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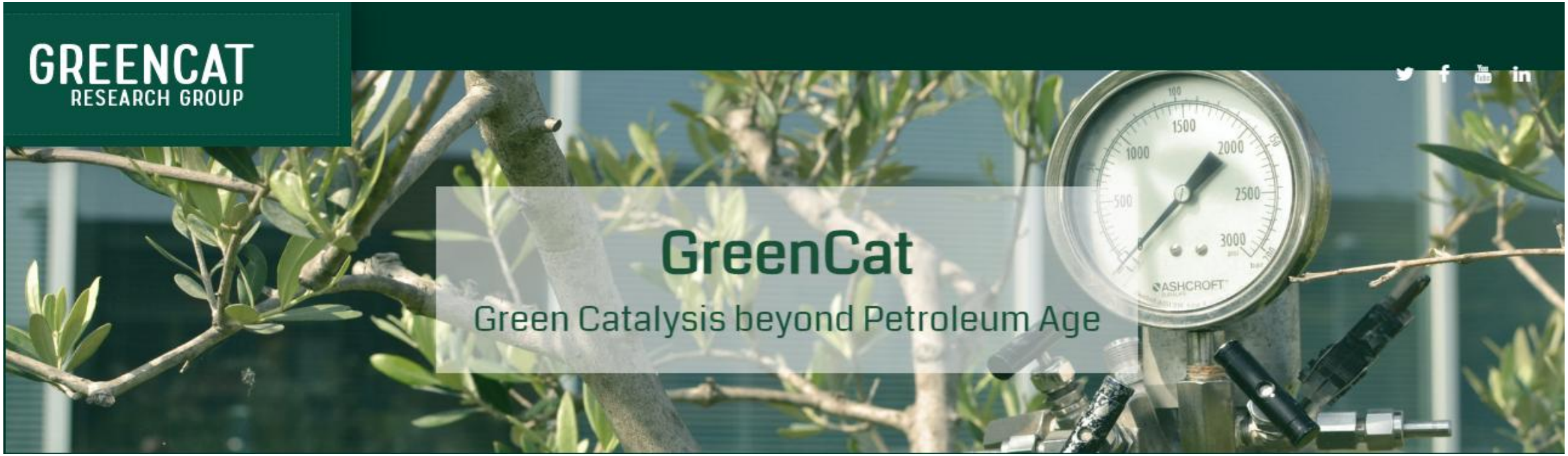
New exploitation strategies of the by-products deriving from the hazelnut supply chain

Dr. Domenico Licursi

Pisa, Italy, 17th -18th June 2022

About the Research Group

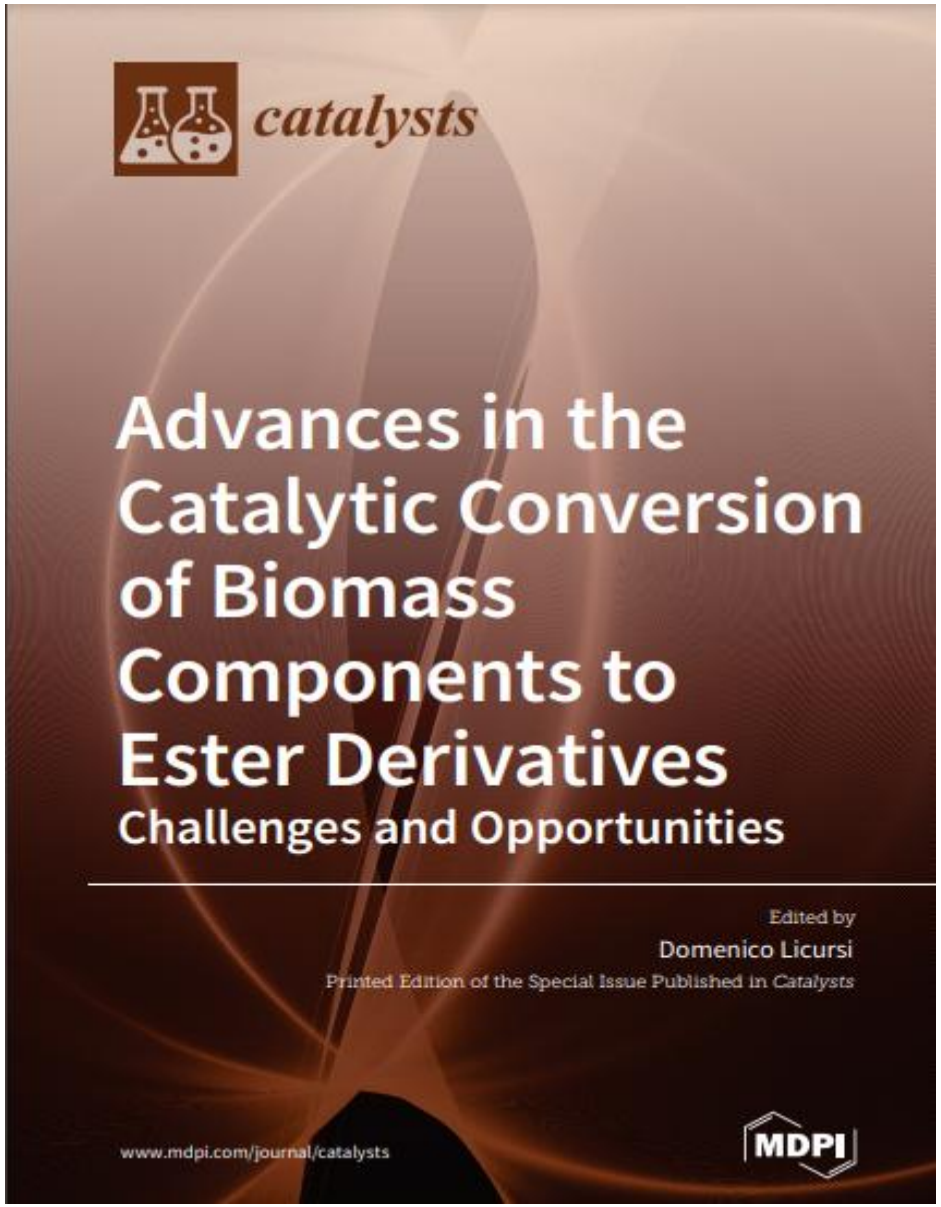


Our key topics:

- sustainable catalysis;
- process optimization;
- ***complete valorization of biomass components;***
- catalytic conversion for chemicals and biofuels;
- process safety;
- synthesis and application of nanostructured heterogeneous catalysts.

Web Site: http://greencat.dcci.unipi.it

About the my recent activities



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Advances in the Catalytic Conversion of Biomass Components to Ester Derivatives: Challenges and Opportunities

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Biomass has received significant attention as a sustainable feedstock that can replace diminishing fossil fuels in the production of value-added chemicals and energy. Many new catalytic technologies have been developed for the conversion of biomass feedstocks into valuable biofuels and bioproducts. However, many of these still suffer from several disadvantages, such as weak catalytic performance, harsh reaction conditions, a high processing cost, and questionable sustainability, which limit their further applicability/development in the immediate future. In this context, the esterification of carboxylic acids represents a very valuable solution to these problems, requiring mild reaction conditions and being advantageously integrable with many existing processes of biomass conversion. An emblematic example is the acid-catalyzed hydrothermal route for levulinic acid production, already upgraded to that of higher value alkyl levulinates, obtained by esterification or directly by biomass alcoholysis. Many other chemical processes benefit from esterification, such as the synthesis of biodiesel, which includes monoalkyl esters of long-chain fatty acids prepared from renewable vegetable oils and animal fats, or that of cellulose esters, mainly acetates, for textile uses. Even pyrolysis bio-oil should be stabilized by esterification to neutralize the acidity of carboxylic acids and moderate the reactivity of other typical biomass-derived compounds, such as sugars, furans, aldehydes, and phenolics. This Special Issue reports on the recent main advances in the homogeneous/heterogeneous catalytic conversion of model/real biomass components into ester derivatives that are extremely attractive for both the academic and industrial fields.

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Hazelnut supply chain: Introduction

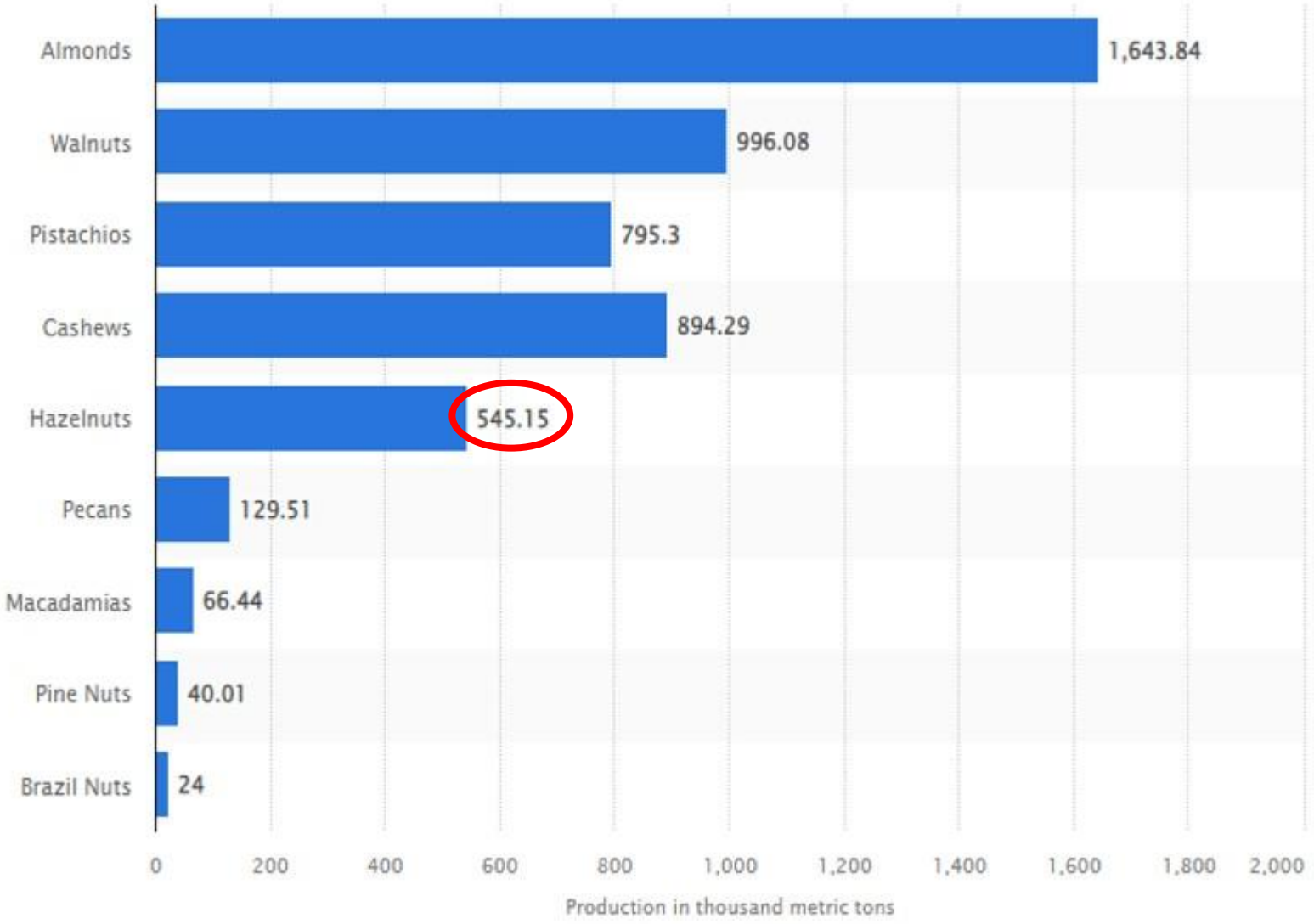


Figure: Production of tree nuts worldwide in 2021/2022, by type [1].

- Hazelnut is the fifth most produced tree nut in the world, with an estimated production of about 545 thousand metric tons in 2022 [1].
- Turkey and Italy (but not only!) are among the main world's leading producers.
- Hazelnut processing into finished food products requires different mechanical operations and generates ***different types of waste streams***.

[1] https://www.statista.com/statistics/1030790/tree-nut-global-production-by-type/ (accessed 13-06-2022).

Hazelnut supply chain: Manufacturing process and produced wastes

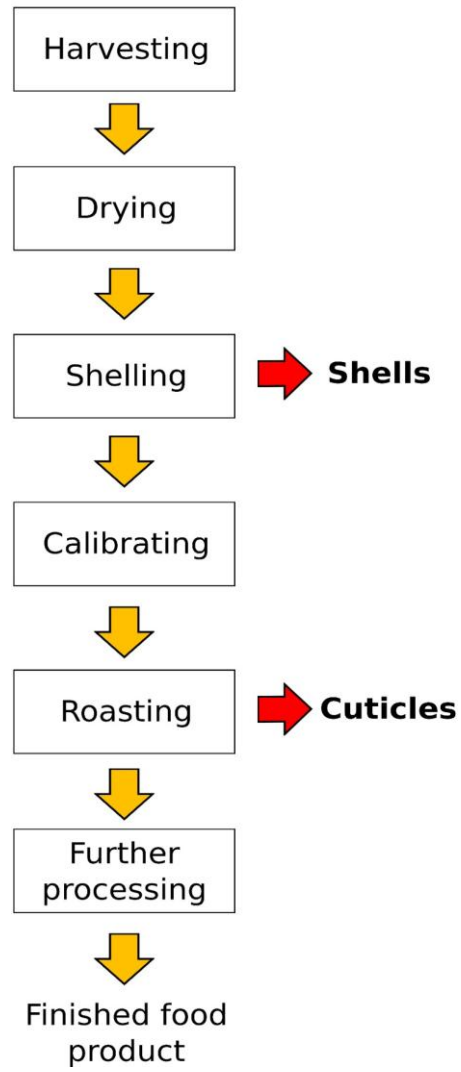


Figure: Manufacturing process of the hazelnut.

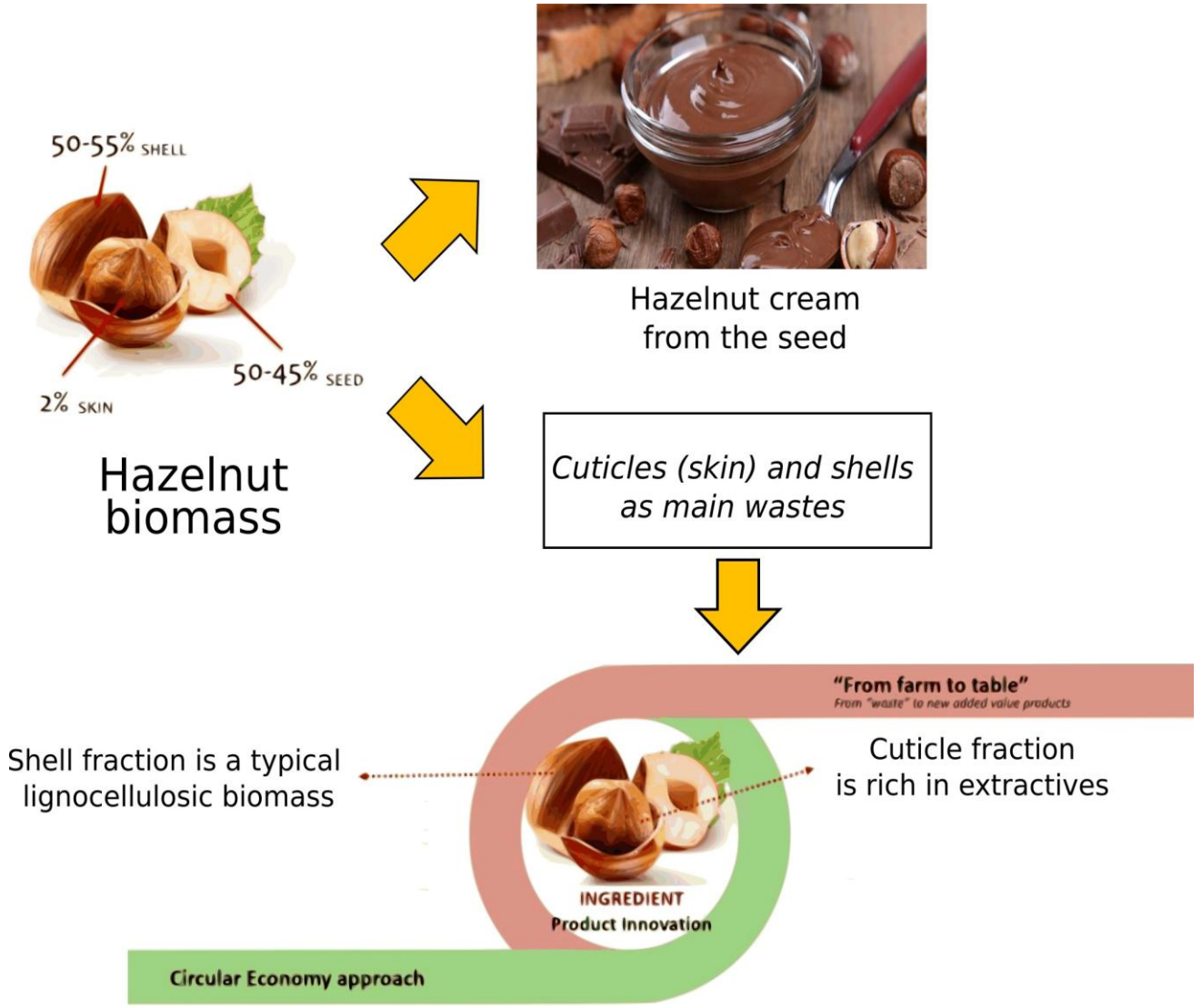


Figure: Main products and wastes originating from hazelnut biomass processing.

- ***Cuticles and shells are the main wastes of the hazelnut processing.***

Exploitation of the cuticles

- Compositional analysis of cuticles and shells was carried out according to standard NREL methods [2]:

Table 1: Compositional analysis of shell and cuticle performed with NREL official procedures. Values are expressed as weight percentages of the total sample. Holocellulose-to-lignin ratios are also reported [2].

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Moisture (%)	Ash (%)	Other (%)	H/L
Shell	22.9	23.6	37.6	1.4	5.1	1.4	8.0	1.2
Cuticle	8.9	4.2	33.2	36.2	8.1	1.5	7.9	0.4

- Cuticle is very rich in extractives, whilst shell is a traditional lignocellulosic biomass.
- This issue was investigated more in-depth by Py(HMDS)-GC/MS and HPLC-DAD techniques.

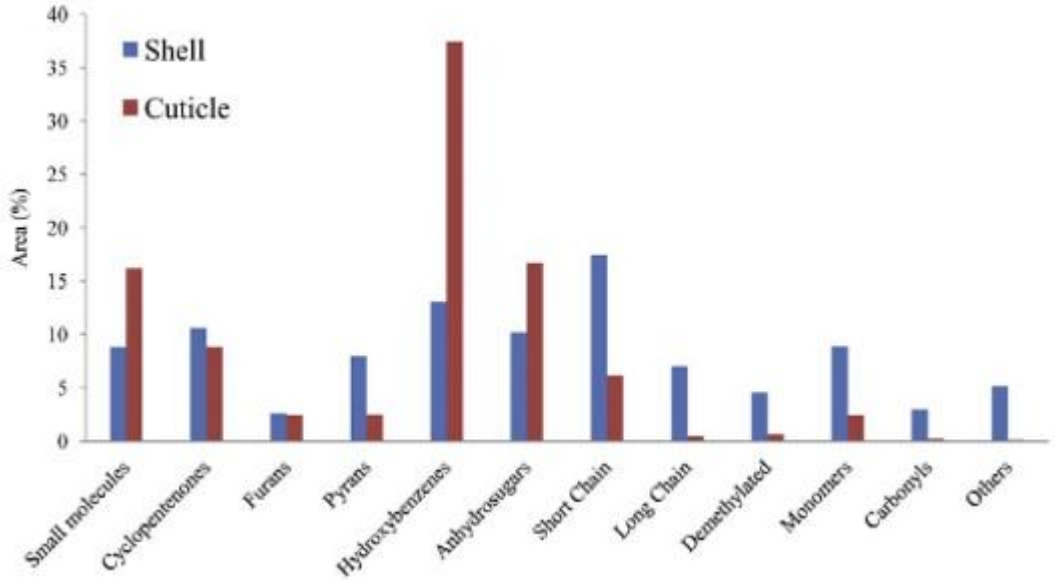
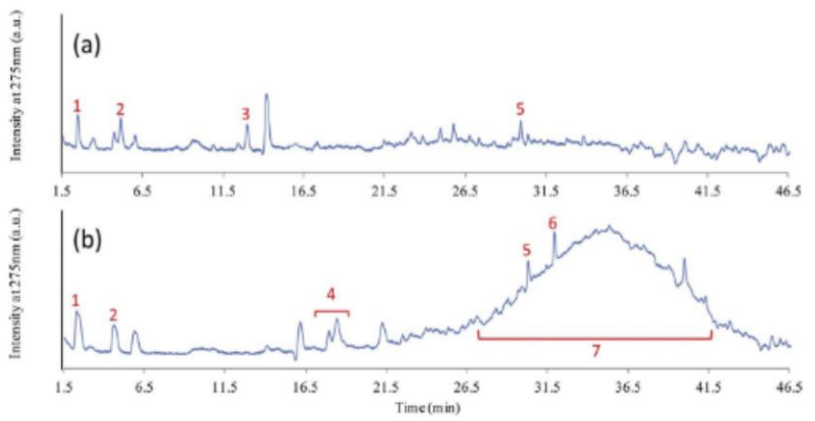


Figure: Percentage composition of each product category for shell and cuticle samples (Py(HMDS)-GC/MS analysis).



n°	Name
1	Gallic acid
2	Protocatechuic acid
3	Vanillic acid
4	Catechin/epicatechin
5	Naringin
6	Quercitrin
7	Procyanidrin

Figure: HPLC-DAD chromatograms of the shell (a) and cuticle (b) samples, both at 275 nm.

- ***Cuticle fraction predominantly includes polyphenols, fatty acids and procyanidrins.*** ➡ ***Nutraceutical applications!***

[2] Licursi *et al.*, *Journal of Analytical and Applied Pyrolysis*, Volume 127, pp. 321-328, 2017. Doi: 10.1016/j.jaap.2017.07.019.

Exploitation of the shells

- ✓ Up to now, shell fraction has been limitedly used as a fuel and for landscaping.
- ✓ C6 carbohydrates in shell fraction can be advantageously converted into **levulinic acid (LA)**, by acid-catalyzed hydrothermal treatment. Levulinic acid is a very valuable platform chemical (upgradable into new bio-fuels, bio-solvents, bio-lubricants, and many more..) [3].
- ✓ We have optimized the LA production from hazelnut shells, both in microwave and in autoclave, anyway achieving a maximum LA yield of 12 wt% [3].
- ✓ However, an abundant waste stream of «*pseudo-lignin*» (45 wt%) is recovered downstream: this is a carbonaceous hydrochar!

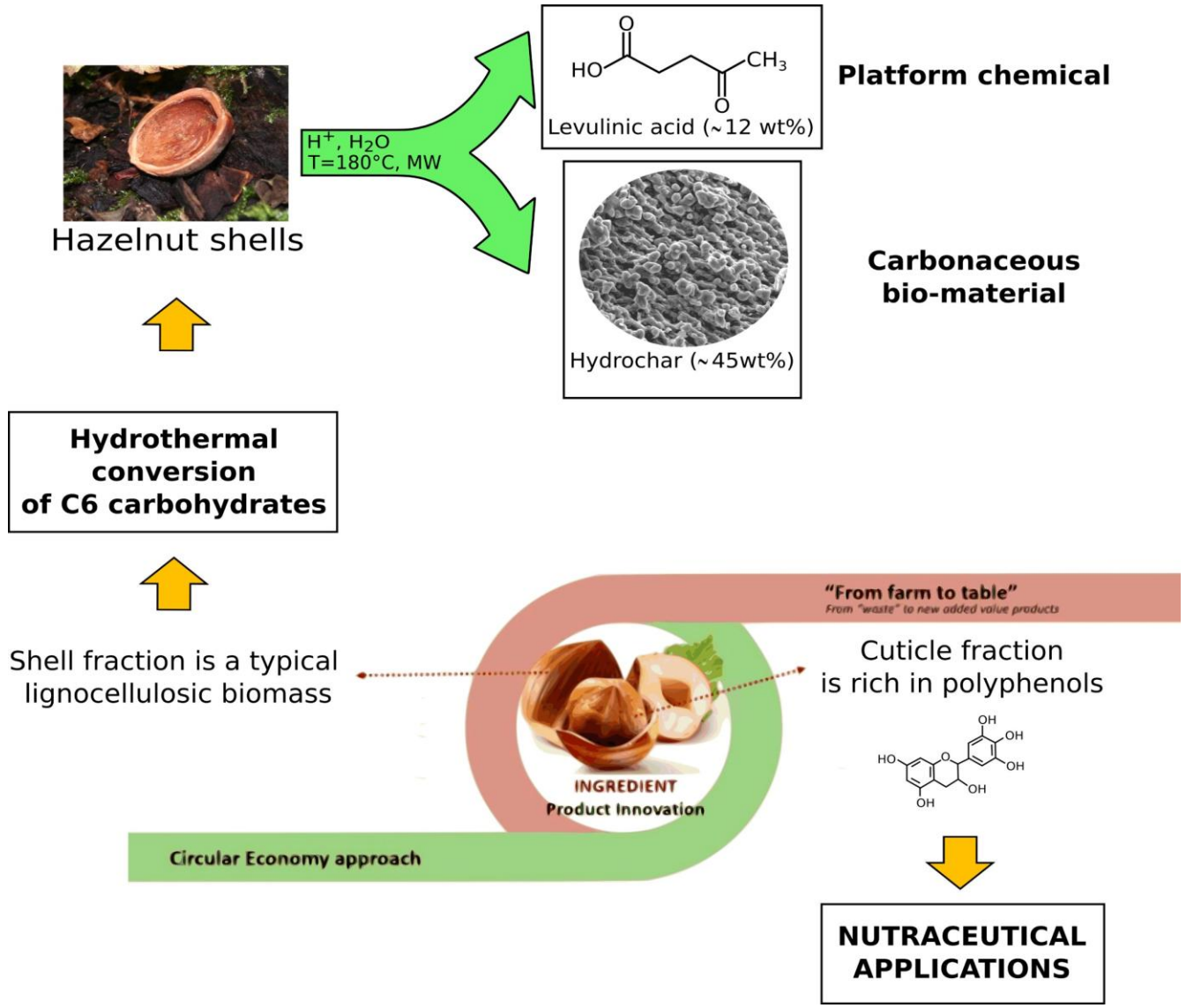


Figure: Further development of our biorefinery approach.

[3] Licursi *et al.*, *Bioresource Technology,* Volume 244, pp. 880-888, 2017. Doi: 10.1016/j.biortech.2017.08.012.

From the hazelnut shells (biomass) to the hydrochar

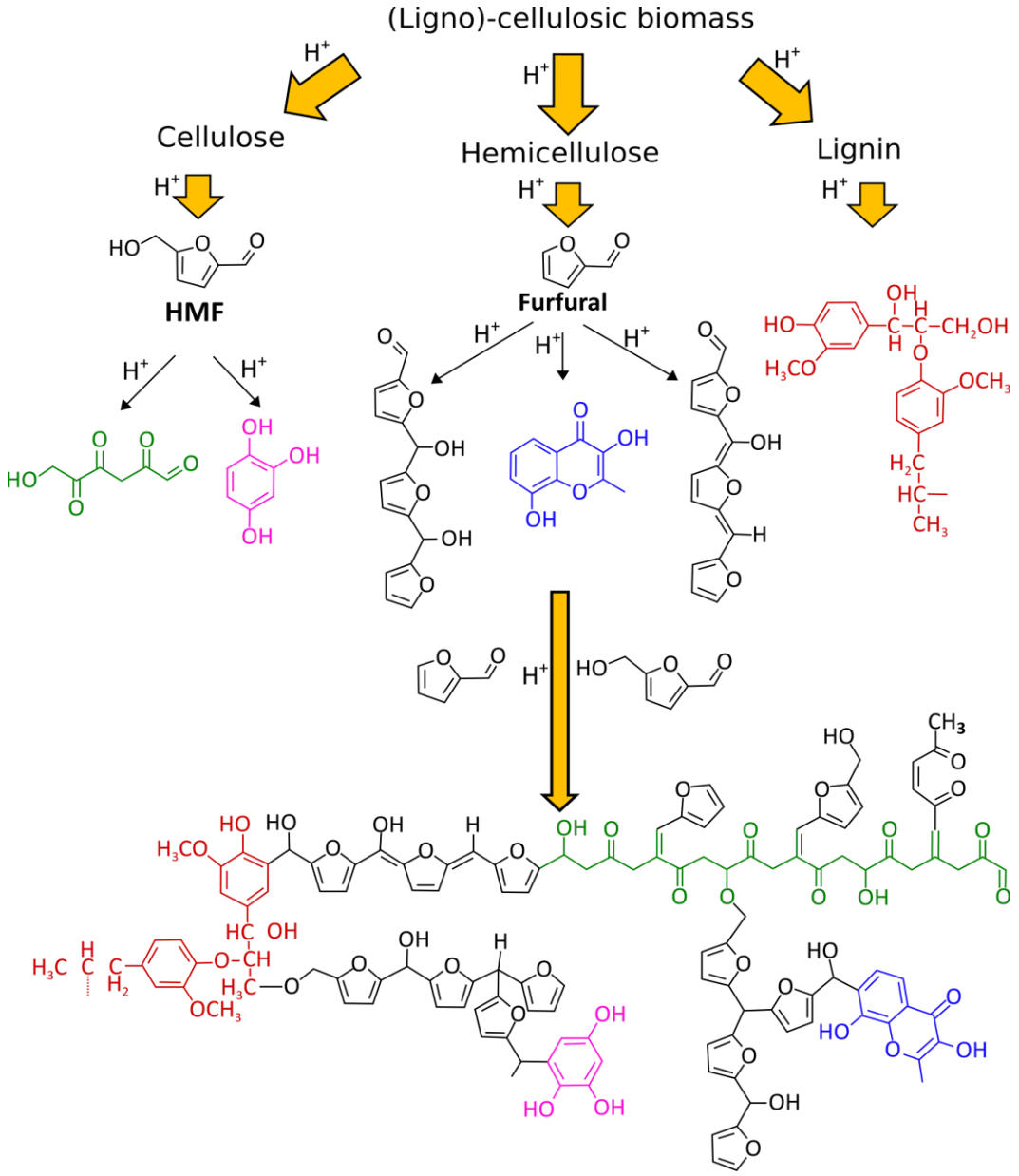


Figure: Humin and «pseudo-lignin» formation, according to Wan *et al.* [4].

- Hydrochar includes both furanics (from C5 and C6 carbohydrates) and aromatics (from lignin).
- It includes many functional groups (-COOH, C-O-C, -OH), as demonstrated by XPS analysis [3].
- ***However, the surface properties of this hydrochar (in particular the specific surface area) are poor, due to the trapped organic compounds.***

Table: Main functional groups of the hazelnut shell hydrochar, according to XPS analysis [3].

Binding energy position [eV]	Structure	Hydrochar Autoclave Auto_3	Hydrochar Microwave MW_3
284.6	C–C	23.3	22.9
286.1	C–O–H; C–O–C	58.7	59.4
288.0	(C=O) COOH (R)	14.0	13.8
290.0	(C–O) COOH (R)	4.0	3.9
532.5	O=C	42.2	42.5
534.6	O–C; –OH	57.8	57.5

[3] Licursi *et al.*, *Bioresource Technology,* Volume 244, pp. 880-888, 2017.

[4] G. Wan *et al.*, *J. Agric. Food Chem.* Volume 67, pp. 10116-10125, 2019.

From the shells to the hydrochar

- Different exploitation possibilities are available for these bio-wastes. Chemical, fuel and agronomic uses are of our prevailing interest.
- In the environmental field, hydrochar can be proposed as cheap & green adsorbents, e.g. for the removal of pollutants from industrial exhausted gases and wastewaters.
- However, this approach requires a preliminary activation step for improving its surface properties.

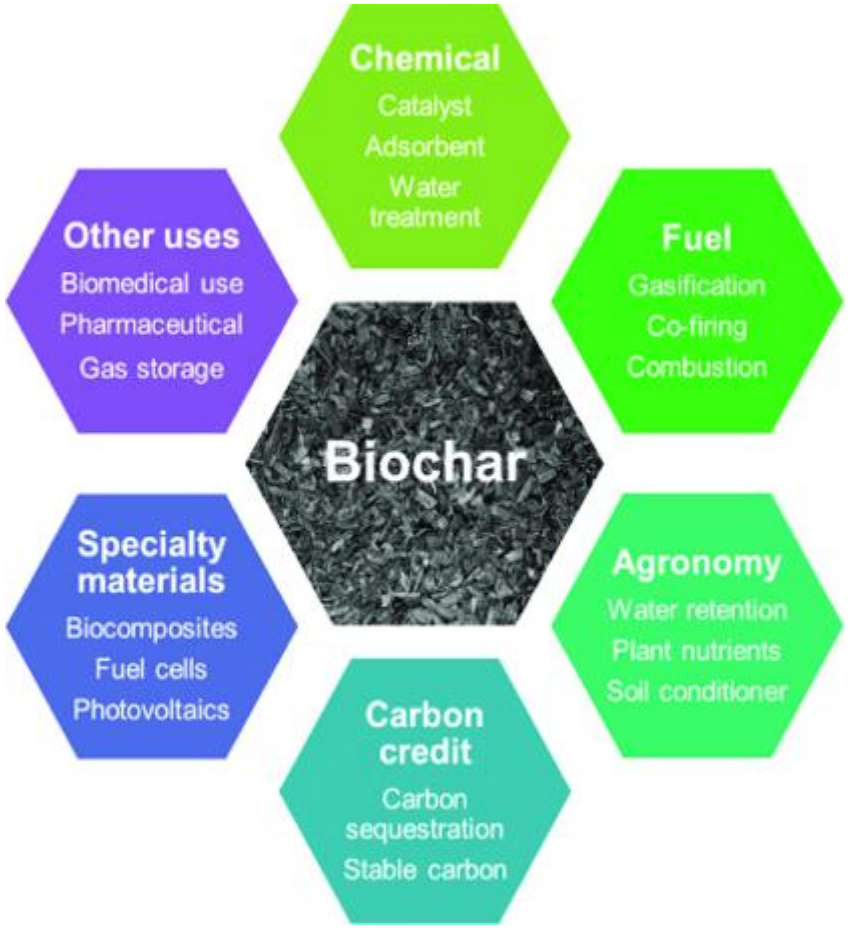


Figure: New emerging char applications.

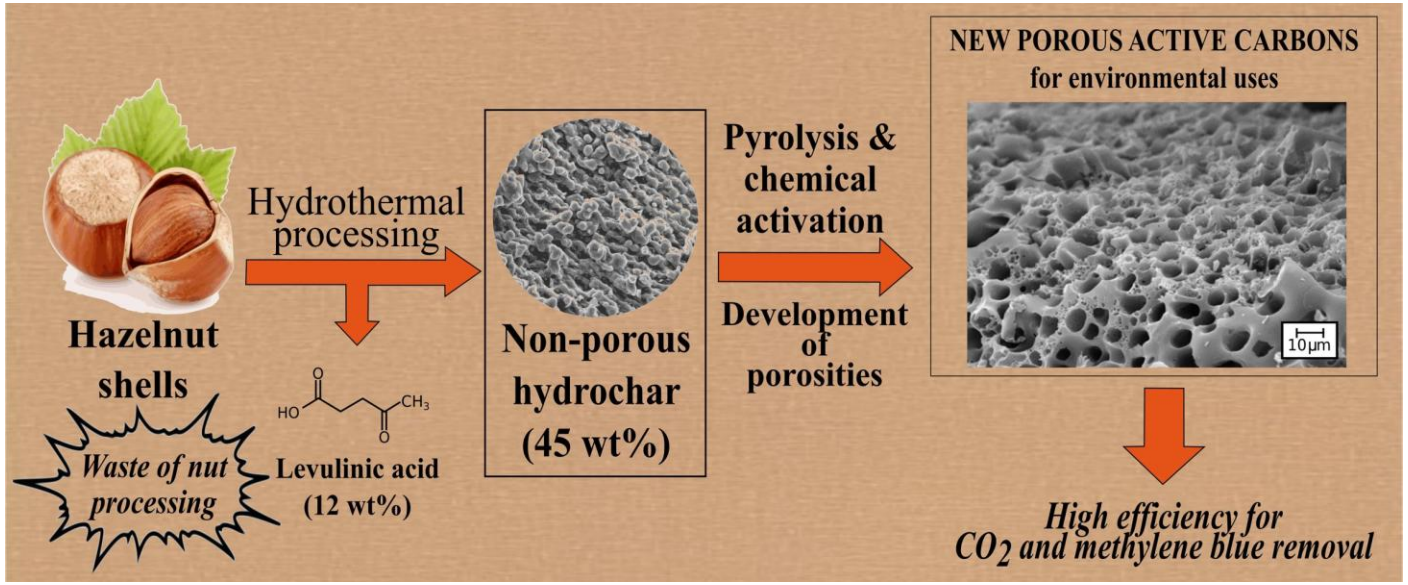
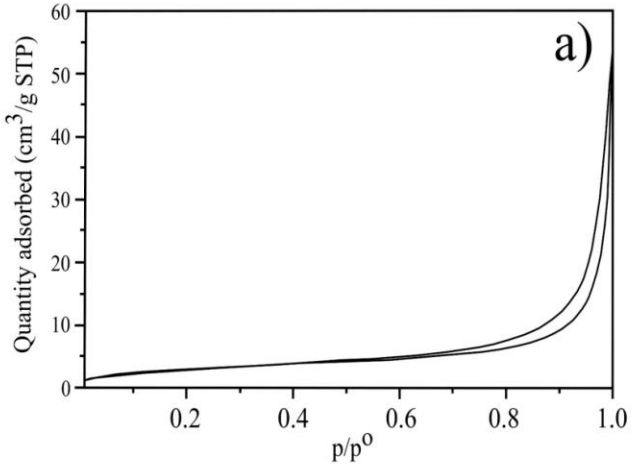


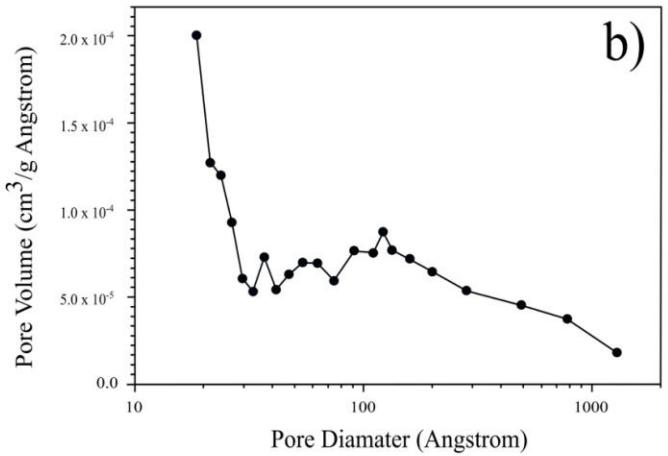
Figure: Proposed approach for the exploitation of our hazelnut shells-based hydrochar.

Different thermo-chemical activation procedures have been carried out, and the synthetised ACs have been characterized for their textural properties.

From the hydrochar to the activated carbons (ACs)

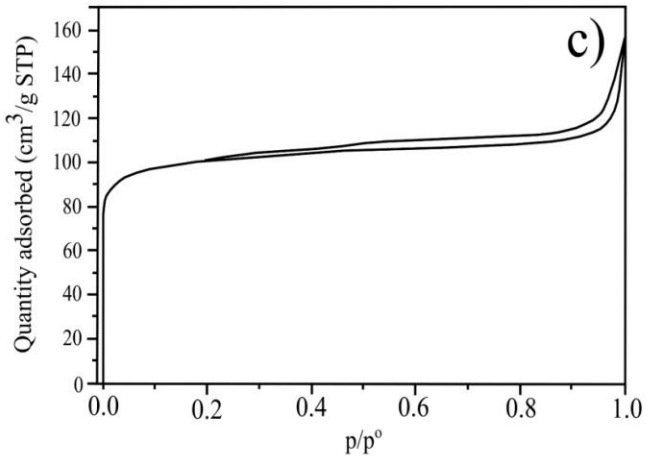
- Pyrolysis is traditionally used for the simultaneous production of bio-oil and biochar from raw biomasses.
- We have been exploiting ***<u>pyrolysis thermal treatment to change the surface properties of the hydrochars</u>***.
- Hazelnut shells pyrolysis already allows to obtain good specific surface areas (SSA max. ~360 m^2/g), starting from the raw hydrochar (SSA ~10 m^2/g) [5].

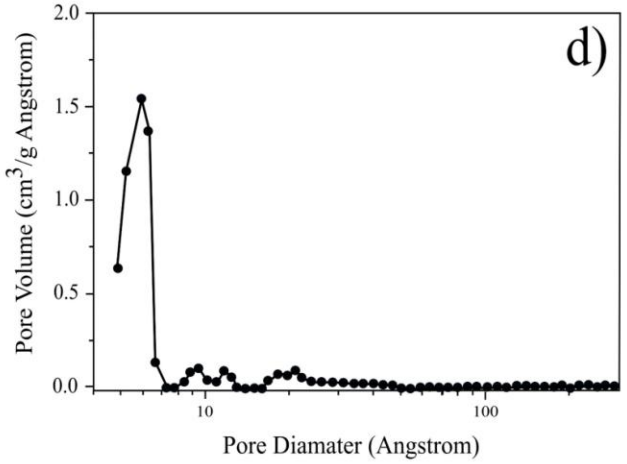




Raw hydrochar

Type II isotherm
(non-porous or macroporous solids)





Pyrolyzed hydrochar

Prevailing Type I isotherm
(microporous solids)

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022

From the hydrochar to the activated carbons (ACs)

- Different chemical activation treatments have been carried out to further improve the properties of the pyrolyzed hyrochar.
- Yield and SSA have been considered to preliminary screen the most interesting ACs [5].

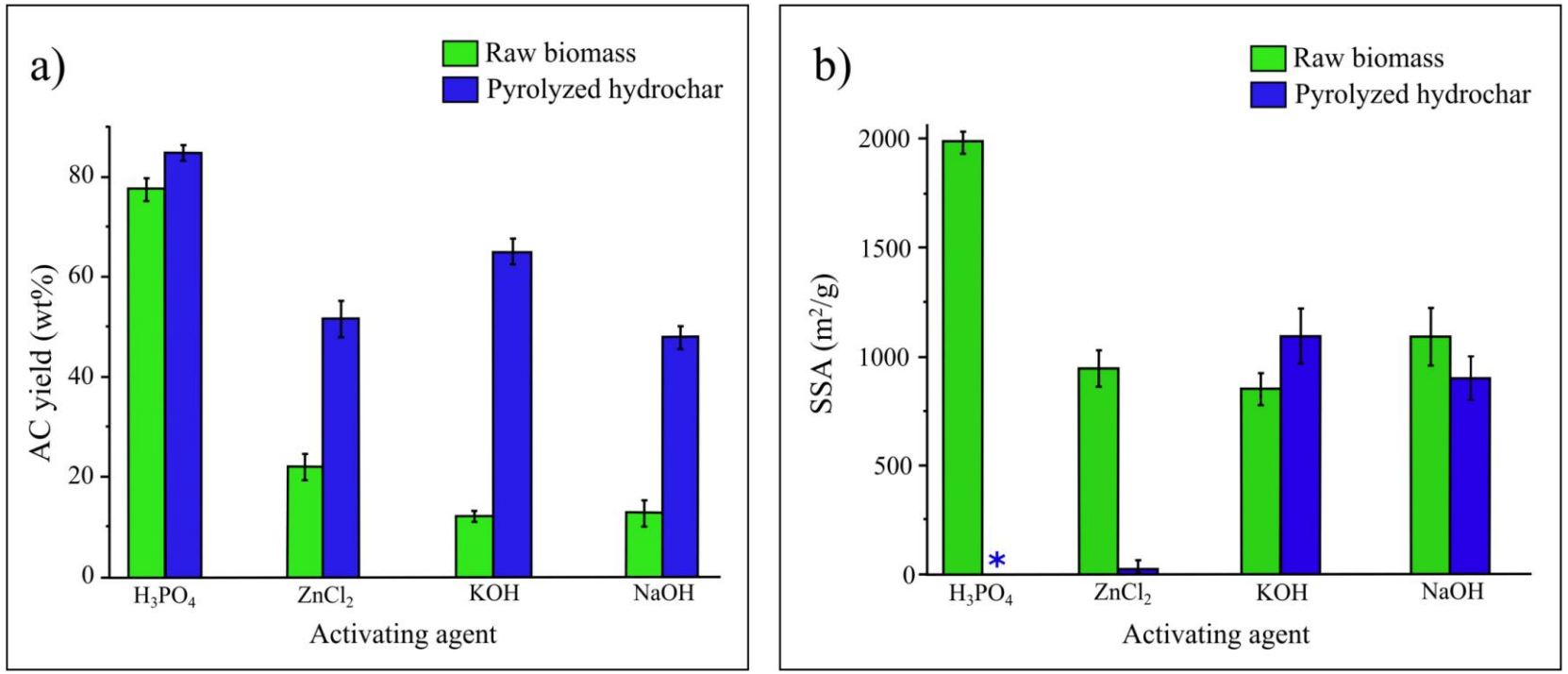


Figure: (a) Yield (wt%) and (b) SSA (m^2/g) of the ACs obtained from different precursors and activating agents. Note *: negligible SSA [5].

✓ ***Alkaline treatment (KOH) is the most suitable activation for the pyrolyzed hydrochar.***

✓ ***Acid treatment (H_3PO_4) is appropriate for the activation of the raw starting biomass.***

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022

From the hydrochar to the activated carbons (ACs)

- Further characterization has been carried out on these promising ACs (ultimate and proximate analysis, FT-IR, SEM, SSA, pore volume and size distribution) [5].

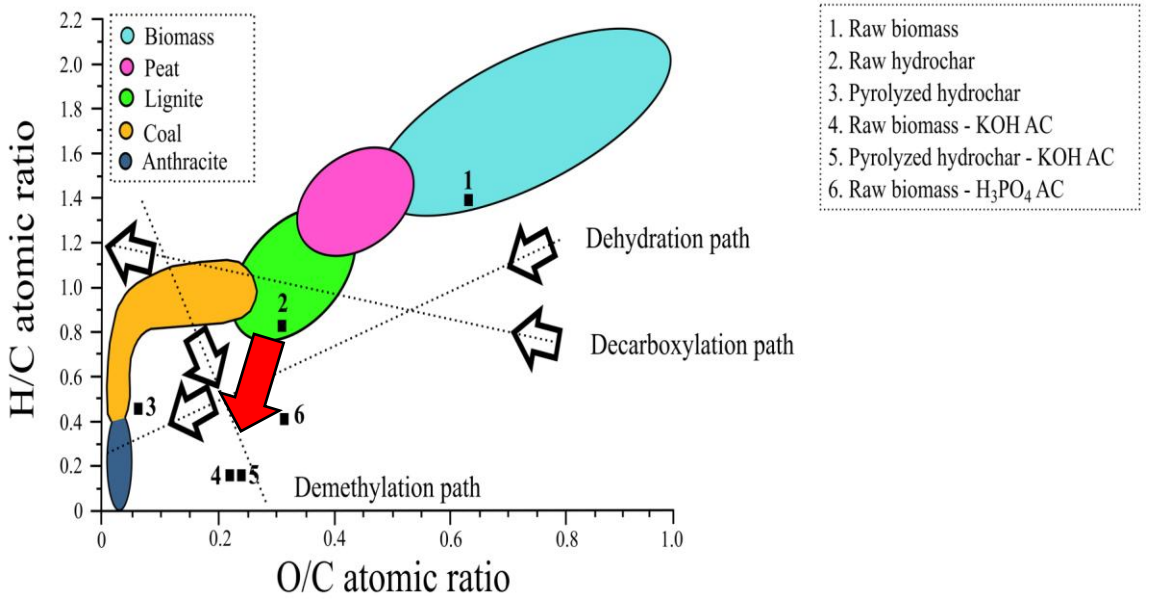


Figure: Van Krevelen diagram of the samples of interest.

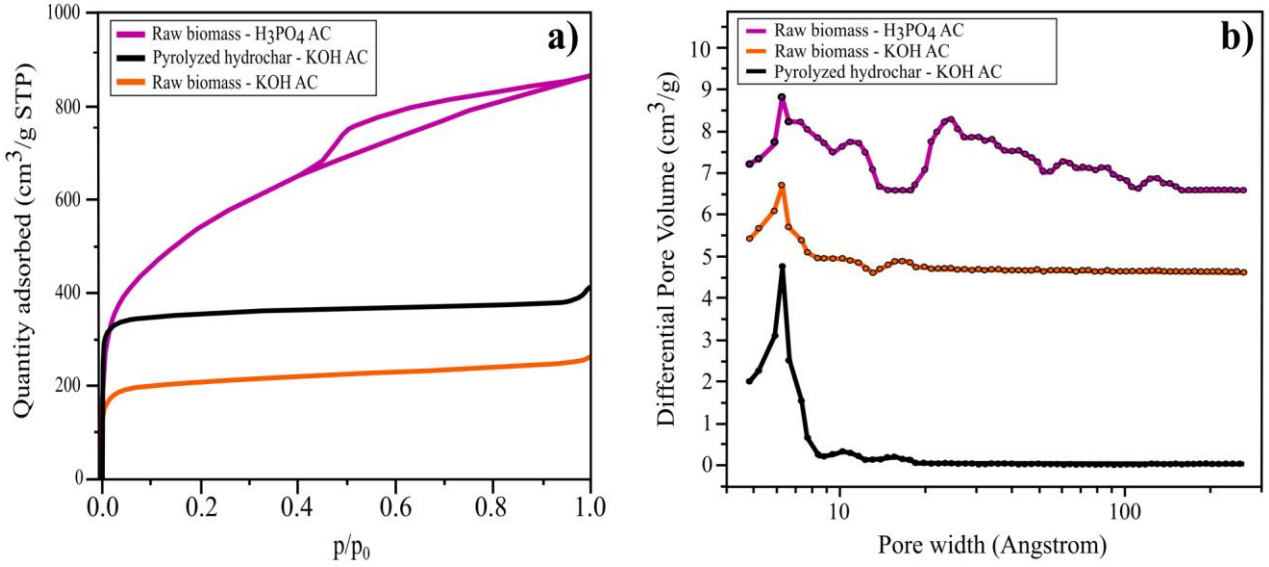


Figure: (a) Adsorption/desorption isotherms of the synthetised ACs and (b) corresponding pore size distributions.

- Van Krevelen diagram confirms the progress of carbonization for the pyrolyzed hydrochar and the ACs of interest.
- KOH activation of the pyrolyzed hydrochar has significantly improved its microporosity (A_{mic}: ~1360 m^2/g).
- H_3PO_4 activation of the raw biomass shows the highest SSA (~1910 m^2g^{-1}), with a high contribution of both micro- (~1100 m^2g^{-1}) and meso-pores (~810 m^2g^{-1}).

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022.

From the hydrochar to the activated carbons (ACs)

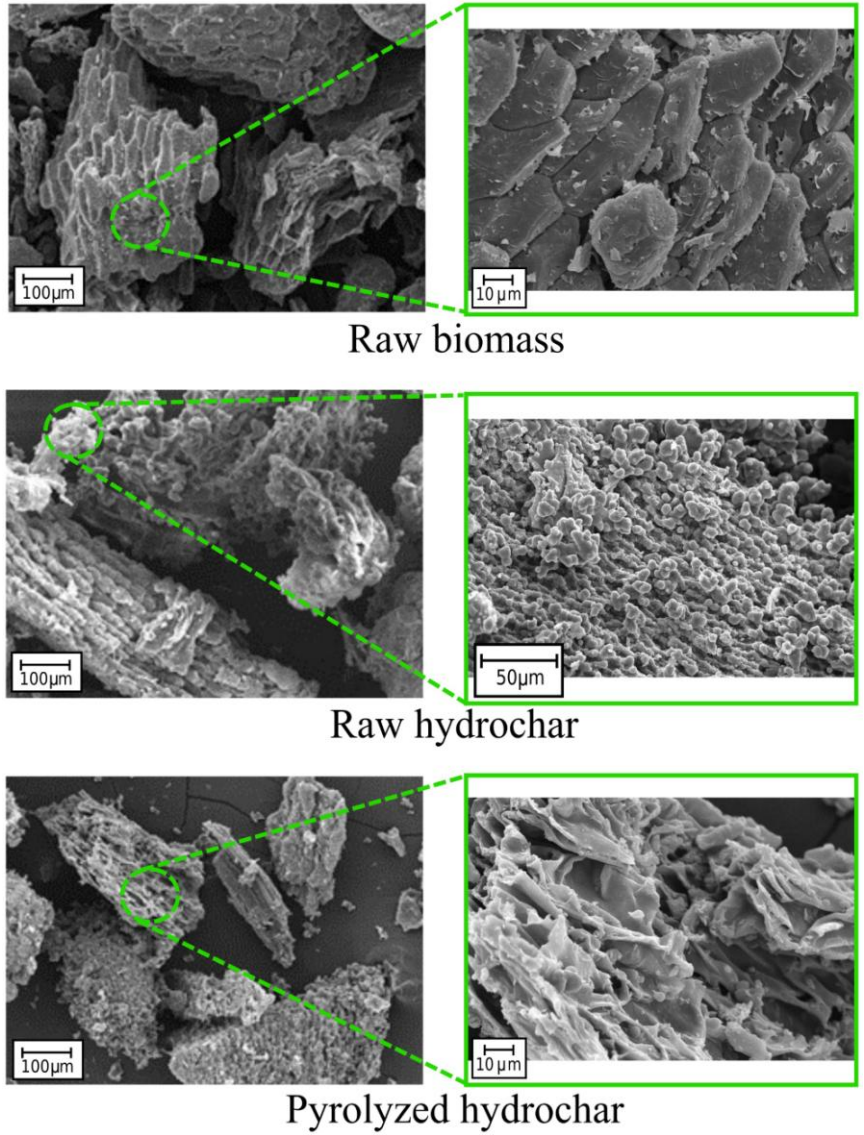


Figure: SEM micrographs of raw biomass, raw hydrochar, and pyrolyzed hydrochar [5].

Chemical Activation

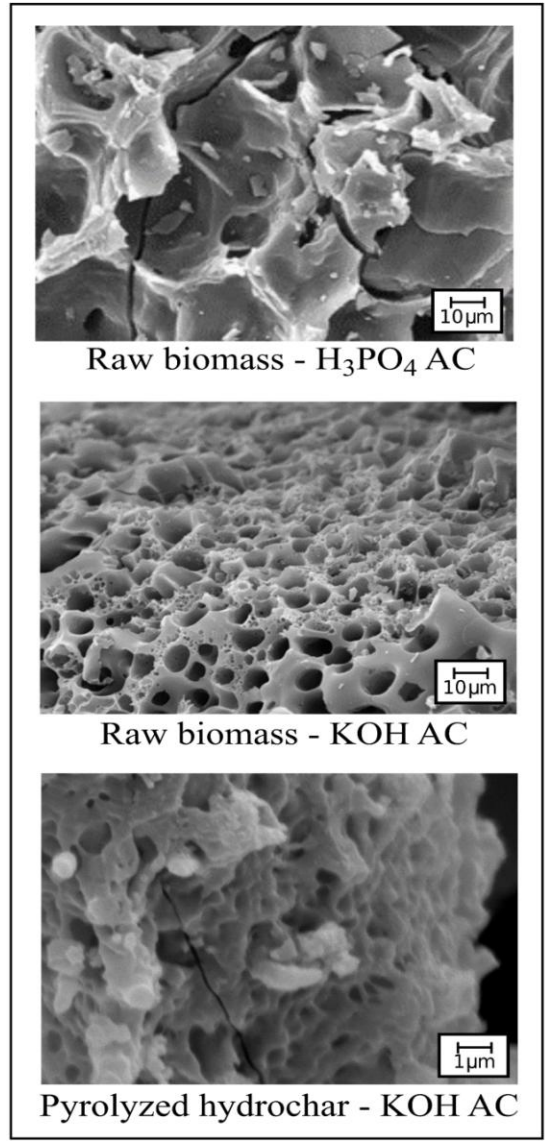


Figure: SEM micrographs of the synthesized ACs [5].

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022.

Activated carbons (ACs) for CO_2 and methylene blue (MB) adsorption

- Precursors and most performing ACs were tested as CO_2 adsorbents at low CO_2 partial pressure (< 1 bar), which is typical for post-combustion CO_2 capture at large power plants [5].

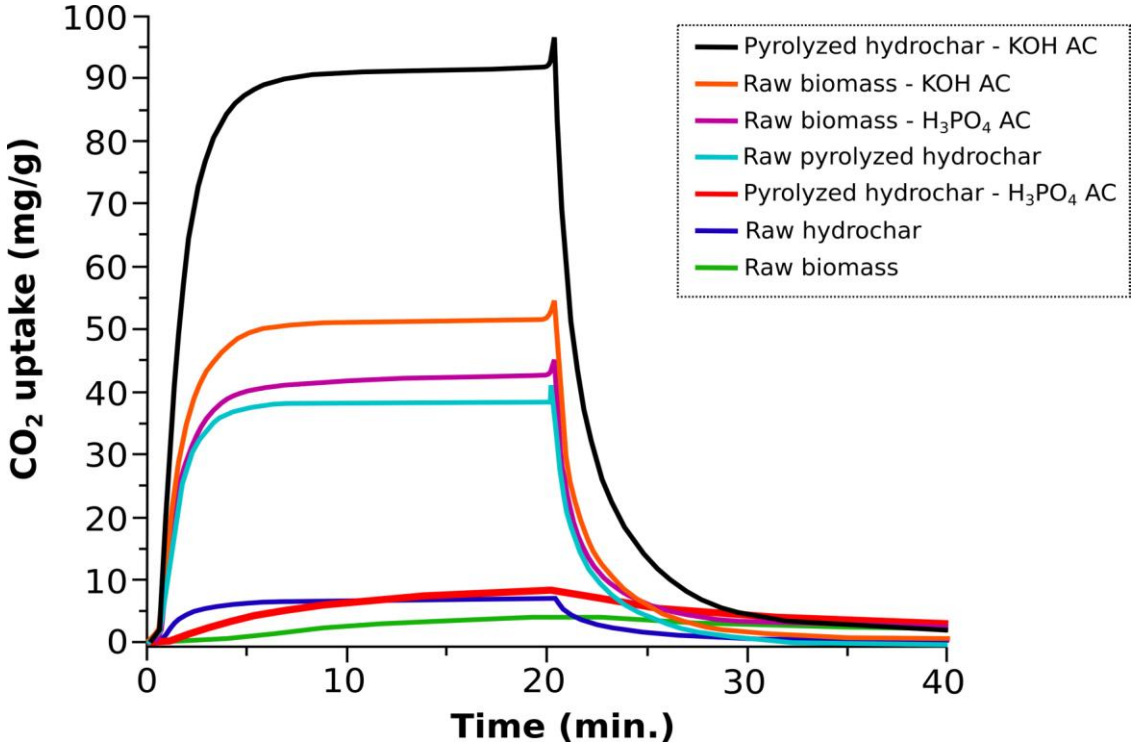


Figure: CO_2 adsorption/desorption curves of the samples of interest [5].

- ✓ CO_2 adsorption/desorption curves of the raw biomass and raw hydrochar confirm, in both cases, poor performances towards CO_2 adsorption, in agreement with their low SSA values.
- ✓ AC obtained from H_3PO_4 activation of the raw biomass gave good adsorption performances (about 50 mg/g).
- ✓ Already the pyrolyzed hydrochar shows good CO_2 sorption capacity (about 35 mg/g).
- ✓ Best CO_2 uptakes were obtained from the pyrolyzed hydrochar-KOH AC (about 90 mg/g).

✓ Remarkably, the pyrolyzed hydrochar-KOH AC shows excellent regenerability, even after 50 adsorption/desorption cycles.

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022.

Activated carbons (ACs) for CO_2 and methylene blue (MB) adsorption

- The most interesting ACs have been preliminarily tested for the removal of methylene blue (MB) from aqueous solutions.
- MB is a well-known cationic dye, which can be found within the wastewaters of the textile industry.
- Moreover, this is a probe molecule, traditionally employed for the evaluation of the adsorption performances of ACs [6].

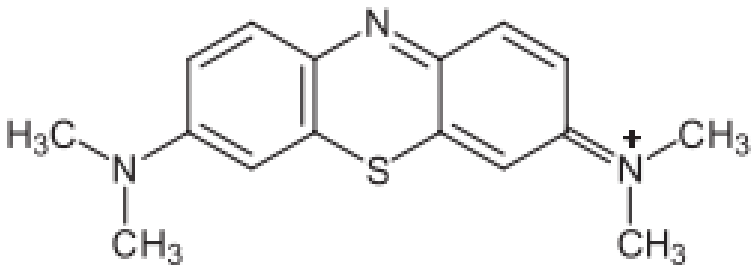


Figure: Chemical structure of MB.

Table: MB adsorbed (in mg/g) and corresponding MB removal efficiency

Test	AC/MB weight ratio	MB adsorbed on raw biomass–H_3PO_4 AC (mg/g)	η %	MB adsorbed on pyrolyzed hydrochar – KOH AC (mg/g)	η %
1	40	25.0	99.9	25.0	100.0
2	4	247.9	99.2	249.9	99.9

The synthesized ACs resulted efficient towards BM removal !

[5] D. Licursi *et al.*, Closing the biorefinery of the hazelnut shells exploitation: Conversion of the hydrochar recovered after levulinic acid production into active carbons and their use for CO_2 and methylene blue adsorption, (Submitted), 2022.

[6] Manuale Unichim 182:1998 M.35, «Acque destinate al consumo umano – Prodotti usati per il trattamento – Metodi di prova».

Conclusions

- New active carbons have been synthesized starting from hazelnut shells and, *more advantageously from hydrochar*, recovered after the biomass conversion to levulinic acid. For this purpose, thermo-chemical activation treatments have been evaluated.

- Acid activation should be advantageously proposed to produce prevailing mesoporous carbons from the raw biomass, whilst *alkaline one is highly required for the selective development of microporosities starting from the pyrolyzed hydrochar*, both these active carbons being recoverable in good yield (~65 wt%).

- CO_2 and methylene blue adsorption tests have highlighted the promising performances of the pyrolyzed hydrochar-KOH activated carbon, *opening the way to its possible exploitation for environmental applications, at the same time smartly closing the biorefinery of the hazelnut shells*.

Thank you for your kind attention