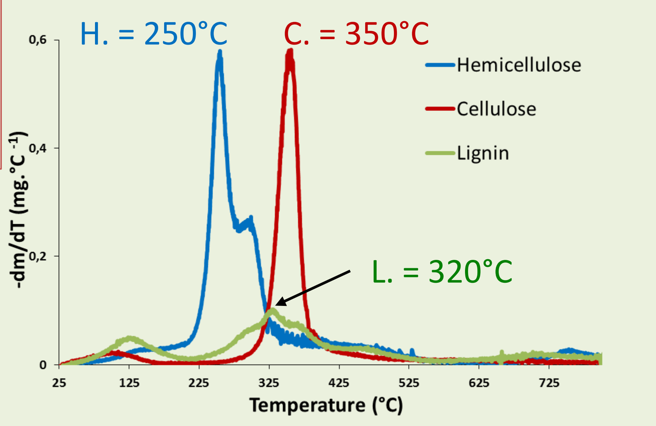
Hemicellulose (H.)

Cellulose (C.)

Lignin (L.)

Raw material from agricultural and agro-alimentary wastes

Experimental conditions:
T_{final}: 800°C-1h
Heating rate: 20°C.min^{-1}
Vector gas: argon
Flow: 160 mL.min^{-1}

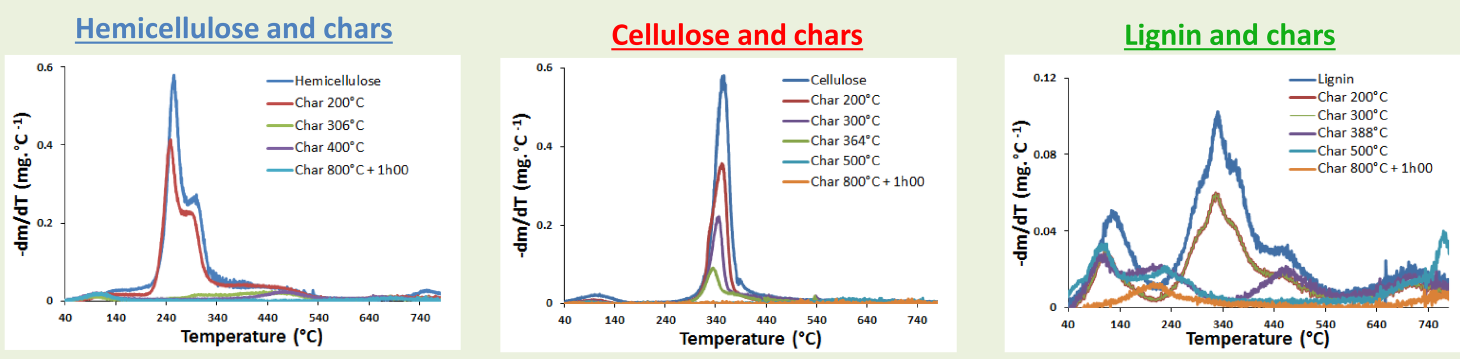


Carbonization of the pure compounds

↓

Lignin decomposes over a wide temperature range whereas hemicellulose and cellulose have characteristic peaks

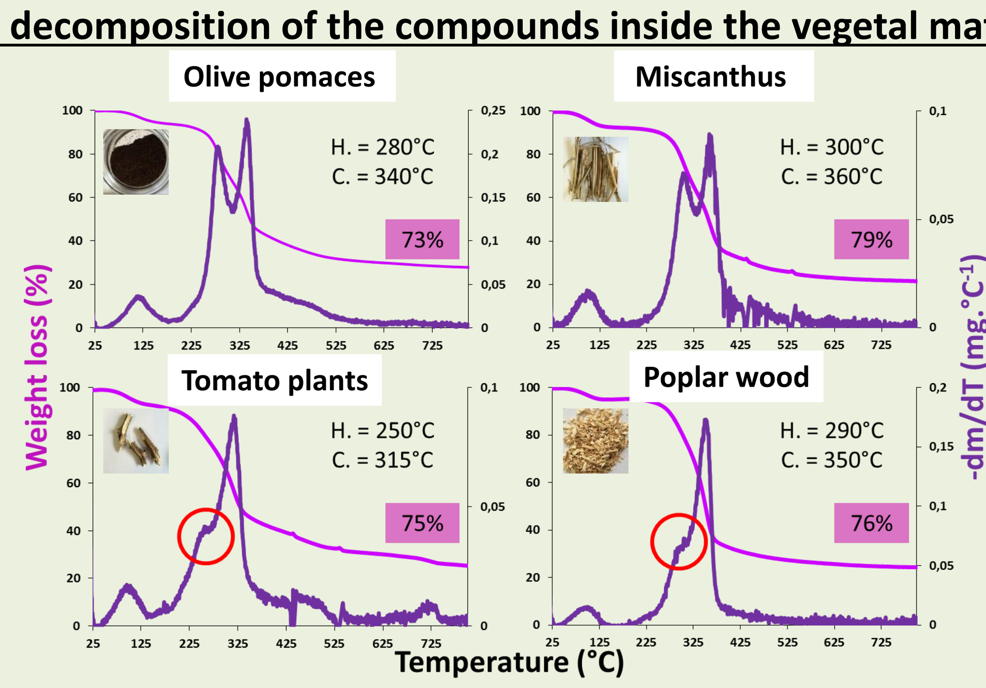
Thermal evolution followed by charring in an oven => Carbonization was done is several steps as a function of the previous thermograms



→ *The thermal decomposition of Lignin seems to be more complex than Hemicellulose and Cellulose.*

Thermal decomposition of the compounds inside the vegetal matrix

→Identification of the characteristic peaks for lignocellulosic compounds



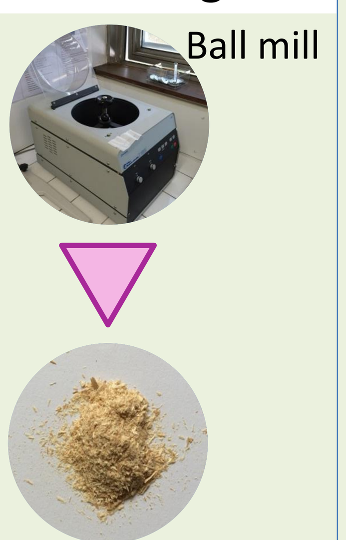
- Different thermal behaviors as a function of the raw material.
- Natural deconvolution of H. and C. for olive pomaces and miscanthus and L. is hidden.
- H. peak is less pronounced for tomato plants and poplar wood.

→ *Analysis of the obtained data by means of a kinetic model required to better understand their thermal decomposition*
→ *Optimization and modelling of the carbonization step required (whatever the activation method) as a function of the raw material in order to control final textural properties of the activated carbon.*

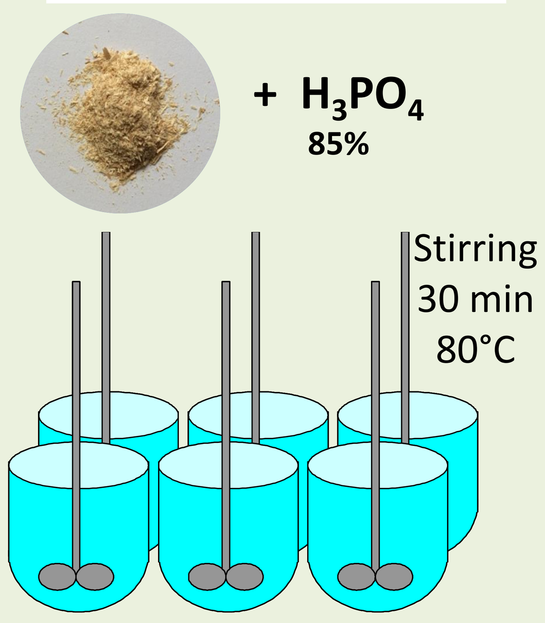
Is it possible to produce activated carbons from tomato plants?

Raw material → **Activated Carbon?**

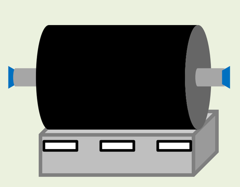
❶ Grinding



❷ Blending

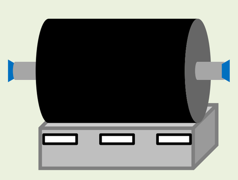


❸ Drying



Under air
15 hours
110°C

❹ Carbonization



Under Argon
500°C
40 min bearing

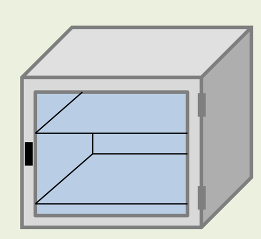
❺ Rinsing/Filtering

Product obtained + HCl 37%

Stirring 20 min

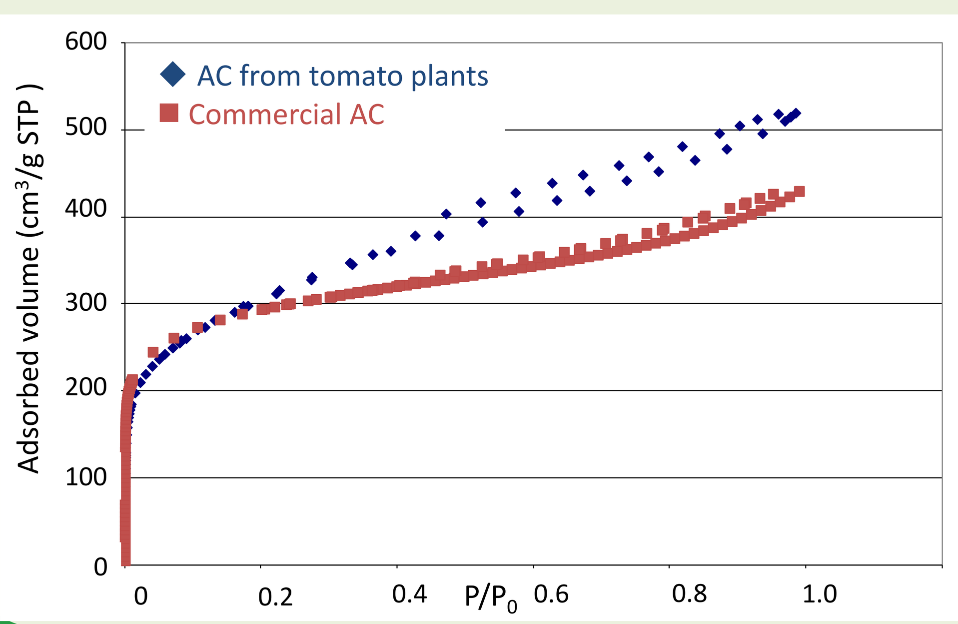
Filtering with distilled water until obtention of a neutral solution (pH = 7)

❻Drying

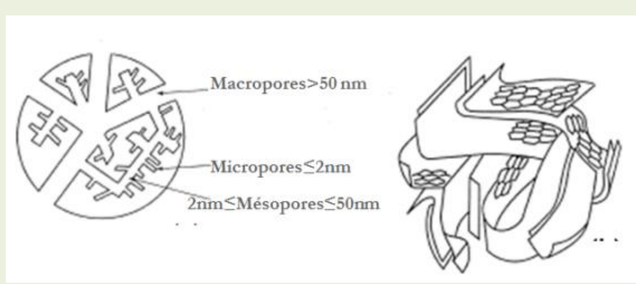


Stove
15 hours
50°C

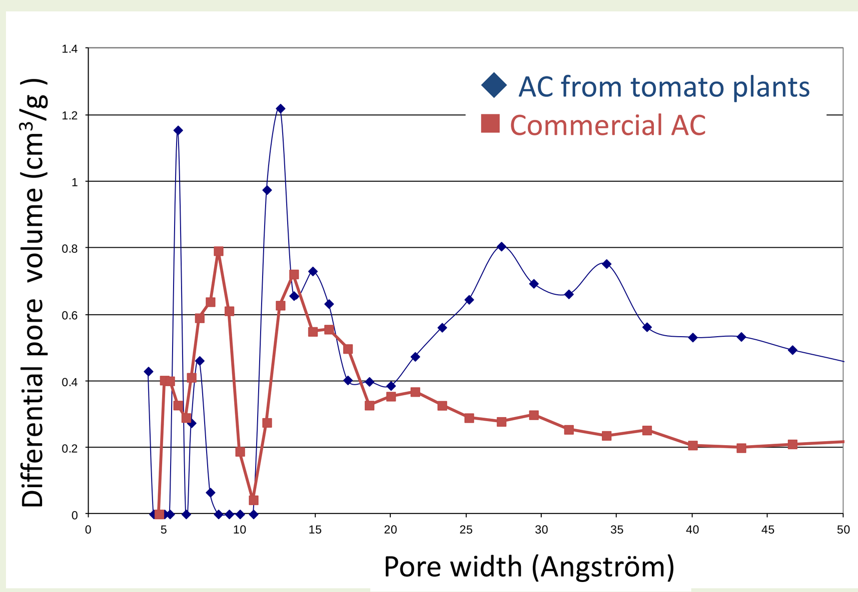
Microporosity characterized by nitrogen adsorption at 77 K and comparison with a commercial AC



→ The isotherm shape indicates presence of micropores and mesopores



→Confirmation by the distribution size of micropores by DFT method ⇨



Textural properties obtained from N_2 77K adsorption isotherm

	W_o (cm³/g)	L_{o1} (Å)	S_{BET} (m²/g)	S_{ext} (m²/g)	S_{micro} (m²/g)	S_{total} (m²/g)
Tomato AC	0.38	22.1	1090	404	344	748
Commercial AC	0.39	12.7	1077	256	614	870

W_o: specific microporous volume; L_{01}: mean microporous size;
S_{BET}: BET surface; S_{ext}: external surface; S_{micro}: microporous surface } *S_{total}: total surface*

→ ***Very good result obtained without any optimization:***
AC from tomato plants has textural properties closed to commercial AC used for water treatment

Conclusion

⇘ **First tests of AC elaboration: very good result (without optimization) with tomato plants: textural properties fitted for water treatment**
⇨ activation optimization required to control porosity for a given application

⇘ **Perspective: development of a predictive method to estimate the mass and the textural properties of the final AC**
based on the study of the raw material: elementary analyses, biochemical composition, FTIR, XRD, Calorimetry, TGA curves, modelling
For activated carbons => control of the porosity => for which application?
For solid fuels => High Heating Value (HHV), modelling of pyrolysis and secondary gas-phase reactions