Biochar: a humble carbon with an exciting future ?

M. Bartoli, P. Jagdale*, M. Giorcelli, M. Rovere, C. Rosso

A. Tagliaferro

Carbon Group, Politecnico Torino, Torino, Italy

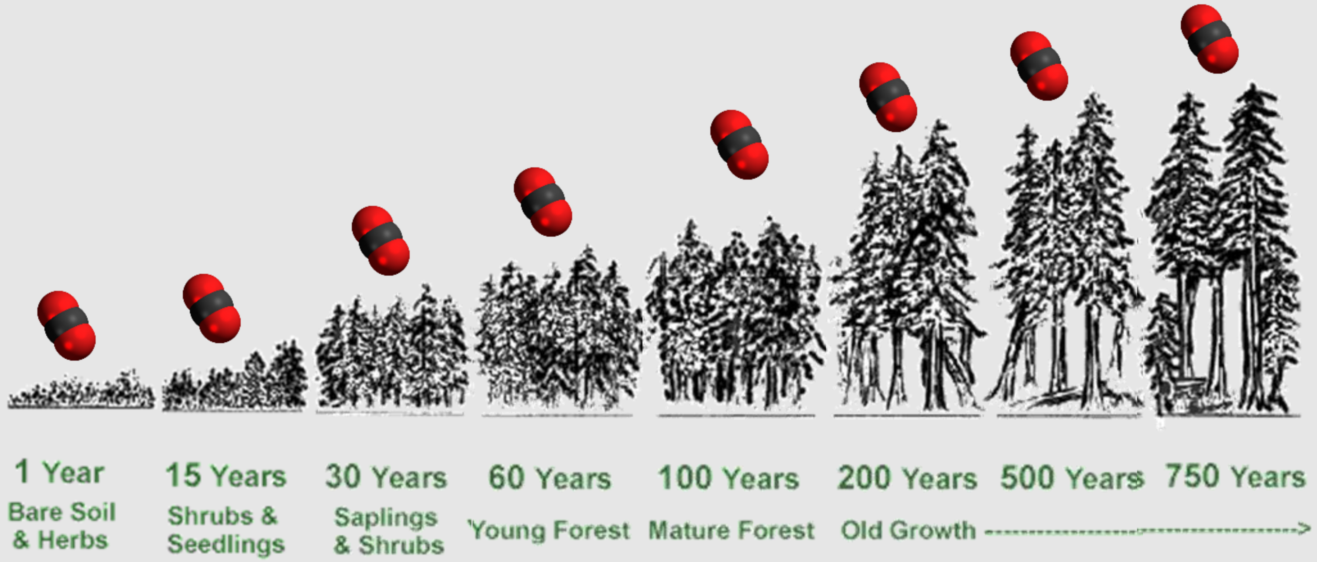
***Center for Sustainable Future Technologies, IIT, Torino, Italy**

Nanoscience and Nanotechnology 2018

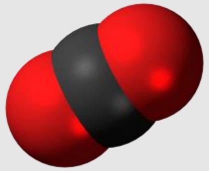
Frascati, 18-20 December 2018

INDEX

CO_2 SEQUESTRATION



Burning biomass produces carbon dioxide



No other ways to exploit biomass ?

PRUNING: A PROBLEM OR AN OPPORTUNITY ?

Hundred of millions of trees are pruned yearly worldwide

Burning residues contributes to the (fake ?) global warming

Alternative disposals are costly

BIOMASS: BEYOND ENERGY

Targets *Replace costly carbon based materials (CNTs, graphene, ...) coming from oil*

Develop a process-to-properties approach

- Rotten foods
- Cooked oils
- Tree waste

Pyrolysis

Biochar

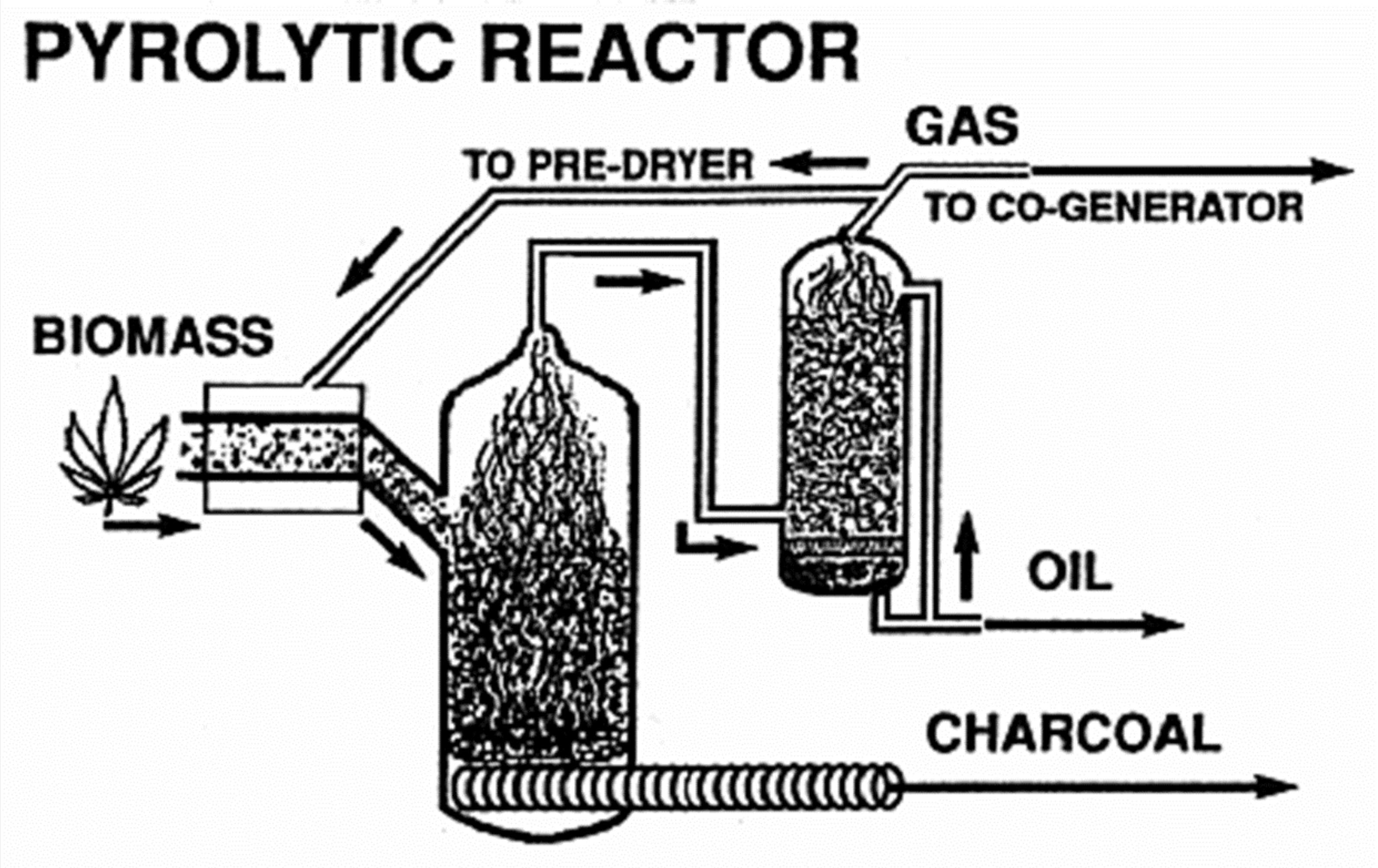
Solid fuels

Sensor applications

Soil amendement

Composite reinforcement

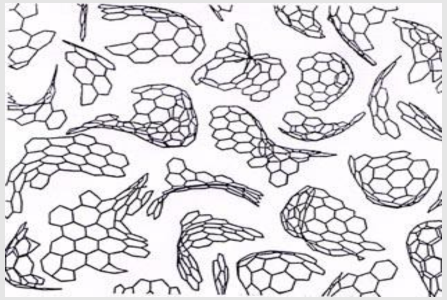
BIOMASS: BEYOND ENERGY (almost)



BIOCHAR(COAL)

BioChar is a
- co-product of pyrolysis of residual biomasses and wastes
- by-product of biofuel production
- by-product of biogas production

BioChar is produced
- using different technologies
- under different operating conditions
- from residues and wastes

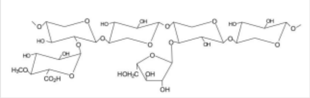


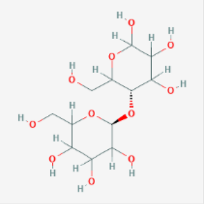
Energy crops	Crop residues	Seeds	Milling residues	Pruning residues	...
Willow Mischantus Switchgrass	Wheat straw Corn stower Canola Straw	Sorghum Sunflower Husks	Olive residue Bagasse	Hardwood Softwood	...

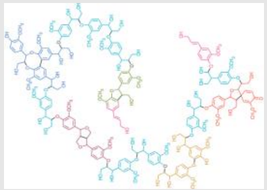
Properties can be tailored to needs by picking up the appropriate feedstock. Easy to activate.
Large surface area can easily be achieved (> 600 m^2/g)

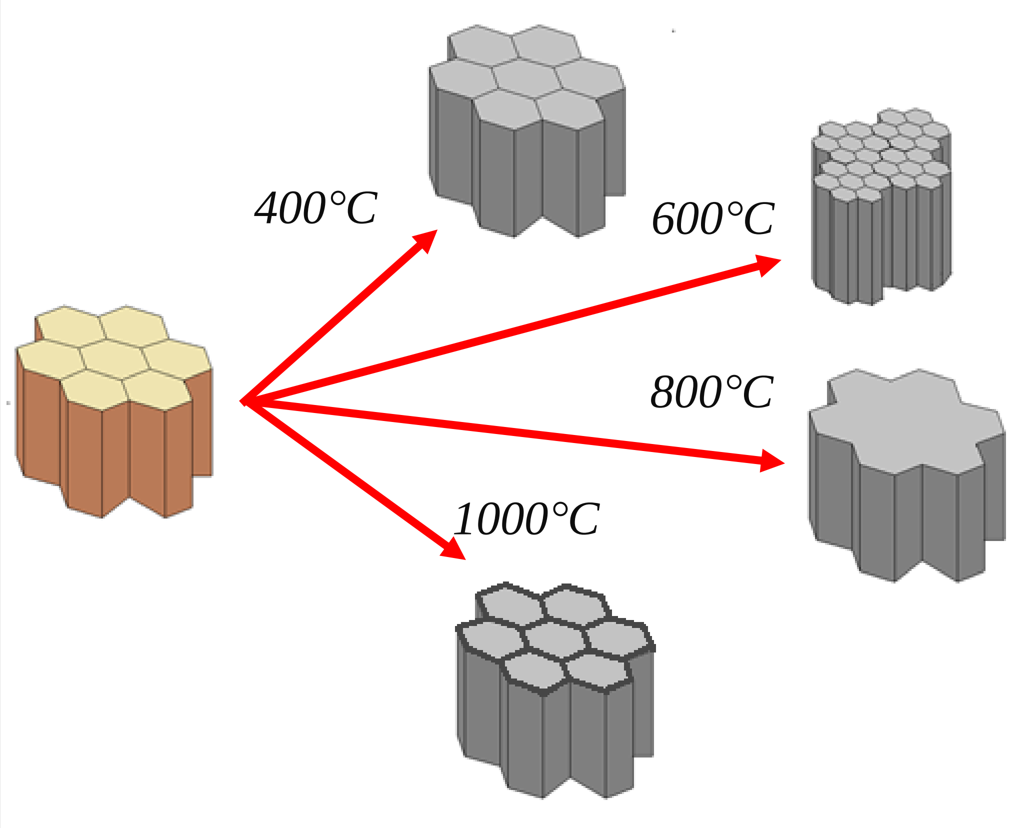
Cost estimate for industrial production: **0.3 - 0.5 €/kg**

PYROLYSIS STEPS



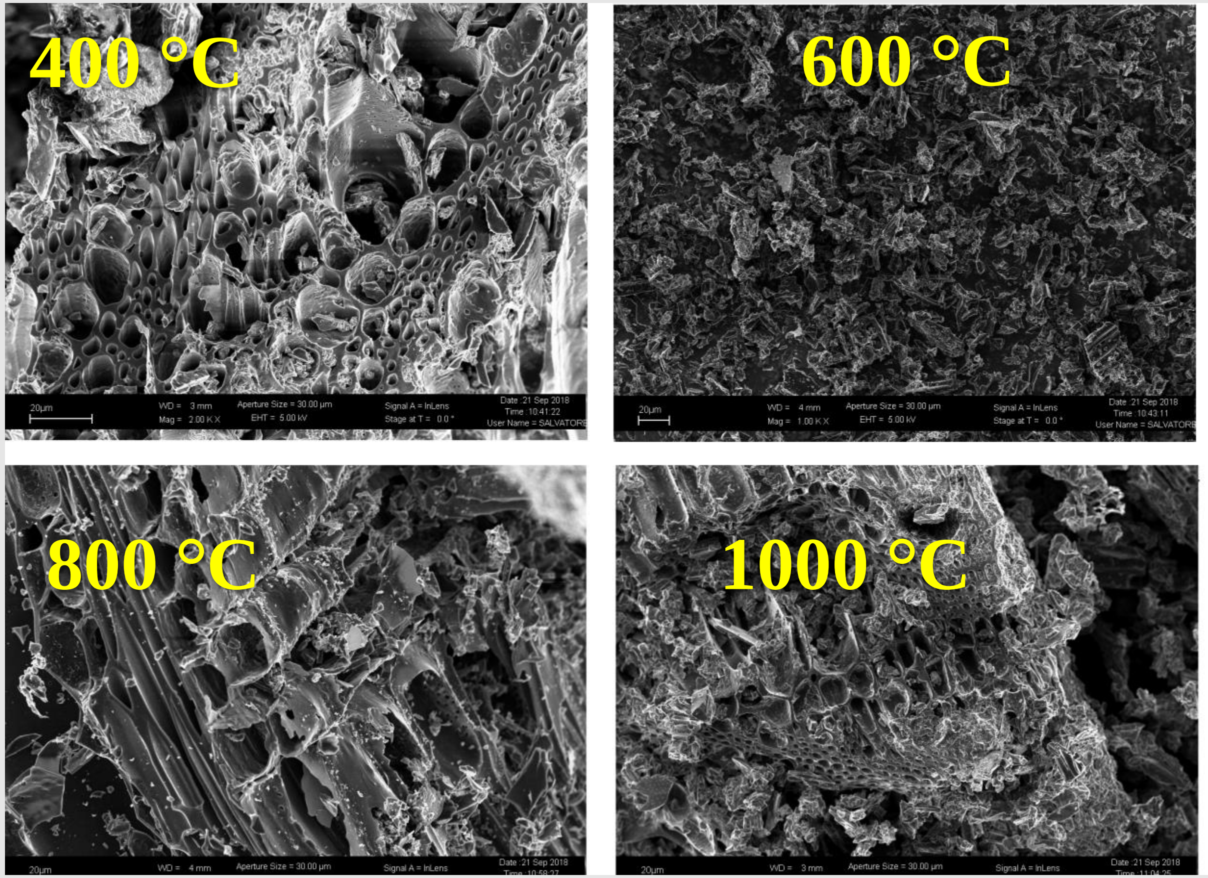


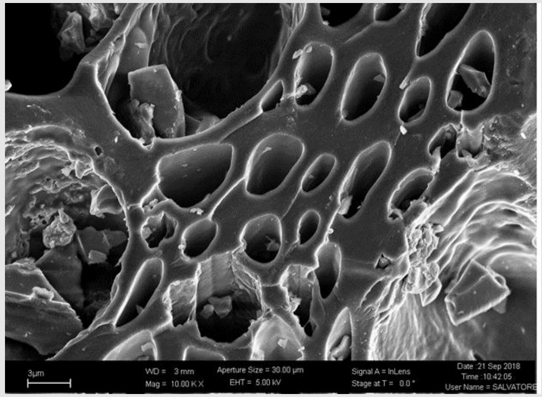


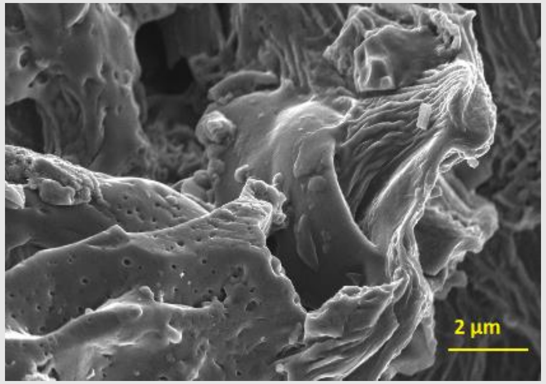


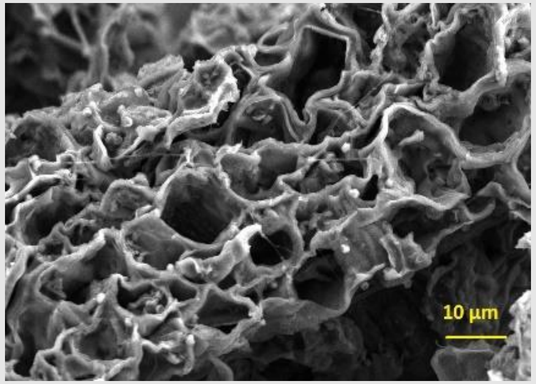
I.	**RT to 130-140°C**	*Release of water and steam extraction of VOCs*
II.	**140°C to 400°C**	*Cellulose-lignin bonds break down, hemicellulose degradation*
III.	**400°C to 600°C**	*Proper pyrolysis reactions, starting massively gas production (550-600°C)*
IV.	**600°C to 800°C**	*Increment of aromatic frames*
V.	**800°C to 2500°C**	*Turbostratic rearrangement*

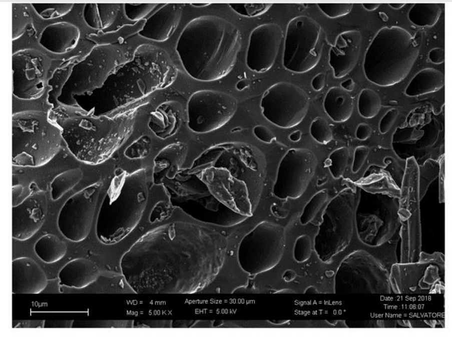
MORPHOLOGIES



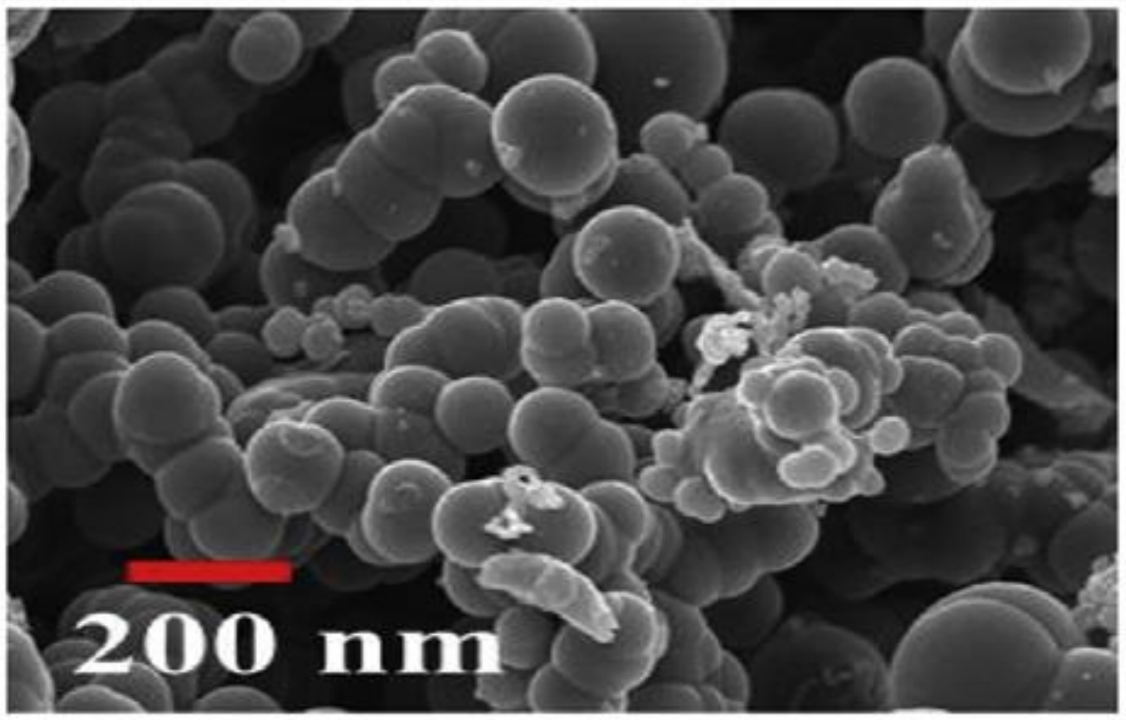




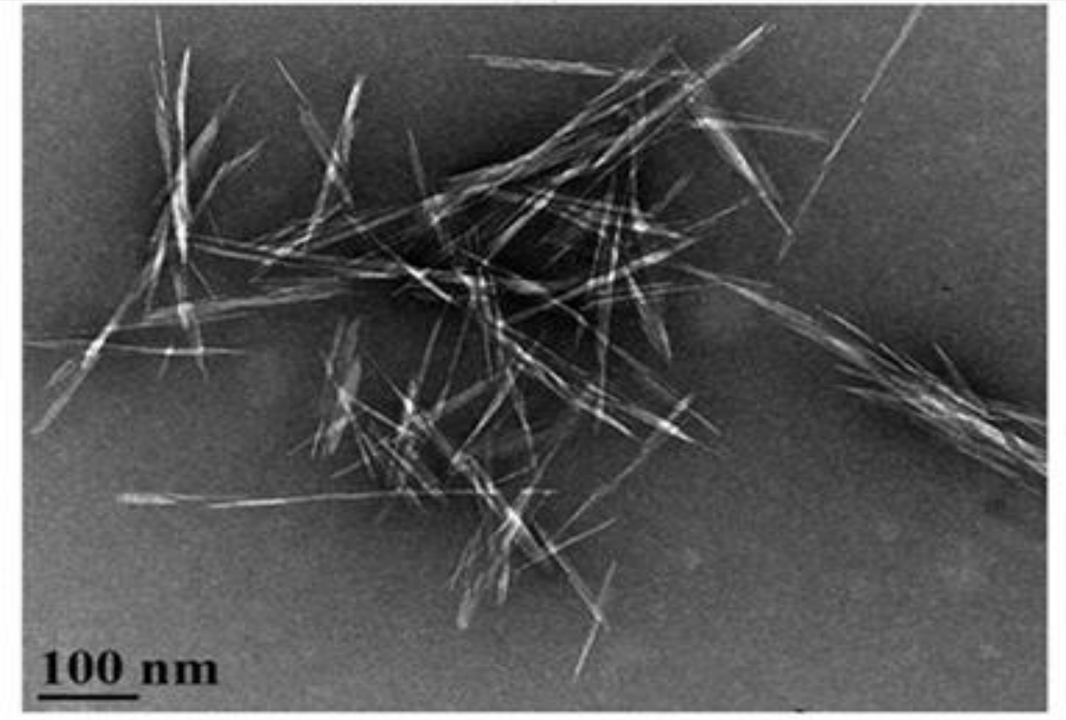




DOWN TO NANO

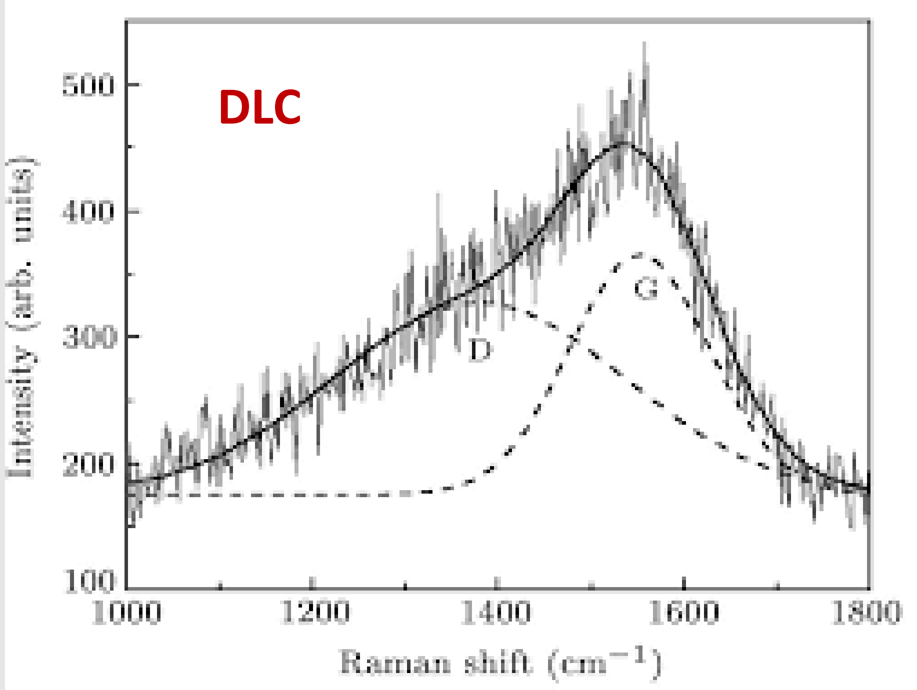


Home made

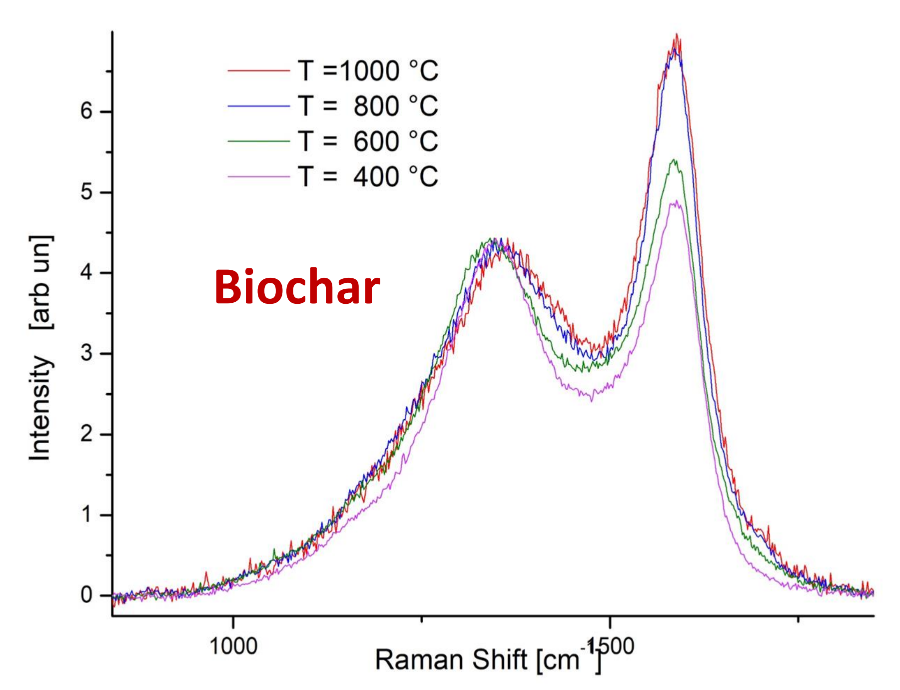


Literature

MORPHOLOGY

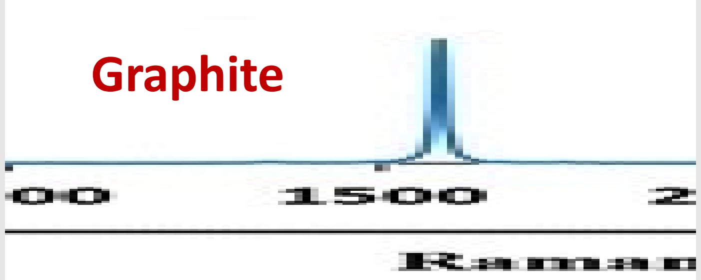


DLC
500
400
300
200
100
Intensity (arb. units)
D
G
1000
1200
1400
1600
1800
Raman shift (cm⁻¹)



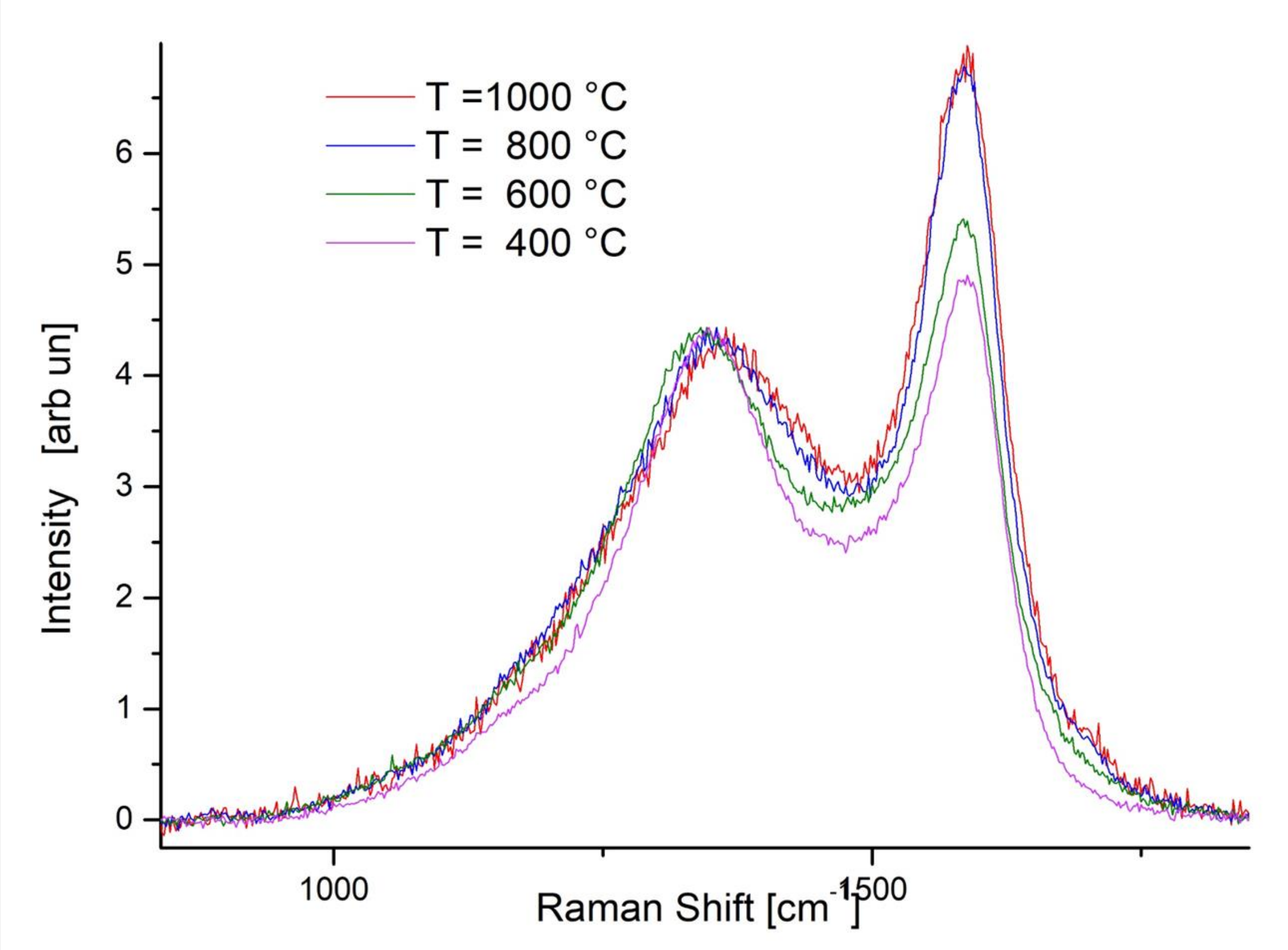
T =1000 °C
T = 800 °C
T = 600 °C
T = 400 °C
Biochar
Intensity [arb un]
0
1
2
3
4
5
6
1000
1500
Raman Shift [cm-1]

Graphite
1500



Graphite
1500

MORPHOLOGY TAILORING



WOOD BIOMASSES TESTED

POLITECNICO DI TORINO

SENSING BIOMOLECULES

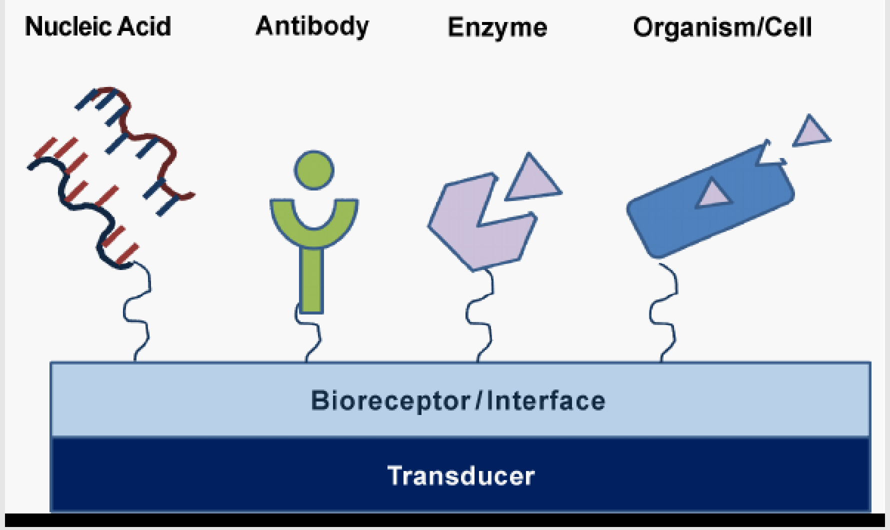
ISTITUTO ITALIANO DI TECNOLOGIA

The **detection of biomolecules** (DNA, proteins, ...) is **of great interest** for academy and industry

Each biomolecule has a specific receptor

Receptors can be **attached** to sensor surfaces or label molecules

Label molecules are targeted and detected by sensing devices in several ways



A technique that combines **high sensitivity with low cost instrumentation is ElectroChemiLuminescence**

ECL **vs PhotoLuminescence**
- no light pollution
- no parassite contribution

ECL **vs Cyclic Voltammetry**
- reduced noise
- no parassitic contribution

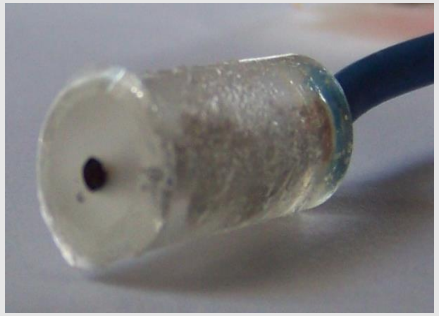
BAMBOO: ELECTRODES FOR ECL

We gave a try to **bamboo toothpicks** !

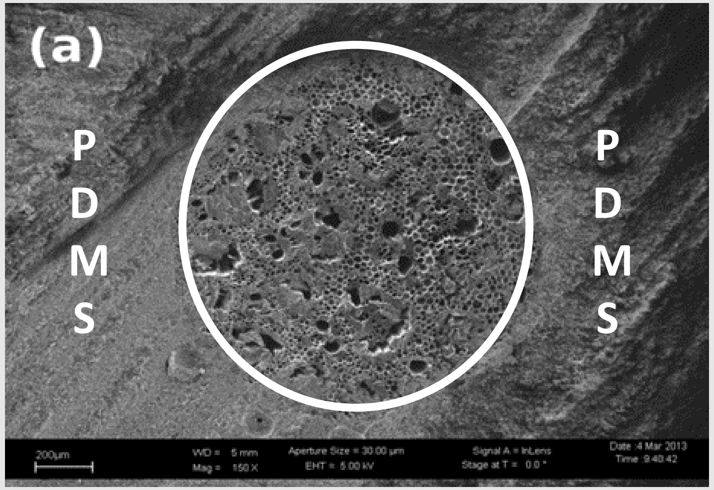
Chop ends

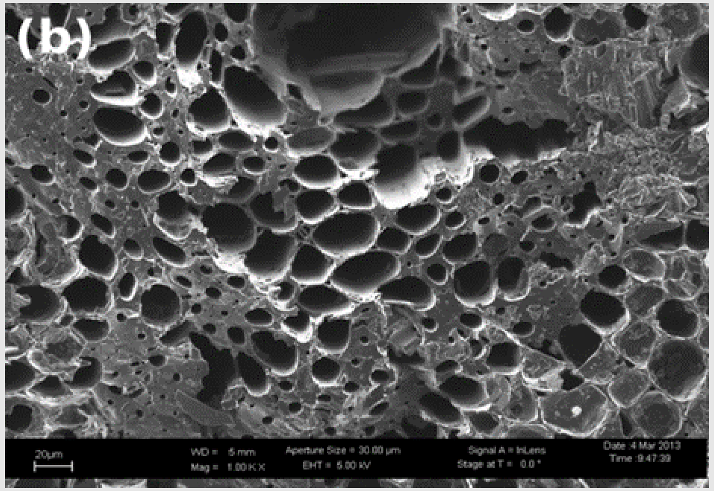
Pyrolize

Wrap in PDMS



SURFACE CHARACTERIZATION

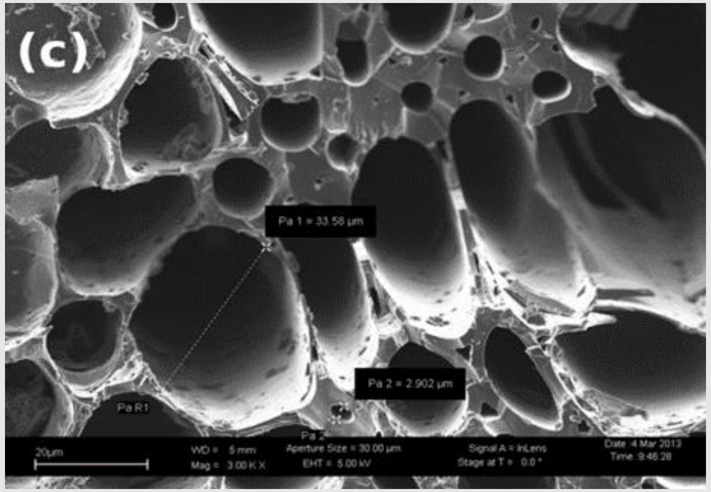




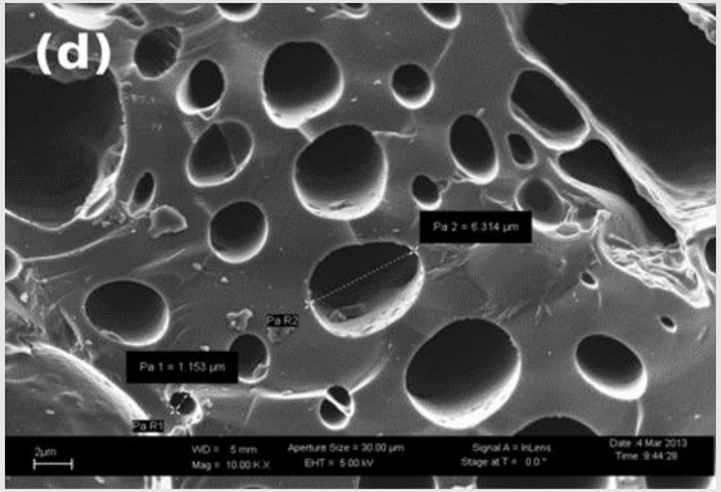
— 20 μm

Highly structured surface
Multi-scale cavities

Diameter ranging from a few hundreds nm to tens of μm



— 20 μm



— 2 μm

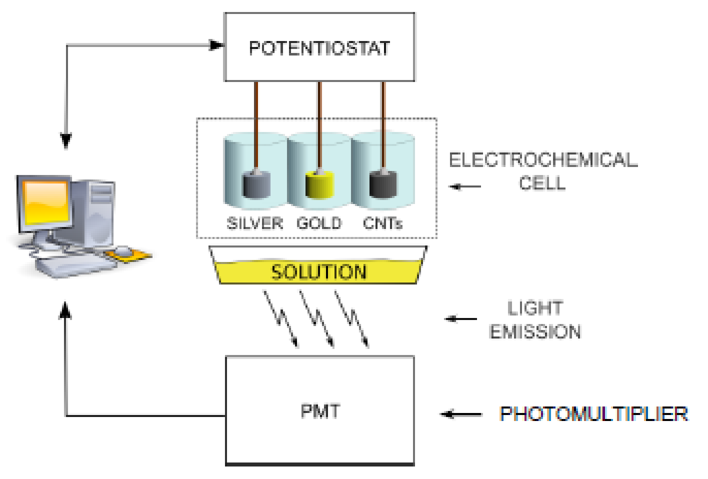
ELECTROCHEMILUMINESCENCE

1) **Bond** a fluorophore to analyte (or surface)

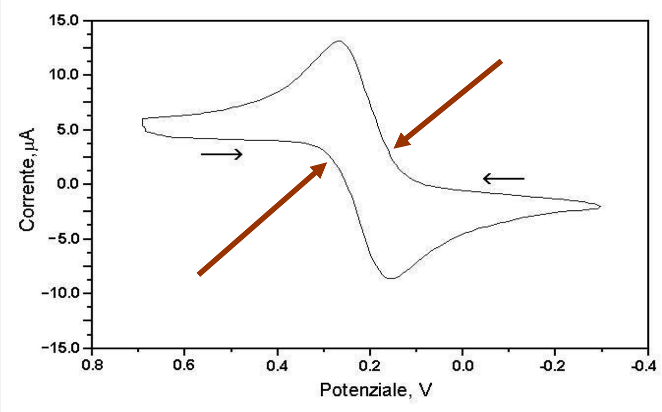
2) **Place** analyte carrying fluorophore **in contact with** electrode **surface**

3) **Excite** the fluorophore (Cyclic Voltammetry)

4) **Detect** the ECL signal intensity (Photomultiplier)



Emission is stimulated at **slope variations** voltages (change in solution resistance due to **reduction** or **oxidation** processes onset)



carbon based sensors are commonly used for ECL (**commercial** ones are often **realized with Glassy Carbon** although CNT sensors have been investigated)

EXPERIMENTAL SETUP

Working electrode
bamboo

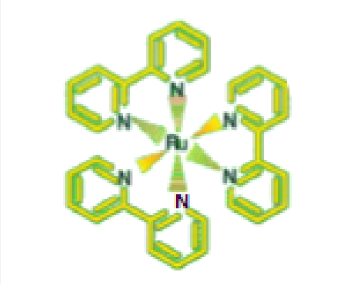
Reference electrode
Ag

Benchmark electrode
glassy carbon (commercial)

Counter electrode
Au

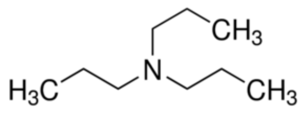
ECL Label Ru(bpy)$_3^{2+}$

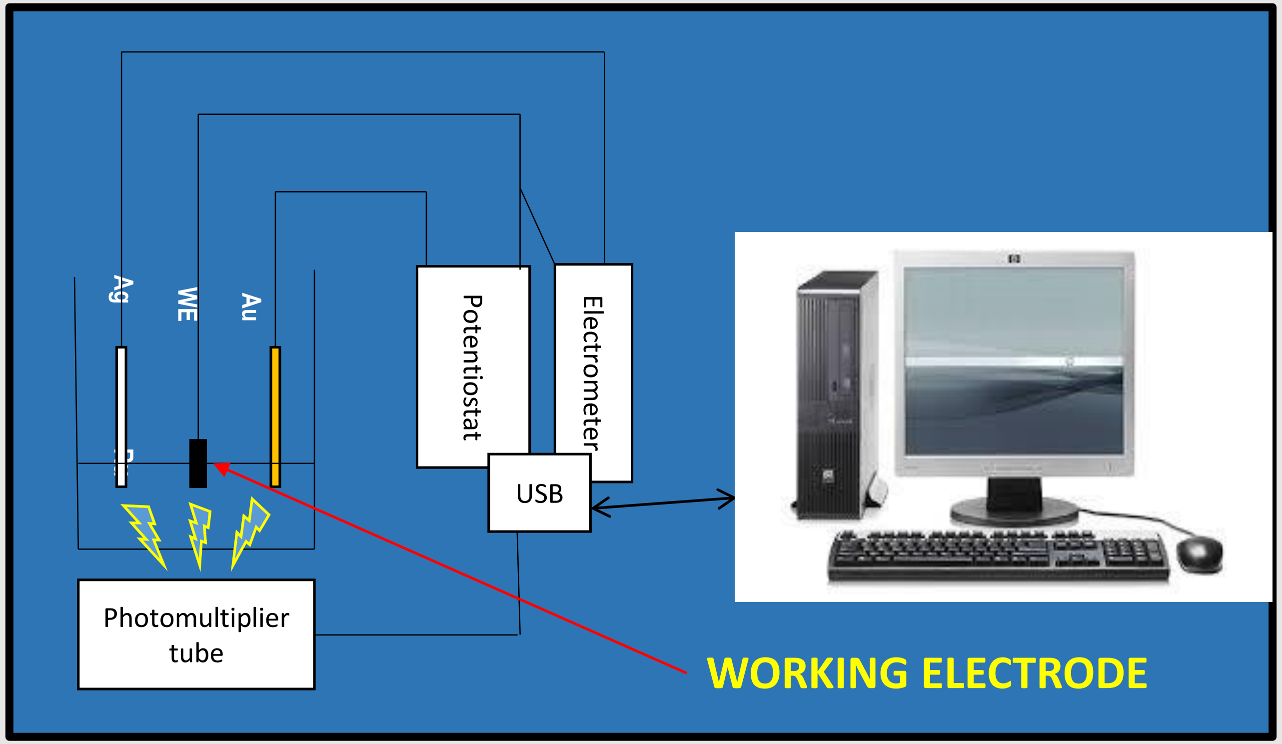
tris(2,2'-**bipy**ridine)**Ru**thenium(2+)

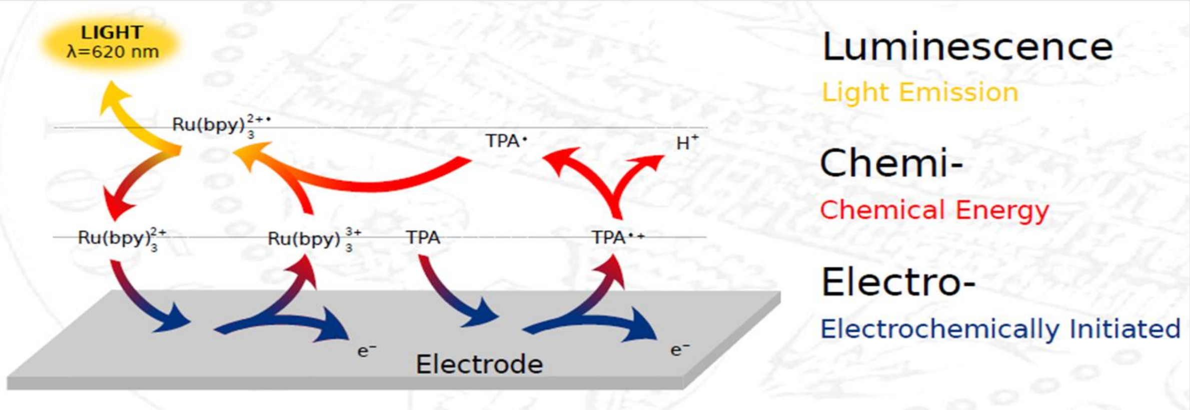


Label regenerator: TPA

Tri**P**ropyl**A**mine
enhances ECL efficiency without losing linearity

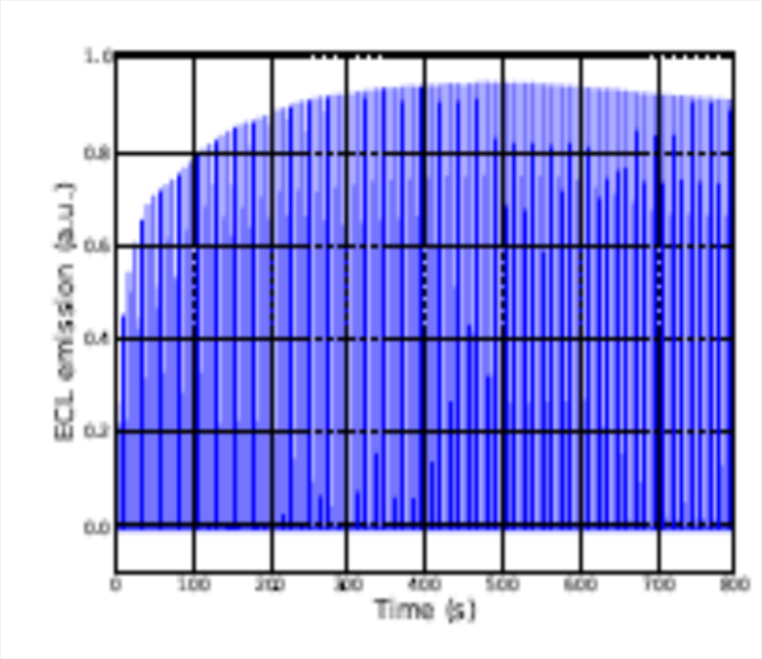


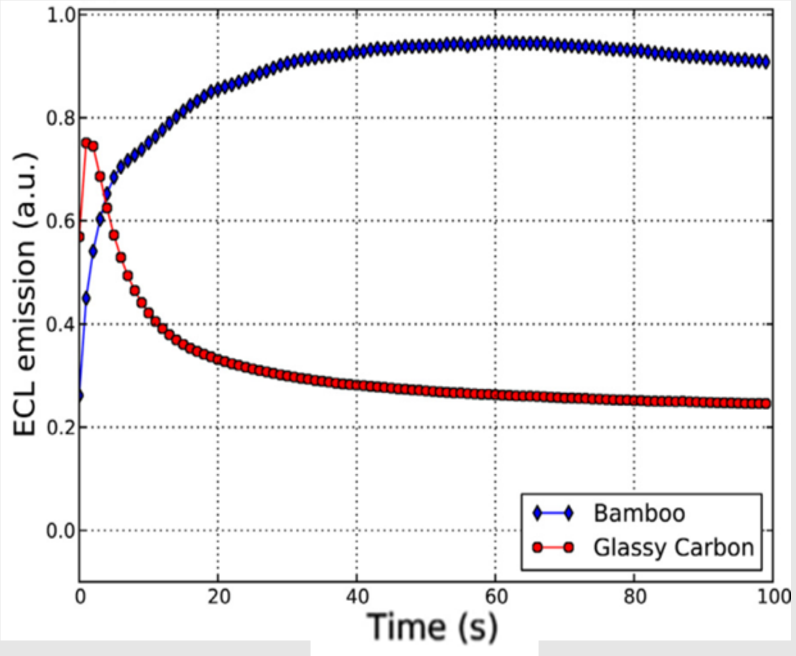




BAMBOO vs BENCHMARK

ECL Signal under cyclic voltammetry excitation





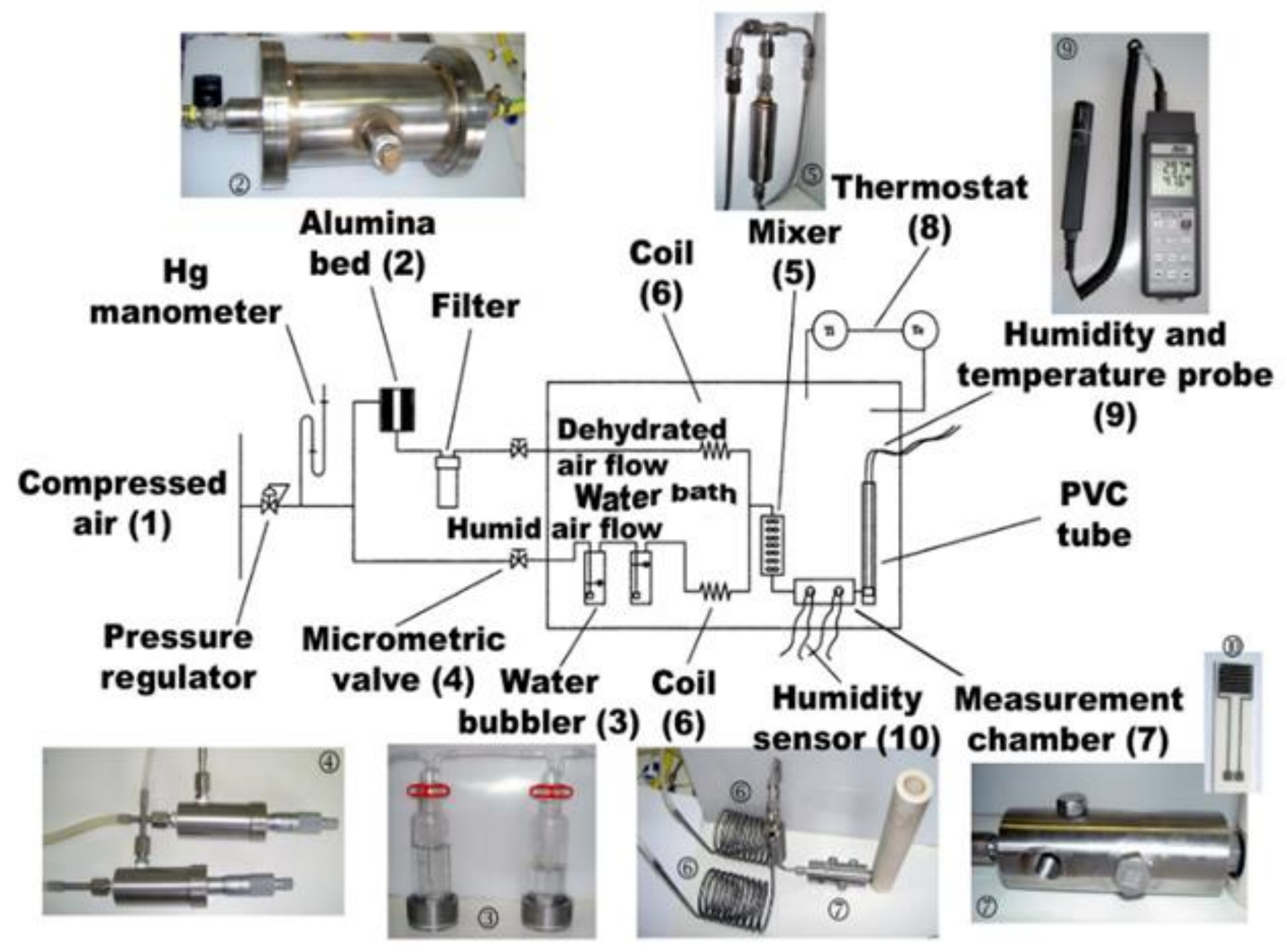
Noman et al. "Pyrolyzed bamboo electrode for electrogenerated chemiluminescence of Ru (bpy) 32+. *Electrochimica Acta* 133 (2014): 169-173.

HUMIDITY SENSING

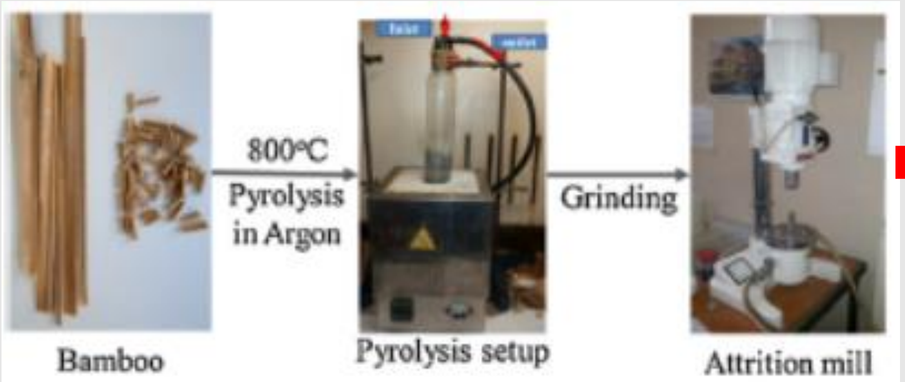
Purpose: Detect humidity level

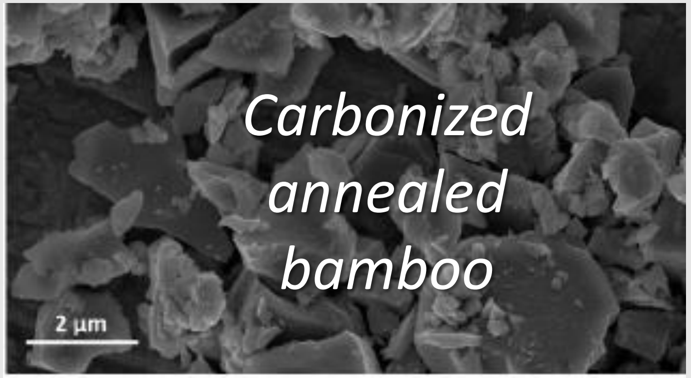
Absolute humidity (g/m^3)
amount of water vapor per unit volume of air

Relative humidity (%)
ratio between partial pressure and saturated pressure of moist at a given temperature

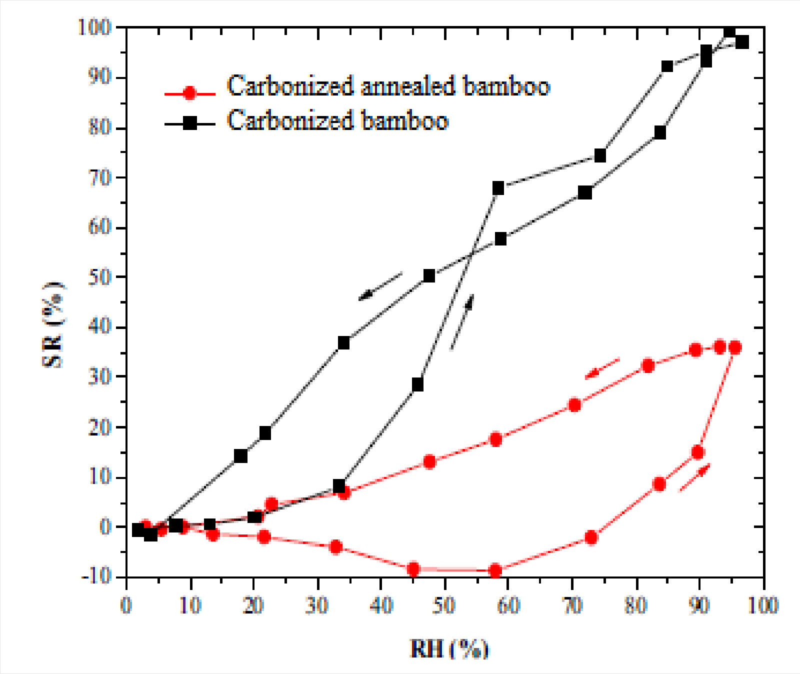


HUMIDITY SENSORS: BAMBOO AGAIN !



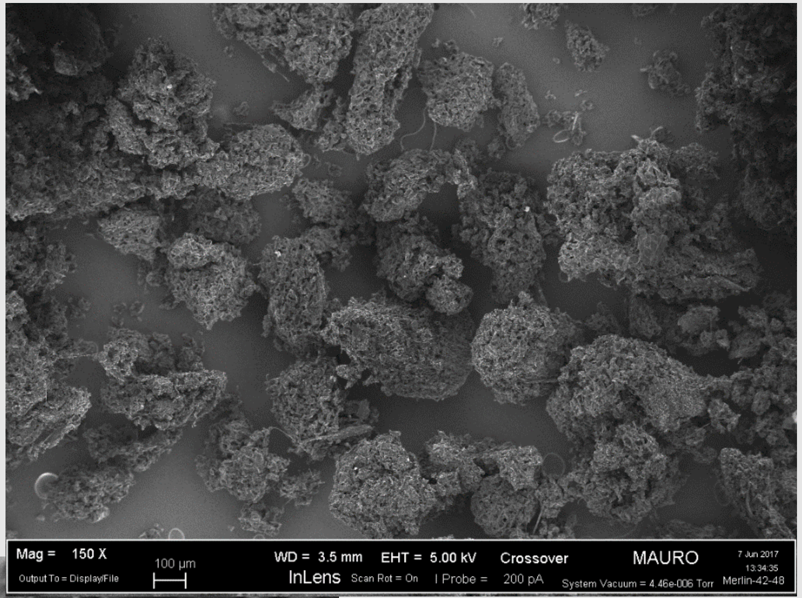


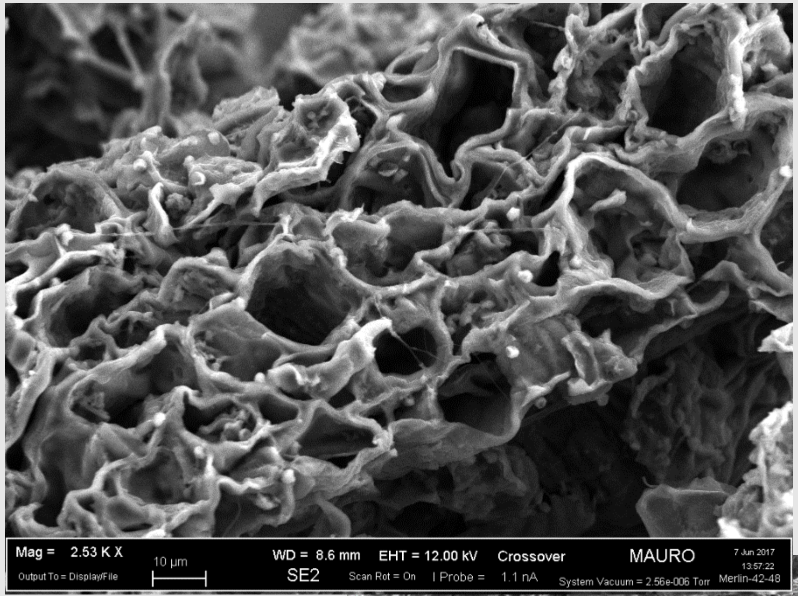
$$SR(\%) = 100 * \frac{|Zo - Zg|}{Zo}$$

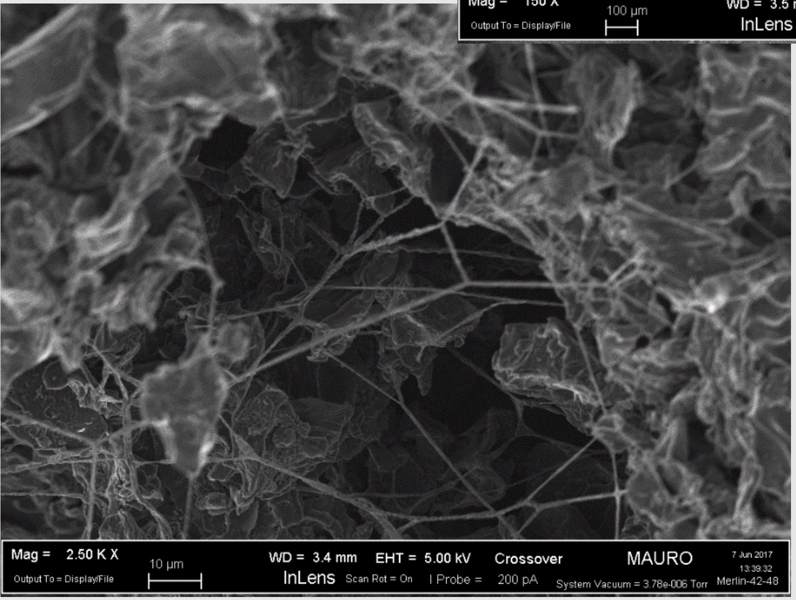


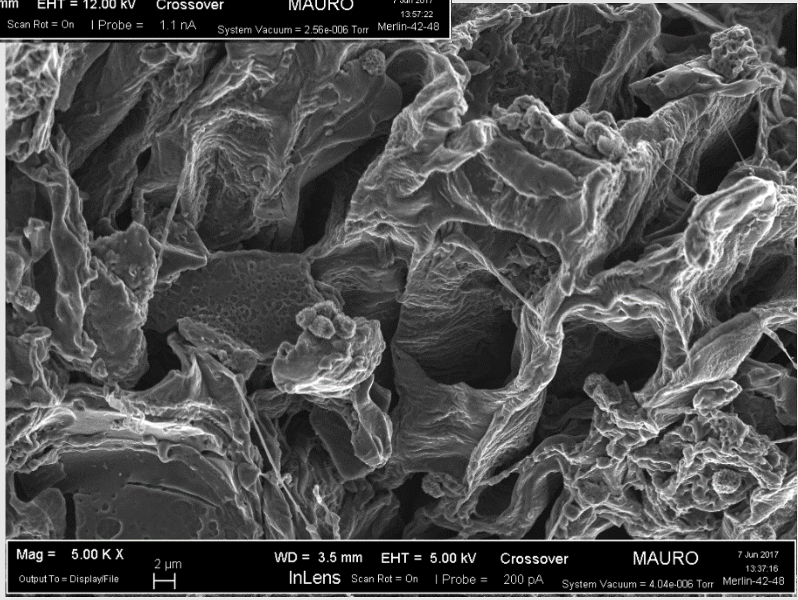
Afify et al. "Elaboration and characterization of novel humidity sensor based on micro-carbonized bamboo particles."
Sensors and Actuators B: Chemical 239 (2017): 1251-1256.

HUMIDITY SENSORS: USED COFFEE GROUNDS

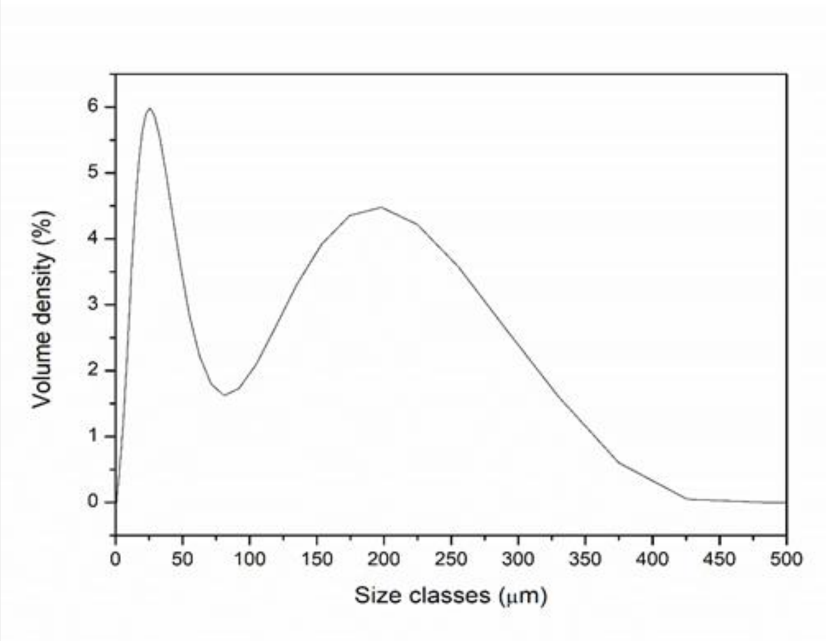


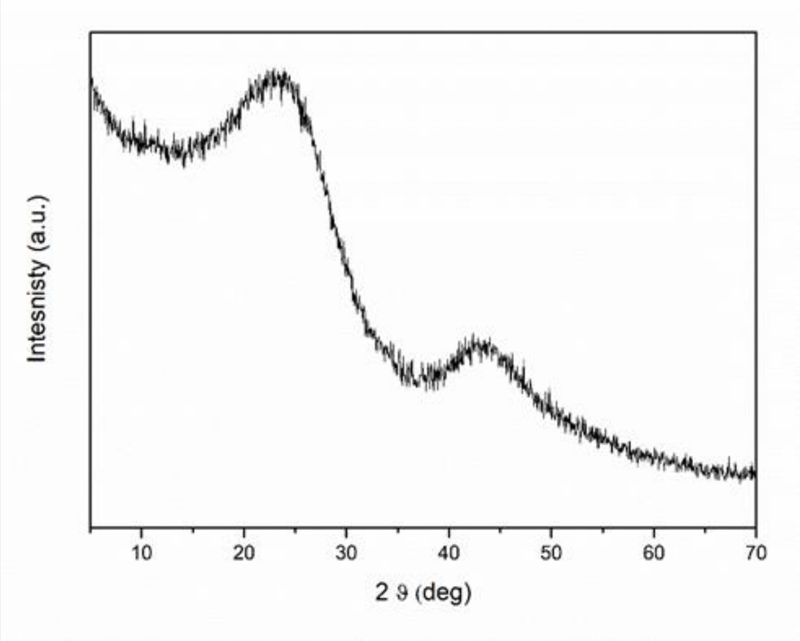


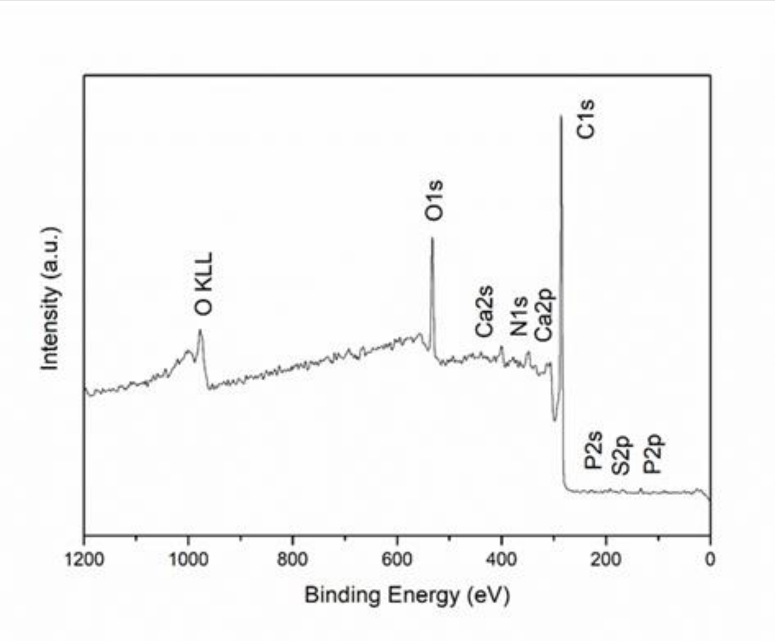




HUMIDITY SENSORS: USED COFFEE GROUNDS

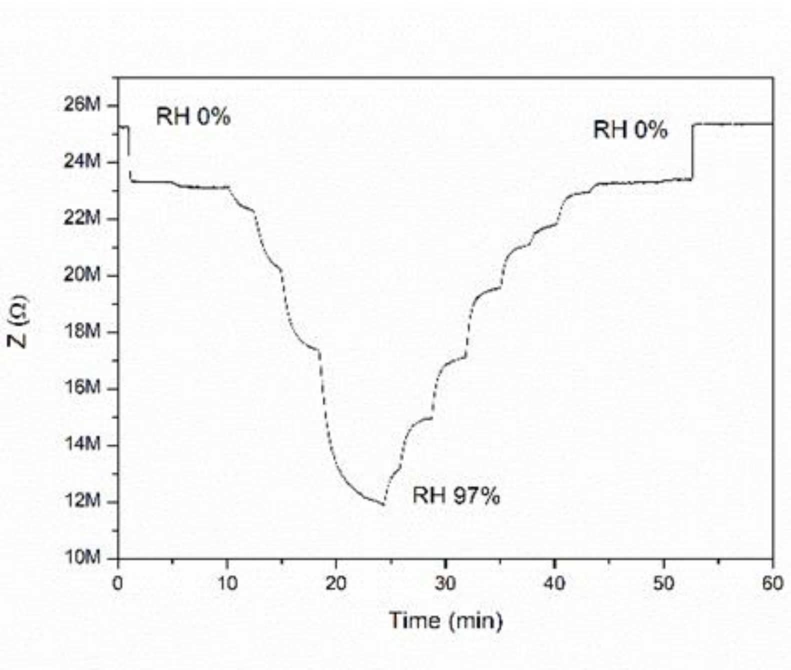


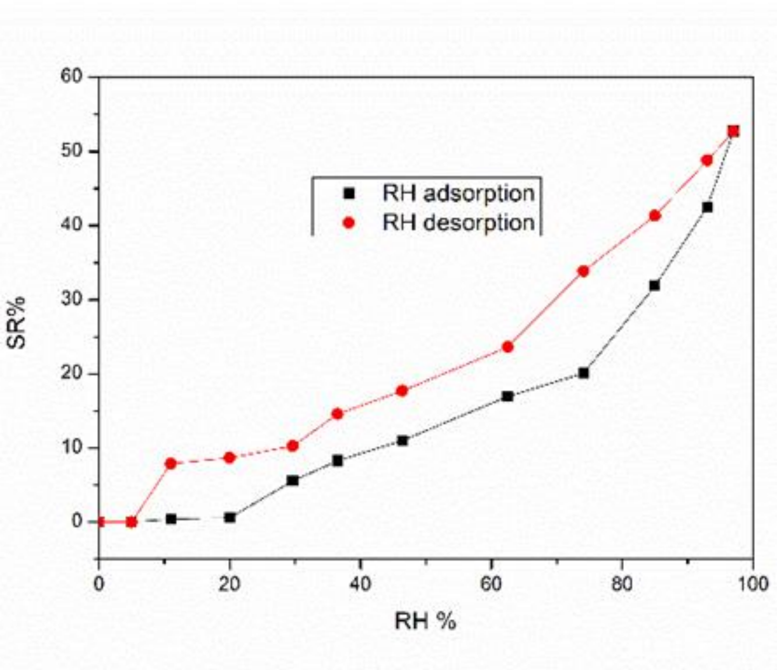


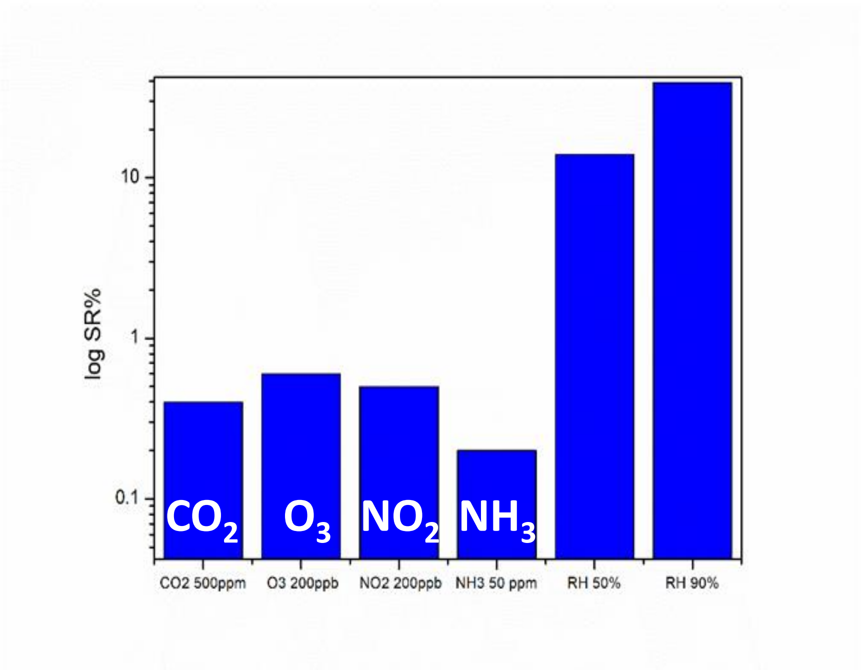


Particle size distribution **XRD** **XPS**

HUMIDITY SENSORS: USED COFFEE GROUNDS







R variation vs humidity

Response curves

Cross sensitivity

HUMIDITY SENSORS: STANDARDIZED BIOCHAR

UK Biochar Research Centre

reducing and removing CO_2 while improving soils: a significant and sustainable response to climate change

www.biochar.ac.uk | biochar@ed.ac.uk

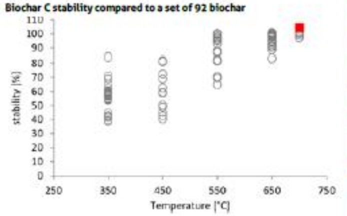
OSR700

Standard biochar specification sheet – Version 1.0 | November 2014

Feedstock: Oil Seed Rape Straw Pellets | **Production:** Pilot-scale rotary kiln pyrolysis unit, nominal peak temp. 700°C

Key features: • Reproducible • Extensively characterised • Readily available

Biochar C stability compared to a set of 92 biochar



Basic Utility Properties		Mean	Run-to-Run Variation, SD(n)
Moisture[a]	wt% (a.r.)	3.63	0.73 (6)
C_{tot}	wt% (d.b.)	67.74	0.86 (5)
H	wt% (d.b.)	1.09	0.14 (5)
O (by difference)	wt% (d.b.)	7.84	1.23 (5)
$H:C_{tot}$	Molar ratio	0.19	0.02 (5)
$O:C_{tot}$	Molar ratio	0.09	0.02 (5)
C_{org}	wt% (d.b.)	tbd	tbd
$H:C_{org}$	Molar ratio	tbd	tbd
Total ash[a]	wt% (d.b.)	21.92	0.52 (6)
Total N	wt% (d.b.)	1.26	0.18 (5)
pH	[-]	10.41	0.49 (4)
Electric conductivity	dS/m	3.11	0.37 (4)
Liming (if pH above 7)	% $CaCO_3$	tbd	tbd
Biochar C stability[b]	% C-basis	104.17	0.19 (4)

Production parameters		Mean	Run-to-Run Variation, SD(n)
Nominal HTT	°C	700	- (1)
Reactor wall temp.	°C	700	- (1)
Max. char HTT	°C	677	- (1)
Heating rate	°C/min	103	- (1)
Kiln residence time	min	12	- (1)
Mean time at HTT	min	5.14	- (1)
Biochar yield	wt% (d.b.)	22.62	2.99 (3)
Pyrolysis liquid yield	wt% (d.b.)	tbd	tbd
Pyrolysis gas yield	wt% (d.b.)	tbd	tbd
Pyrolysis liquid HHV	MJ/kg	tbd	tbd
Pyrolysis gas HHV	MJ/kg	tbd	tbd

Advanced Analysis & Soil Enhancement Properties		Mean	Run-to-Run Variation, SD(n)
Mineral N (ammonium & nitrate)	mg/kg (d.b.)	<3	- (5)
Total P[c]	wt% (d.b.)	0.258	0.079 (5)
Total K[c]	wt% (d.b.)	2.98	0.396 (5)
Available P	mg/kg (d.b.)	tbd	tbd
Volatile Matter[a]	wt% (d.b.)	13.18	3.47 (6)
Total Surface Area	m^2/g (d.b.)	25.20	- (1)
External Surface Area	m^2/g (d.b.)	tbd	tbd

Toxicant Reporting - Total Content	Unit	Mean	Run-to-Run Variation, SD(n)	IBI	EBC (premium)	BQM (high grade)
Germination Inhibition Assay	pass/fail	tbd	tbd			
Polycyclic Aromatic Hydrocarbons (EPA16)[d]	mg/kg dry wt	<0.11	- (5)	6-20	4	20
Dioxin/ Furan (PCDD/ Fs)[e]	ng/kg dry wt	4.50	- (1)	9	20	20
Polychlorinated Biphenyls (PCBs)[f]	ng/kg dry wt	0.001	- (1)	0.2-0.5	0.2	0.50
As	mg/kg dry wt	1.09	0.79 (3)	12-100	n/a	10
Cd	mg/kg dry wt	2.98	0.13 (3)	1.4-39	1	3
Cr	mg/kg dry wt	4.36	0.95 (3)	64-1200	80	15
Co	mg/kg dry wt	3.17	0.17 (3)	40-150	n/a	n/a
Cu	mg/kg dry wt	13.78	0.93 (3)	63-1500	100	40
Pb	mg/kg dry wt	bdl	- (3)	70-500	120	60
Hg	mg/kg dry wt	bdl	- (3)	1-17	1	1
Mo	mg/kg dry wt	1.68	0.14 (3)	5-20	n/a	10
Ni	mg/kg dry wt	3.27	0.22 (3)	47-600	30	10
Se	mg/kg dry wt	bdl	- (3)	1-36	n/a	5
Zn	mg/kg dry wt	8.80	0.24 (3)	200-7000	400	150

modified dry ashing followed by ICP-OES

comparison vs. recommended standard thresholds+

8 different types

specific surface up to 500 m^2/g

UK Biochar Research Centre

reducing and removing CO_2 while improving soils: a significant and sustainable response to climate change

www.biochar.ac.uk | biochar@ed.ac.uk

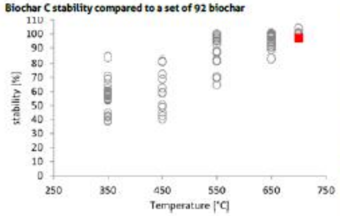
SWP700

Standard biochar specification sheet – Version 1.0 | November 2014

Feedstock: Soft Wood Pellets | **Production:** Pilot-scale rotary kiln pyrolysis unit, nominal peak temperature 700°C

Key features: • Reproducible • Extensively characterised • Readily available

Biochar C stability compared to a set of 92 biochar



Basic Utility Properties		Mean	Run-to-Run Variation, SD(n)
Moisture[a]	wt% (a.r.)	1.00	0.24 (8)
C_{tot}	wt% (d.b.)	90.21	0.39 (9)
H	wt% (d.b.)	1.83	0.15 (9)
O (by difference)	wt% (d.b.)	6.02	0.74 (8)
$H:C_{tot}$	Molar ratio	0.24	0.02 (8)
$O:C_{tot}$	Molar ratio	0.05	0.01 (8)
C_{org}	wt% (d.b.)	tbd	tbd
$H:C_{org}$	Molar ratio	tbd	tbd
Total ash[a]	wt% (d.b.)	1.89	0.43 (8)
Total N	wt% (d.b.)	<0.1	- (9)
pH	[-]	8.44	0.69 (4)
Electric conductivity	dS/m	0.16	0.06 (4)
Liming (if pH above 7)	% $CaCO_3$	tbd	tbd
Biochar C stability[b]	% C-basis	97.27	0.50 (7)

Production parameters		Mean	Run-to-Run Variation, SD(n)
Nominal HTT	°C	700	- (1)
Reactor wall temp.	°C	700	- (1)
Max. char HTT	°C	680	- (1)
Heating rate	°C/min	87	- (1)
Kiln residence time	min	12	- (1)
Mean time at HTT	min	5	- (1)
Biochar yield	wt% (d.b.)	17.34	2.46 (6)
Pyrolysis liquid yield	wt% (d.b.)	27.64	- (1)
Pyrolysis gas yield	wt% (d.b.)	54.05	- (1)
Pyrolysis liquid HHV	MJ/kg	1.06	- (1)
Pyrolysis gas HHV	MJ/kg	12.6	- (1)

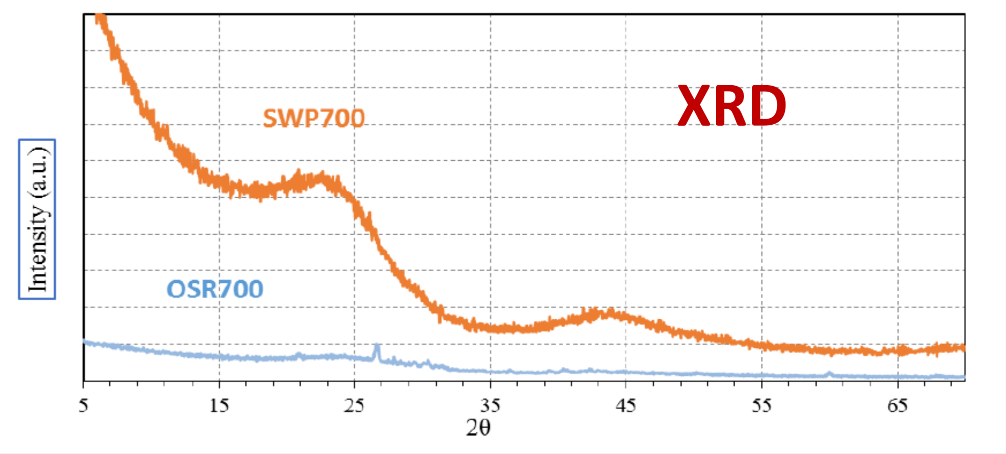
Advanced Analysis & Soil Enhancement Properties		Mean	Run-to-Run Variation, SD(n)
Mineral N (ammonium & nitrate)	mg/kg (d.b.)	<3	- (4)
Total P[c]	wt% (d.b.)	0.07	0.04 (4)
Total K[c]	wt% (d.b.)	0.28	0.09 (4)
Available P	mg/kg (d.b.)	tbd	tbd
Volatile Matter[a]	wt% (d.b.)	6.66	0.46 (8)
Total Surface Area	m^2/g (d.b.)	162.3	- (1)
External Surface Area	m^2/g (d.b.)	tbd	tbd

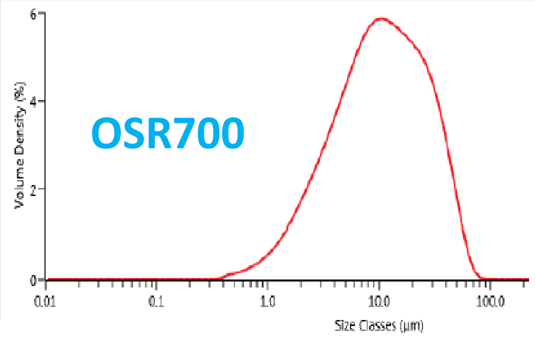
Toxicant Reporting - Total Content	Unit	Mean	Run-to-Run Variation, SD(n)	IBI	EBC (premium)	BQM (high grade)
Germination Inhibition Assay	pass/fail	tbd	tbd			
Polycyclic Aromatic Hydrocarbons (EPA16)[d]	mg/kg dry wt	0.18	0.08 (9)	6-20	4	20
Dioxin/ Furan (PCDD/ Fs)[e]	ng/kg dry wt	3.30	- (1)	9	20	20
Polychlorinated Biphenyls (PCBs)[f]	ng/kg dry wt	0.17	- (1)	0.2-0.5	0.2	0.50
As	mg/kg dry wt	0.61	0.69 (3)	12-100	n/a	10
Cd	mg/kg dry wt	8.16	13.86 (3)	1.4-39	1	3
Cr	mg/kg dry wt	123.35	49.92 (3)	64-1200	80	15
Co	mg/kg dry wt	4.37	1.73 (3)	40-150	n/a	n/a
Cu	mg/kg dry wt	9.66	3.03 (3)	63-1500	100	40
Pb	mg/kg dry wt	bdl	- (3)	70-500	120	60
Hg	mg/kg dry wt	bdl	- (3)	1-17	1	1
Mo	mg/kg dry wt	38.54	26.17 (3)	5-20	n/a	10
Ni	mg/kg dry wt	74.07	31.09 (3)	47-600	30	10
Se	mg/kg dry wt	bdl	- (3)	1-36	n/a	5
Zn	mg/kg dry wt	99.60	141.28 (3)	200-7000	400	150

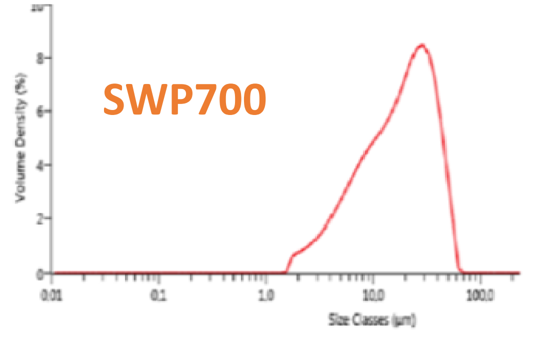
modified dry ashing followed by ICP-OES

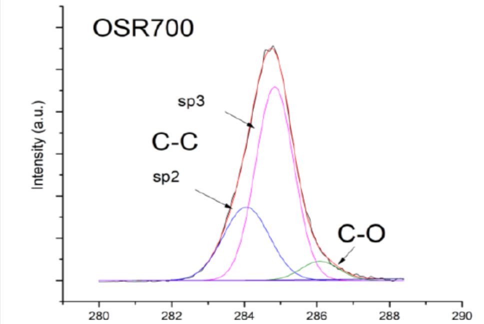
comparison vs. recommended standard thresholds+

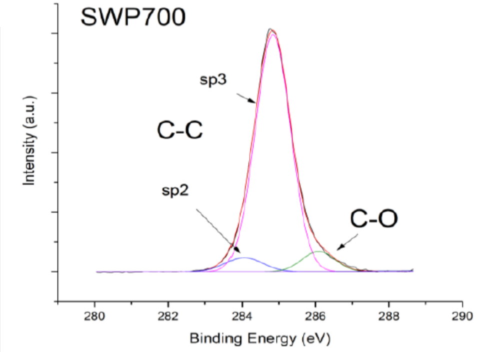
HUMIDITY SENSORS: STANDARDIZED BIOCHAR

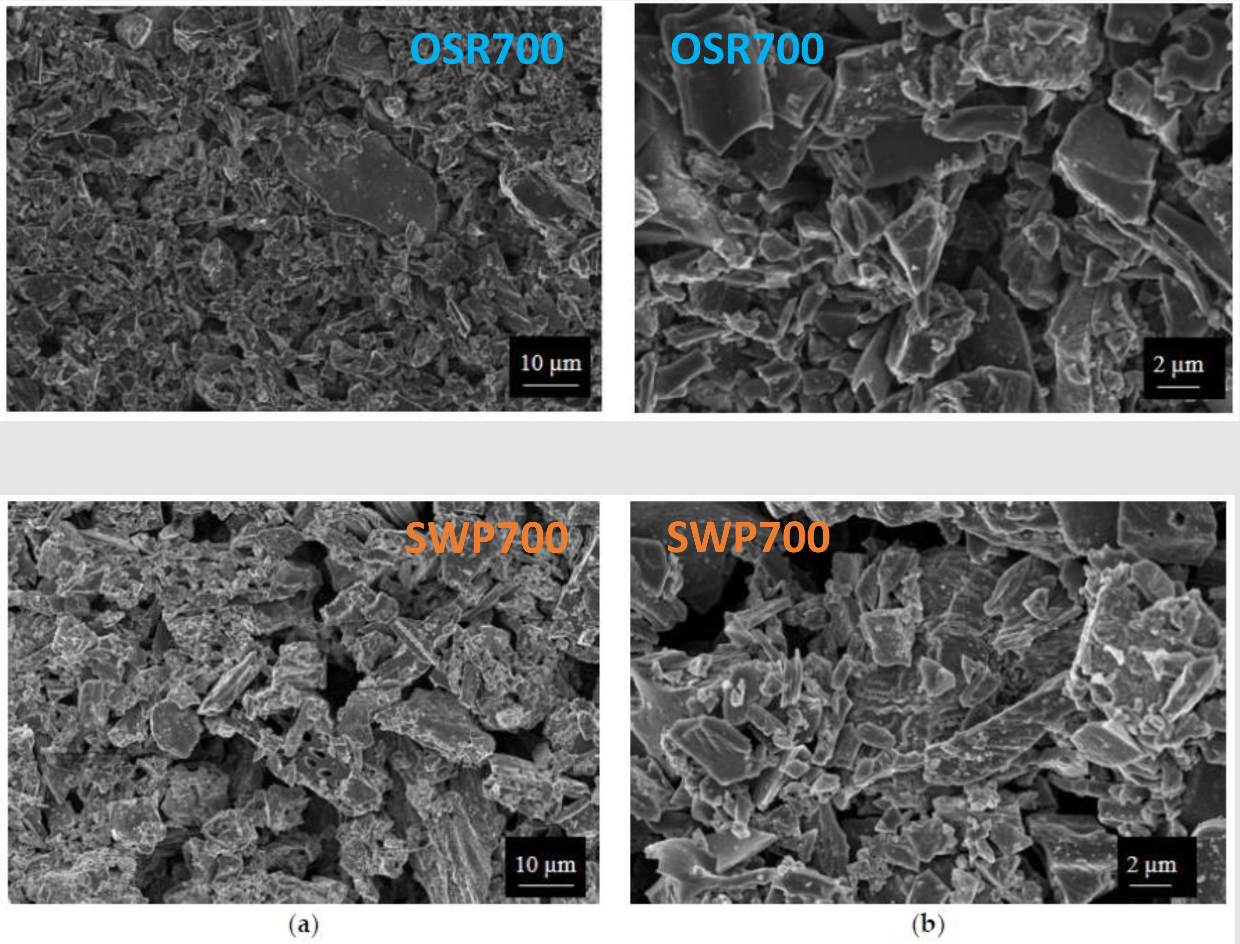




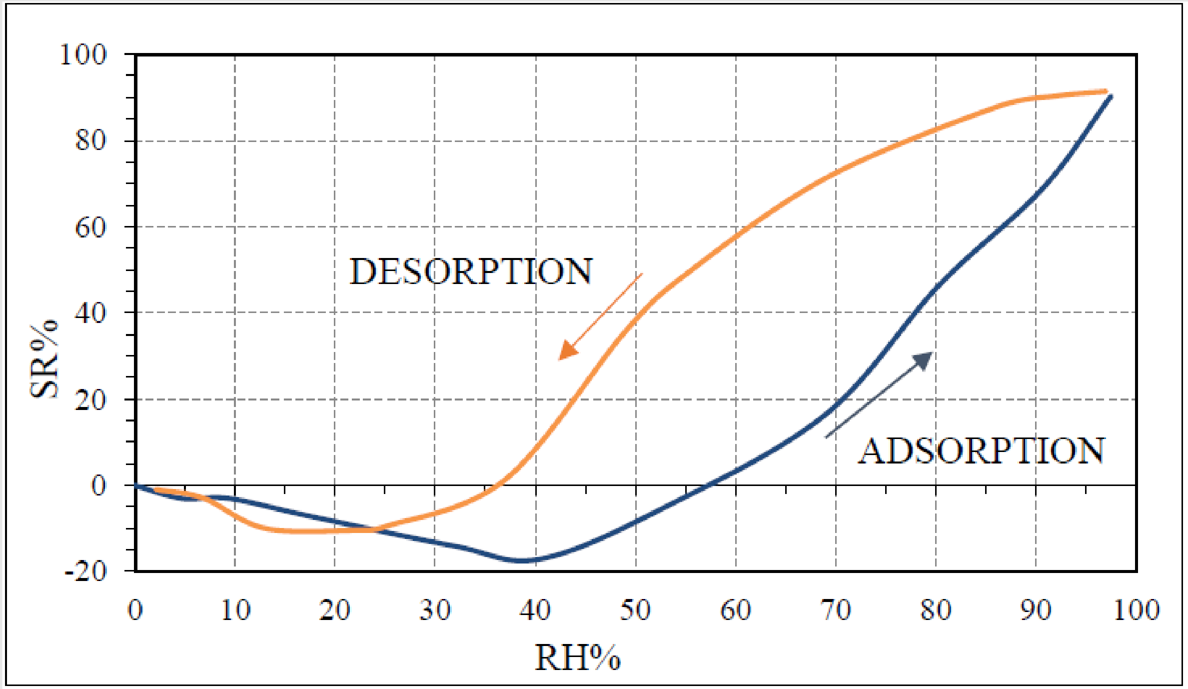




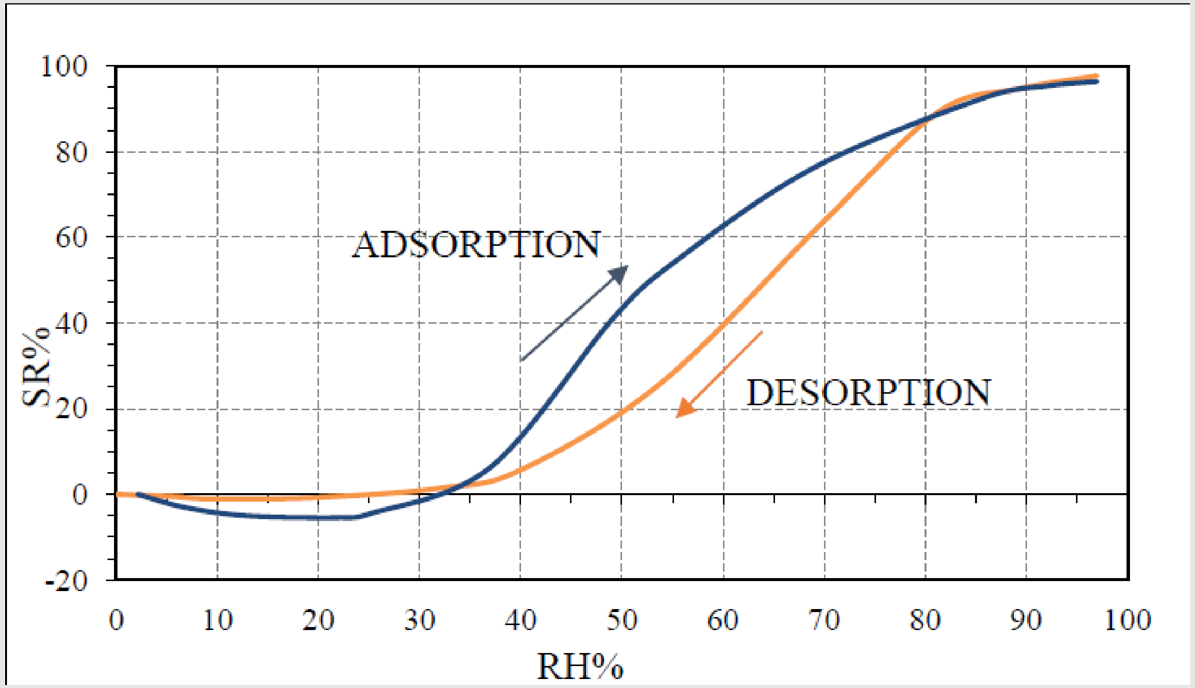




HUMIDITY SENSORS: STANDARDIZED BIOCHAR



OSR700



SWP700

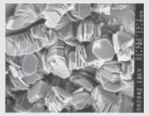
Ziegler et al "Biochars as Innovative Humidity Sensing Materials" Chemosensors 5 (2017) 35

FILLERS IN POLYMERS

Fillers used in polymers for:

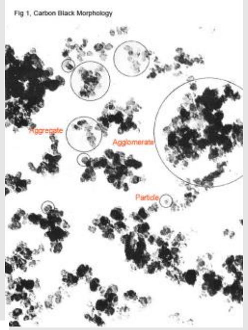
cost reduction improved processing density control
optical effects (color) thermal conductivity
electrical properties magnetic properties
flame retardancy control of thermal expansion
improved mechanical properties (hardness , …) …

In electrical cable applications,

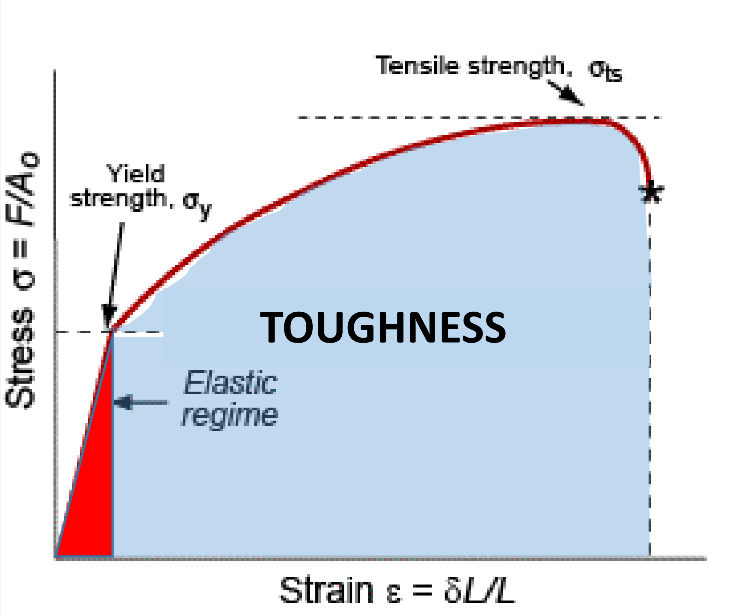
metakaolinite  provides better **electrical stability**

 **alumina trihydrate** is a **fire retardant**.

carbon black is added to elastomers used in tyres



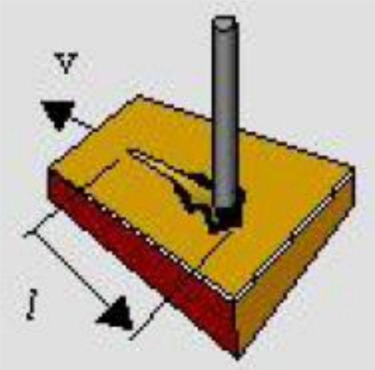
MECHANICAL TESTING



Elastic modulus = stress/strain ratio in the linear region
Young modulus = elastic modulus under tensile (compressive) stress

Yield strength (stress) = stress limit for elastic behaviour
(ultimate) **Tensile strength** = the maximum stress a material can withstand

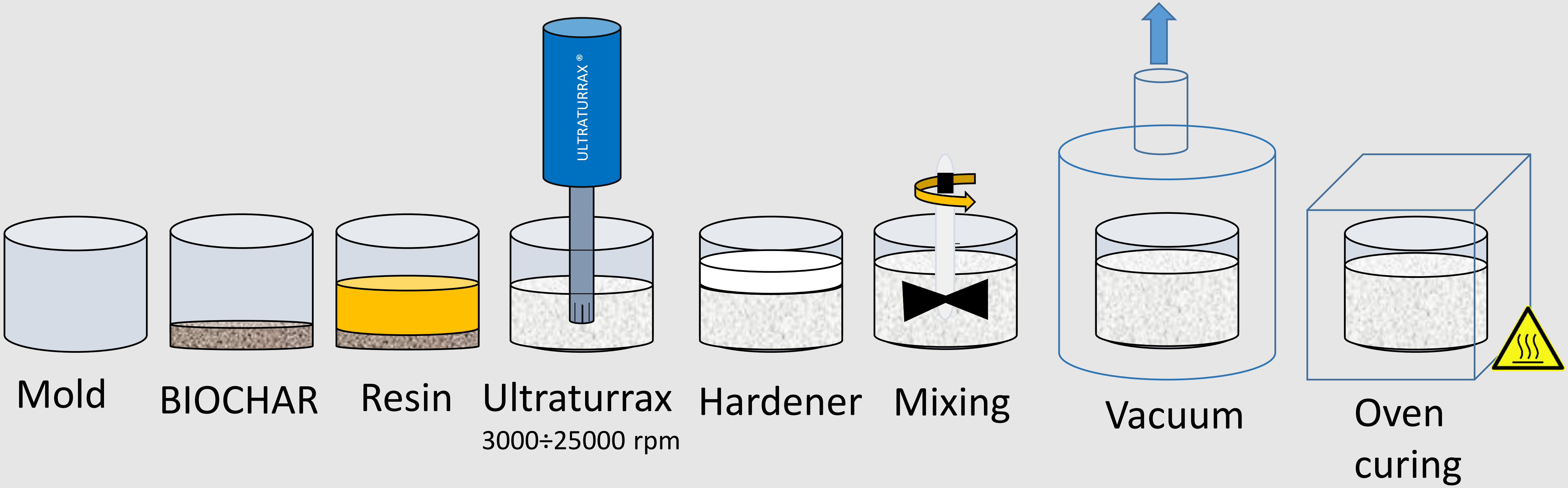
Maximum Elongation = strain at breakdown
Resilience = energy per unit volume needed to overcome the elastic behaviour
Toughness = energy per unit volume needed to break the sample



Reduction of friction coefficient is of high interest.

Target is to reach self-lubrication limit
(Friction coefficient = 0.08)

SAMPLE PREPARATION

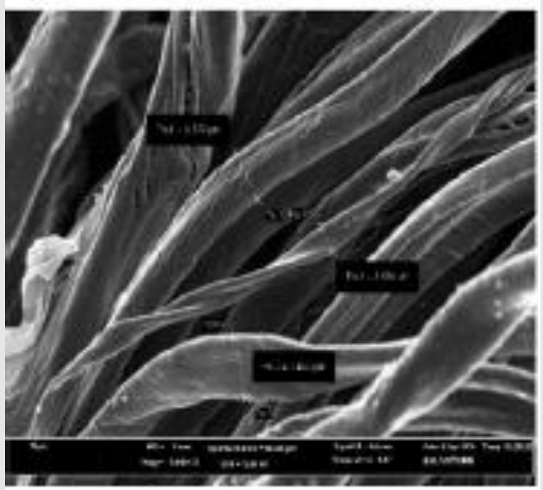


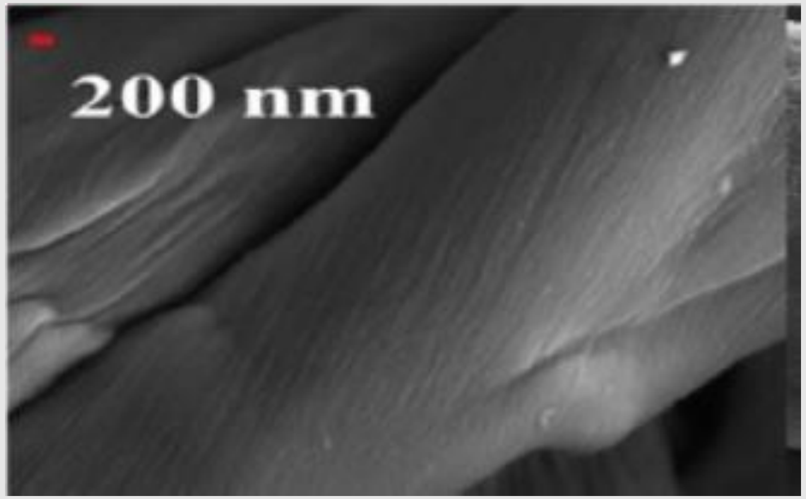
Composite dogbone for testing

BIOCHAR FROM WASTE COTTON CLOTHES

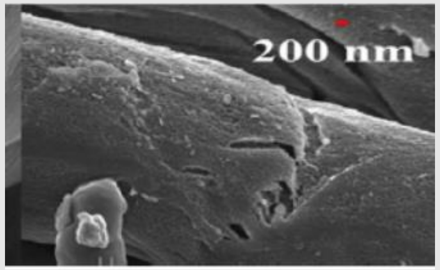
Cut !

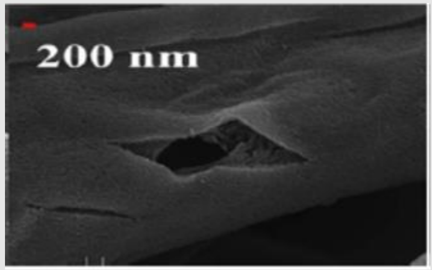
Pyrolyze

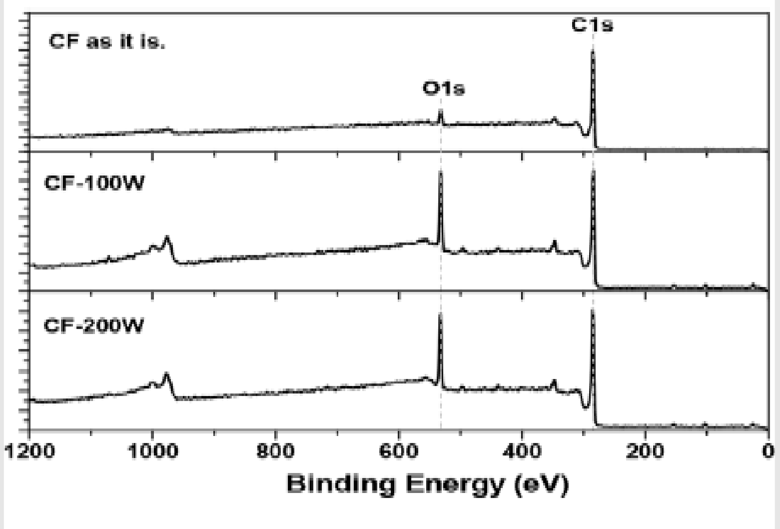




Functionalize with O_2 plasma







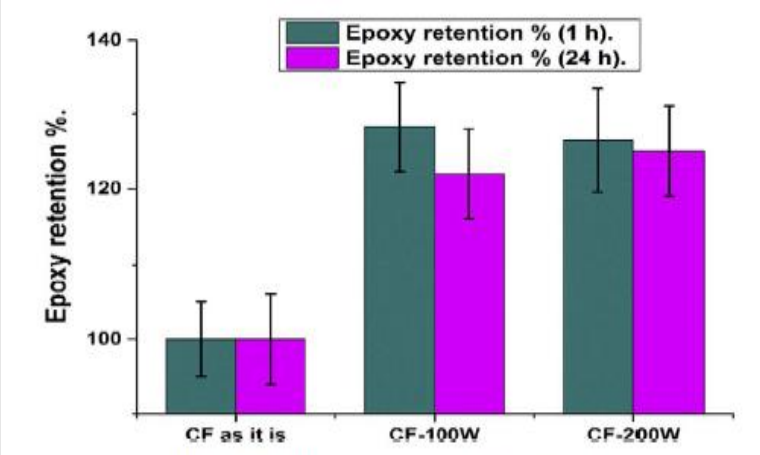
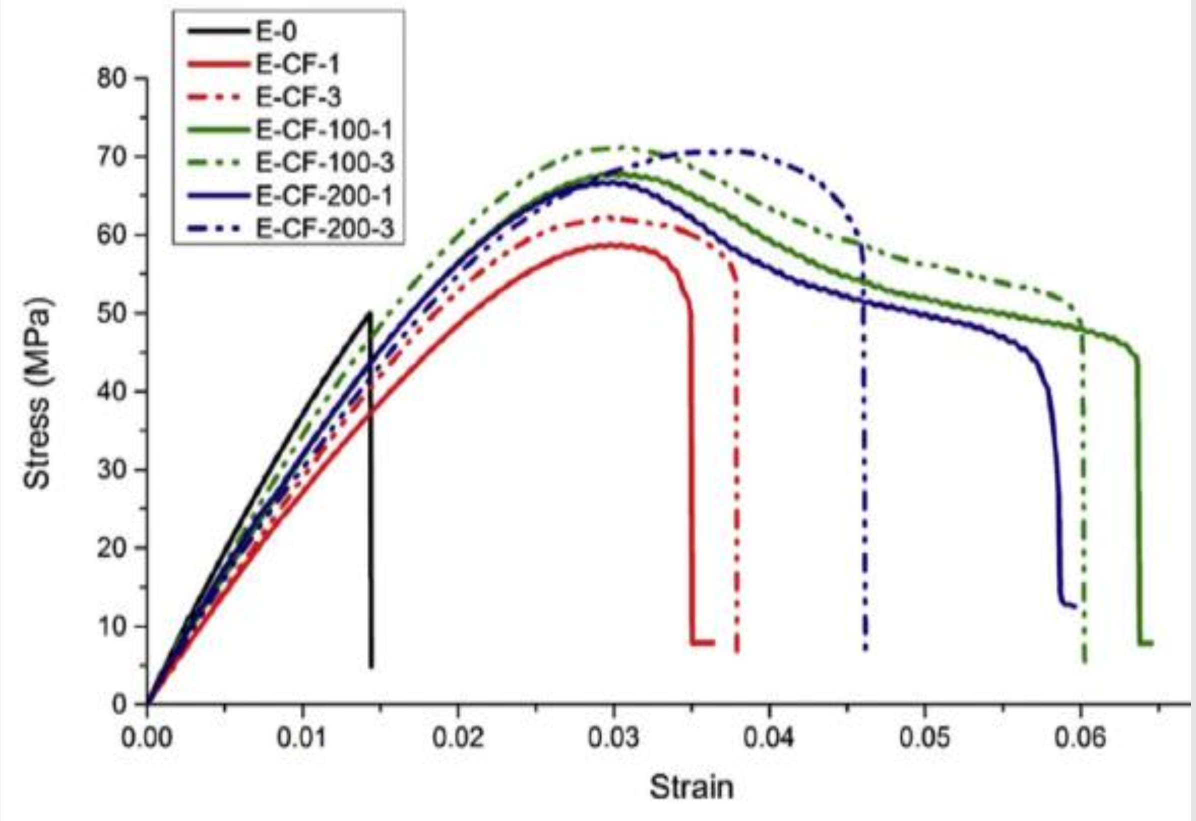
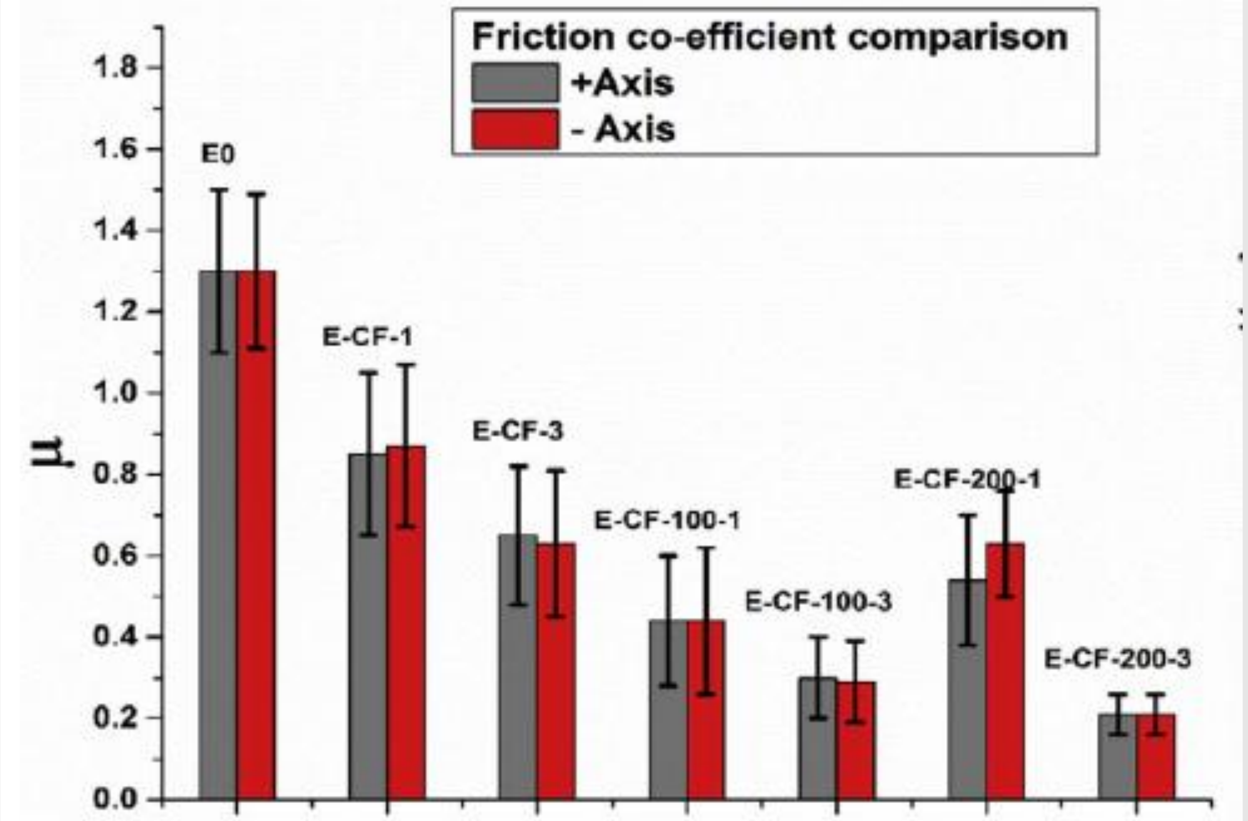


Fig. 8. Wettability test on untreated and treated CF.

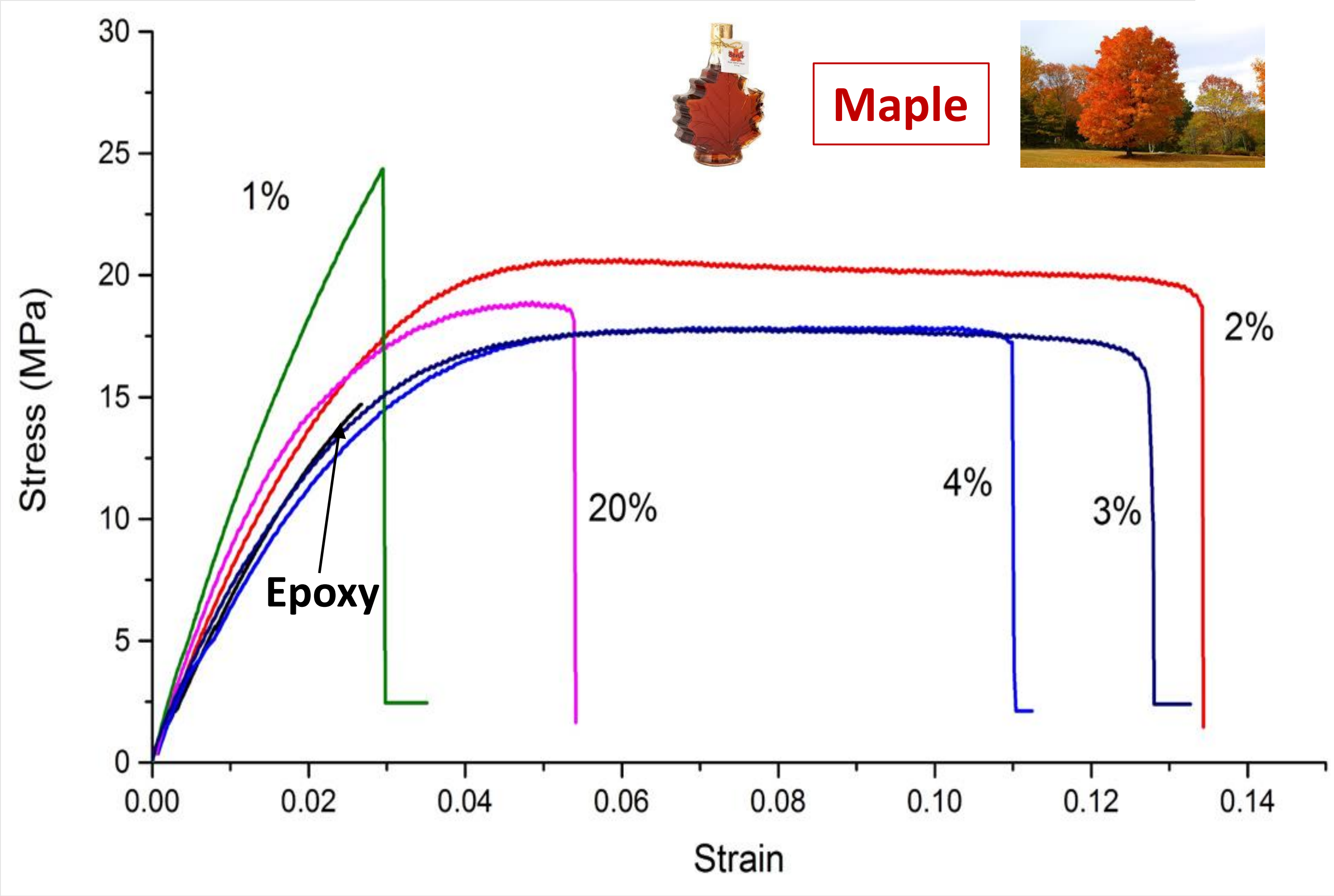
BIOCHAR FROM WASTE COTTON CLOTHES

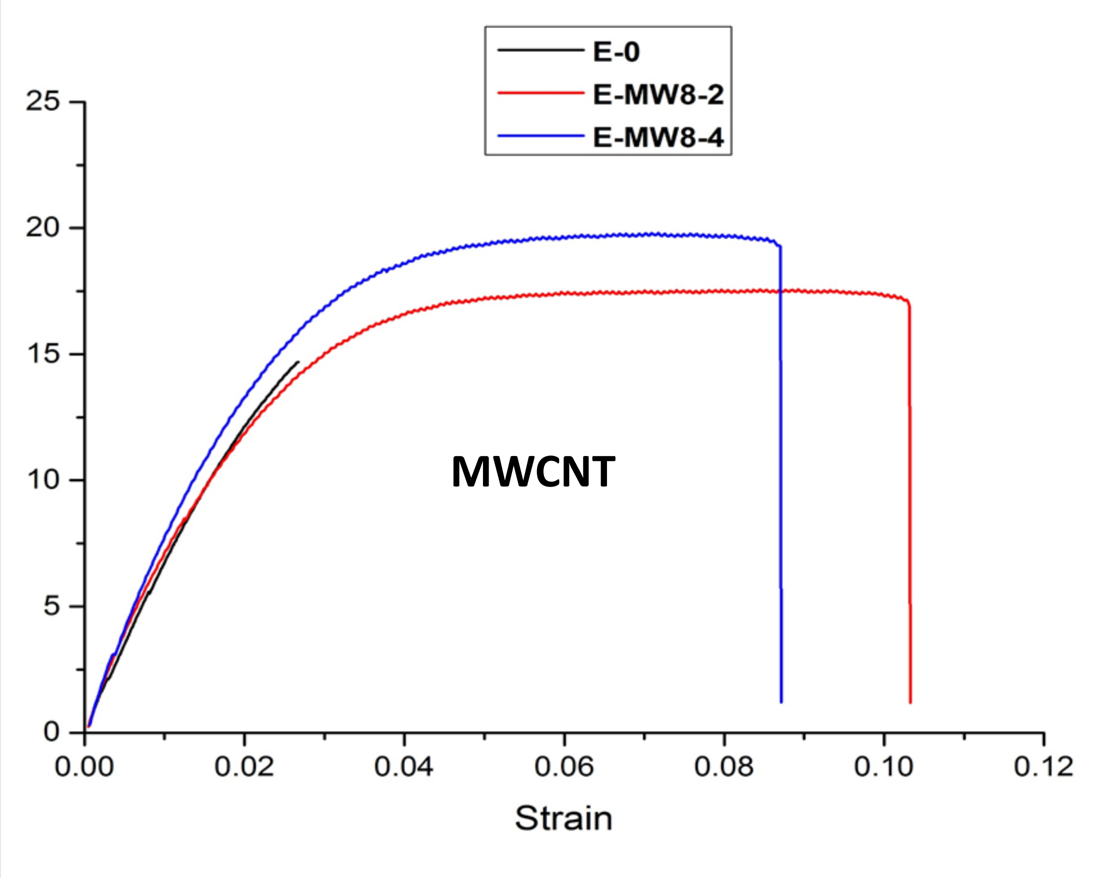




A.A. Khan et al - Low-cost Carbon fillers to improve mechanical properties and conductivity of polymers
Polymers 9 (2017) 642-655

FROM COTTON TO WOOD

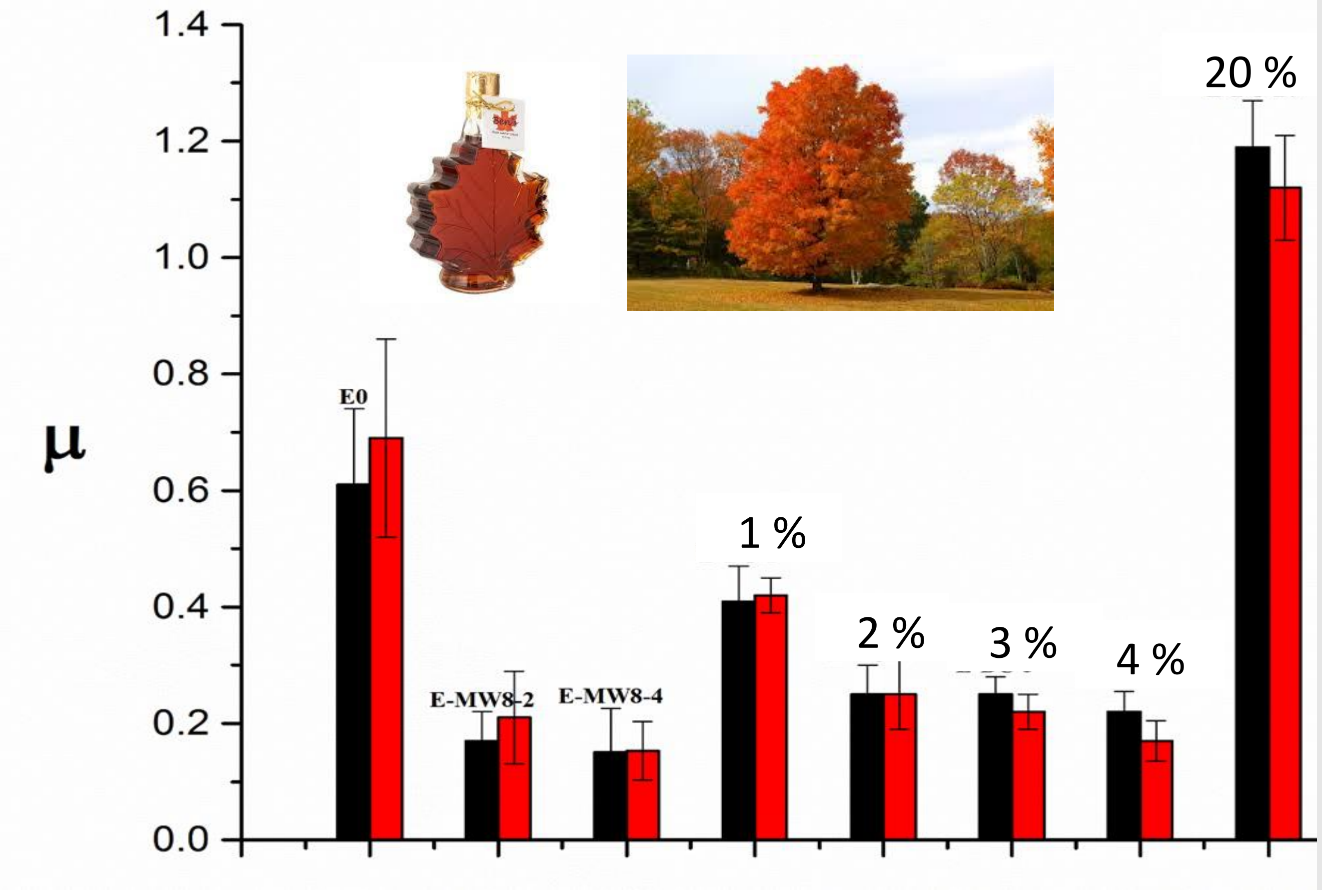




30% increase in Young modulus (1 wt%)

5-fold increase in elongation (2 wt%)

FROM COTTON TO WOOD



M. Giorcelli et al - Biochar as a cheap and environmental friendly filler able to improve polymer mechanical properties
Biomass and Bioenergy 120 (2019) 219-223

HAS THE TYPE OF WOOD A ROLE ?

Ash Tree
light, resistant

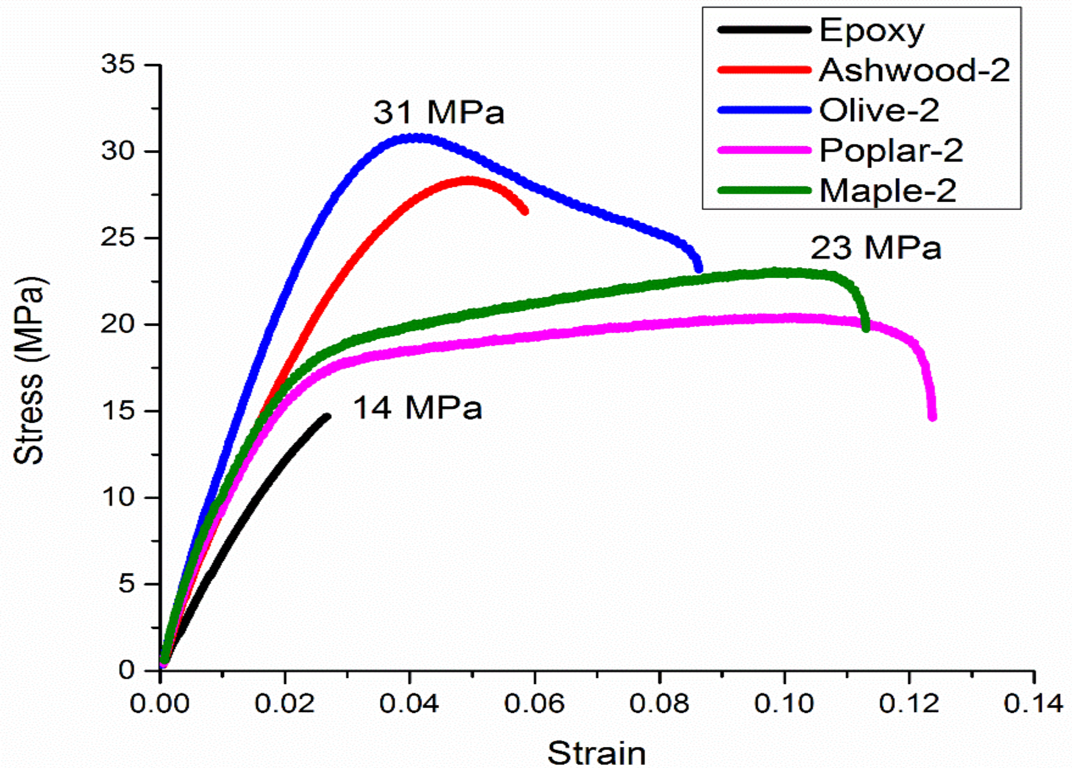
Poplar
flexible, easy to work

Olive
hard, high YM

WOOD TYPE	Hardness [kN]	Rupture Modulus [MPa]	Elastic Modulus [GPa]	Crushing strength [MPa]
Poplar	1.8	65	8.9	not available
Maple	6.5	109	12.6	54
Ash tree	6.6	104	12.3	51
Olive	12.0	155	17.8	77

STRESS STRAIN CURVES

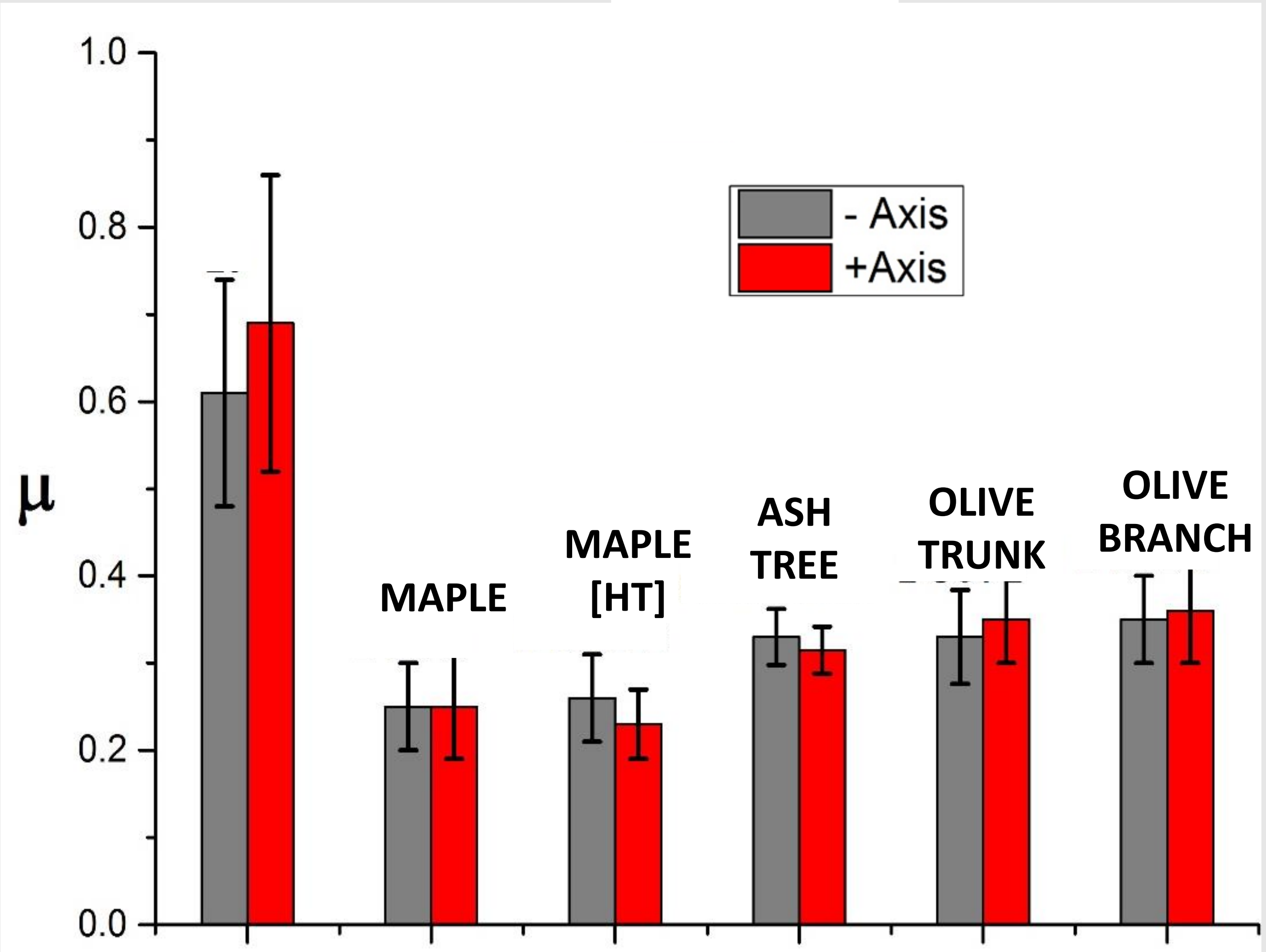
2 wt% biochar



	Young (MPa)	UTS (MPa)	Resilience (MJ/m^3)	Toughness (MJ/m^3)
RESIN	640	14.7	0.13	0.2
MAPLE	850	20.6	0.08	2.4
MAPLE [HT]	875	21.7	0.08	2.5
ASH TREE	1095	28.4	0.07	1.2
OLIVE TRUNK	1040	31.2	0.11	1.2
OLIVE BRANCH	**1305**	**30.8**	**0.14**	2.1
POPLAR	*1030*	*26.8*	*0.07*	***2.8***

FRICTION COEFFICIENT

2 wt% biochar



SUMMARY

Biochar is a promising candidate for a number of added value applications

- sensors
- improvement of mechanical and electrical properties of composites
- …

Advantages of Biochar and bio-waste:

- carbon dioxide sequestration
- added value to the biofuel chain
- reduction of waste disposal needs and costs
- worldwide available at low cost

Drawbacks of Biochar:

- feedstock variability
- not fashion enough to raise research funds …

ACKNOWLEDGMENTS

D. Ziegler, J.M. Tulliani. A.A. Khan	**DISAT – Politecnico Torino**
D. Demarchi, A. Sanginario, P. Savi	**DET – Politecnico Torino**
N. Pugno	**Università Trento (Italy)**
C. Jia	**University of Toronto (Canada)**
F. Berruti	**University Western Ontario (Canada)**
K.H. Wei	**National University Singapore**
O. Masek	**University of Edinburgh (UK)**
E. Kumoulous, C. Charitidis	**National Technical University Athens**

…


THANK YOU
FOR YOUR
TIME


Questions?