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Production of activated carbon from barley biochar precursor

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PRODUCTION OF ACTIVATED CARBON FROM BARLEY BIOCHAR PRECURSOR

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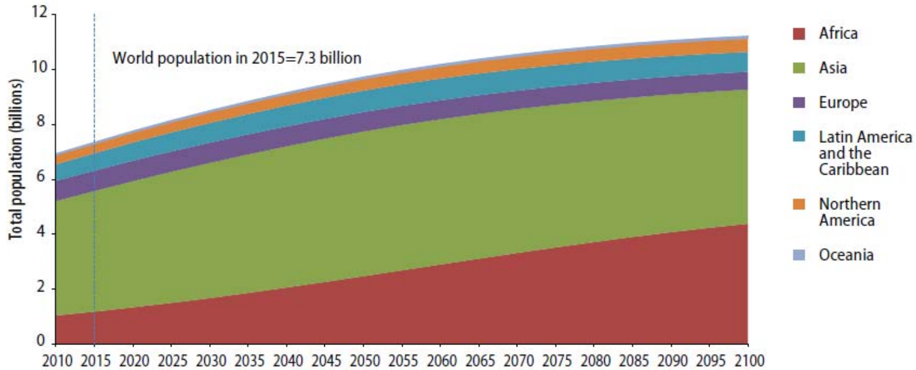
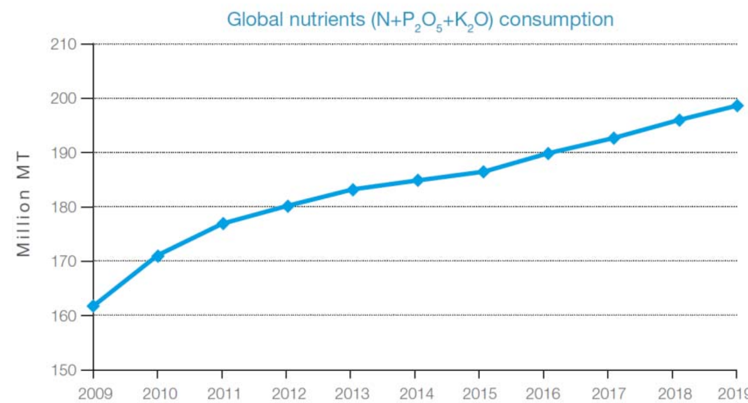
1. Introduction

Biochar is considered a product of great interest in **agriculture** since several studies have demonstrated its effectiveness in increasing agricultural yields, increasing the water retention capacity and nutrients in the soil, increasing the development of arbuscular mycorrhizal fungus (AMF), and ultimately improving the efficiency of fertilizers. However, to maintain the development of our society where the world population and food production in the last 50 years have doubled and tripled, respectively, **inorganic fertilizers** will remain a fundamental pillar.



World population prospects (United Nations)



World fertilization trends and outlook to 2019 (FAO)

An alternative solution to this problem is the use of **activated carbon (AC)** of biomass nature as a complement to nitrogen fertilization. There are numerous studies that demonstrate the **positive effect that AC has on the fertility of agricultural soils**, with the consequent increase in crop yields (Steinbeiss et al., 2009). In addition, their use as an amendment may have significant reductions in N_2O emissions (Singh et al. 2010), NH_3 (Spokas et al., 2012) and nitrogen leachate (Knowles et al., 2011).

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2. Barley as precursor material for the production of activated biochar

In Spain, an average of 6 million hectares of cereals (representing 12% of the whole geographical area and 44% of the total cultivated area) are cultivated, of which, in the current 2016/17 season, it is estimated that **42.8%** of the production corresponds to **barley**. **It is the crop with greater territorial base and with distribution throughout the whole territory.**

Barley is characterized by its morphological structure constituted by a trunk with cane structure and spikes, which provides grains (seeds) that are used, as the main use of the plant, for food, both human and animal, being one of the **main contributors to the world's food diet**.

Excluding grain as the main product, of the **remaining available residual biomass** (excluding secondary uses such as cattle feeding, livestock beds, energy production), between **15 - 50% of the waste straw is not used**.

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2. Barley as precursor material for the production of activated biochar

Barley has favorable characteristics for the production of activated carbon (low ash and a high volatile content), similar to other biomass residual materials that have been already reported in literature such as almond shells (Marcilla et al., 2000), pistachio shells (Okutucu et al., 2011) and maize corncob (El- Hendawy et al., 2001). Moreover, it presents a great variety of macro and micro nutrients (P, K, Ca, Mg, S, Fe, Mn,…) which supports its potential use in agriculture

Dry basis (% wt.)	
Moisture	9.0
Volatiles	77.2
Fixed Carbon	17.3
Ash	5.5
C	45.4
H	6.1
O	41.92
N	0.7
S	0.07
Cl	0.31

Oxide/metal	% wt	Oxide/metal	% wt	Oxide/metal	% wt
Al_2O_3	1.5	P_2O_5	2.9	Mn	0.054
CaO	10	SO_3	2.8	Na	0.50
Fe_2O_3	0.60	SrO	0.026	P	1.3
K_2O	21	ZnO	0.024	S	1.1
MgO	3.3	Al	0.082	Si	2.1
Na_2O	0.67	Ba	0.021	Sr	0.022
SiO_2	45	Ca	7.2	Ti	0.046
BaO	0.024	Mn_2O_3	0.10	K	18
Mg	2.0	TiO_2	0.077	Fe	0.42

Proximate, ultimate and ash analysis (barley)

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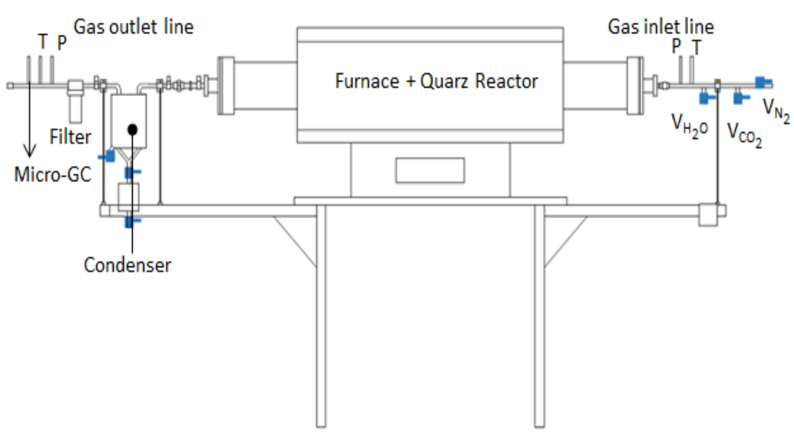
3. Physical activation

In this study the production of activated carbon was carried out through a **physical activation process** in two stages: **carbonization** with nitrogen and **activation** with carbon dioxide in a quartz tubular reactor (L = 1730 mm, ϕ = 162 mm).



The installation is completed with the gas inlet line that has independent valves that allow the regulation of the gases used in the process from compressed gas cylinders. Futhermore, in the exit zone there is installed a condenser that allows to cool and to separate tar formed in the process and a coalescent filter. The installation has pressure and temperature measurements on both lines, flow rate meter and a gas chromatograph to determine the composition of the exhaust gas.

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3. Physical activation

The conditions in which each of these stages takes place, such as the final temperature, residence time, heating rate (°C/min) and gas mass flow, are determinant in the properties reached in the final activated carbon. Through an extensive **experimental campaign**, these conditions were **optimized** in order to obtain a final product with a greater **surface area** and **microporosity**.

CARBONIZATION				CO_2 ACTIVATION			
N_2 (cm^3/min)	T (°C)	β (°C/min)	tr (h)	CO_2 (cm^3/min)	T (°C)	β (°C/min)	tr (h)
2500	500	10	1	2500	800	10	1

Optimized conditions barley physical activation process

After the tests, the **BET area**, **total pore volume** and **pore size distribution** (DFT model) were determined by the N_2 adsorption isotherm. These analyses were complemented with **XRF** and **ICP** to determine the elements present in the sample and **SEM/EDX** microscopy to characterize morphologically the surface of the solids.

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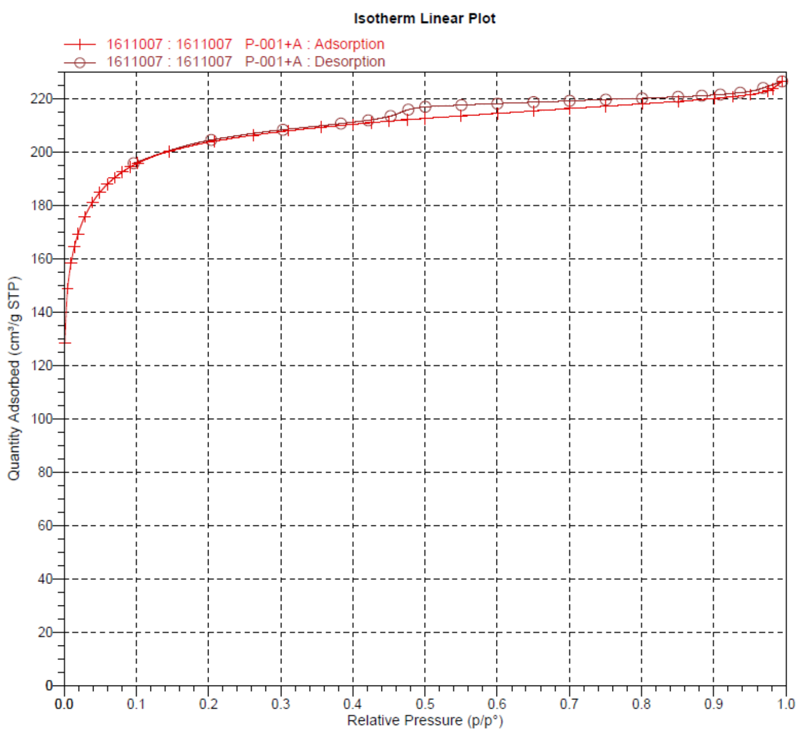
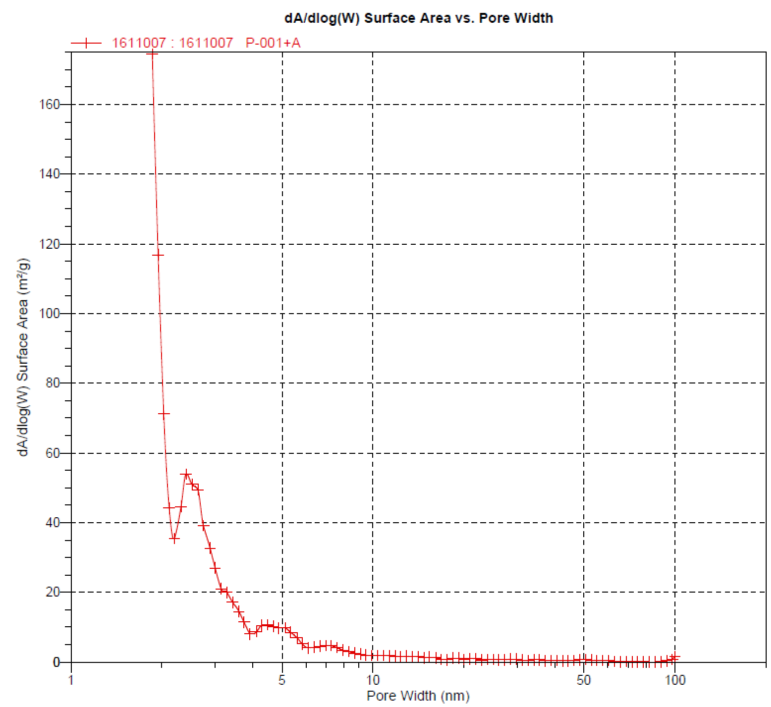
4. Results

N_2 adsorption isotherm





Initial mass (g)	Final mass (g)	Conversion (%)	S_BET (m^2/g)	Vpore (cm^3/g)	Vmicropore (cm^3/g)
25.141	3.4858	13.86%	788.5214	0.349508	0.326836

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4. Results

XRF, ICP

Element	XRF (% wt)	ICP (mg/g)	Element	XRF (% wt)	ICP (mg/g)
K	43.07	75.05	Pb	0.103	
Si	21.16		Ti	0.0955	0.109
Ca	20.2	21.65	Al	0.046	2.121
Cl	7.27		Fe	0.04	1.021
Mg	2.67	6.313	S	0.038	1.788
P	1.99	3.697	Pt	0.034	
Na	0.54	1.021	Zn	0.032	0.081
Mn	0.17	0.164	Cu	0.0228	0.023
Sn	0.145		Sr	0.0105	

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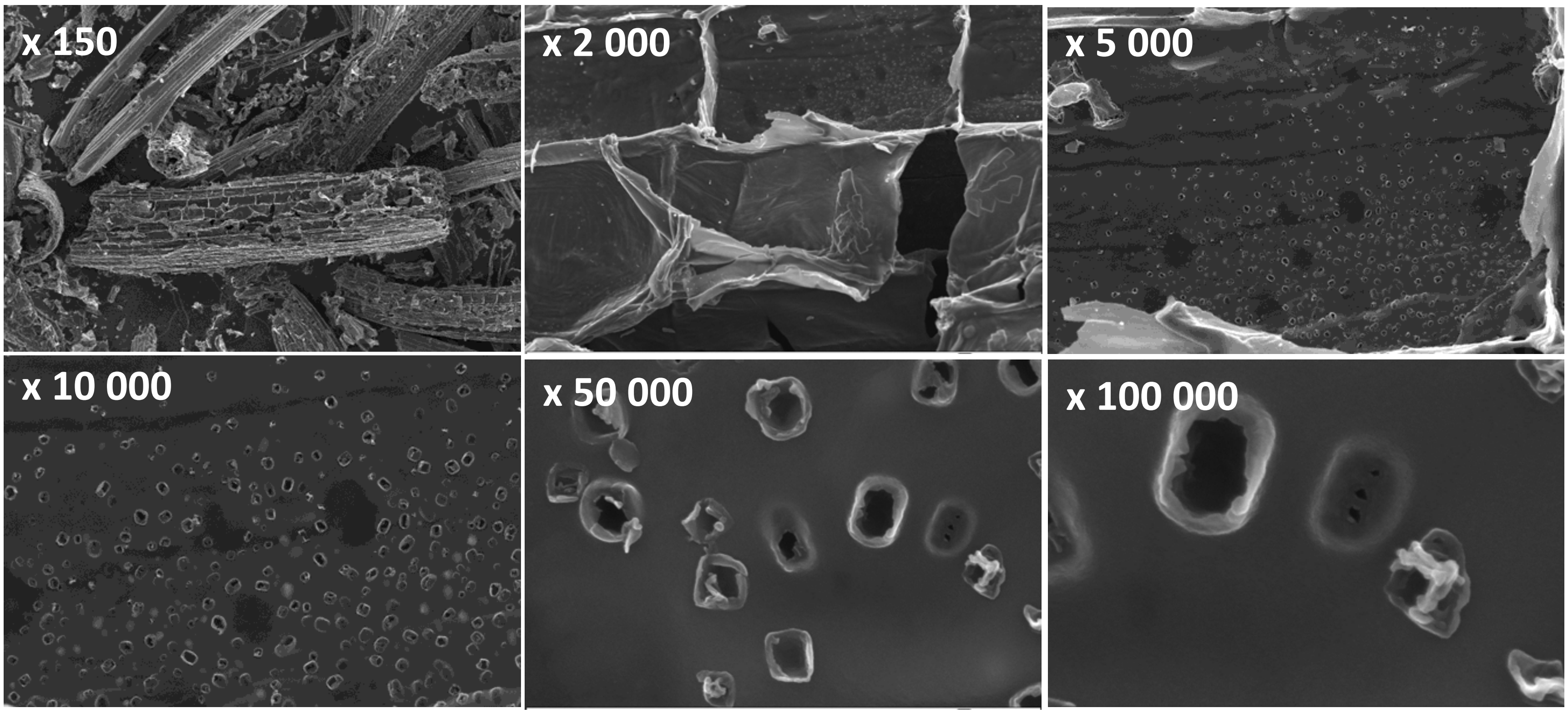
4. Results

SEM



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5. Conclusions

The results demonstrate the **potentiality of barley as precursor material** for the production of activated biochar, **improving the results** obtained in terms of **BET area** and **microporosity** developed to those obtained from other similar precursors with physical activation process (e.g. El-Hendawy et al. 2001, Fan et al. 2004, Aworn et al. 2008, Okutucu et al. 2011, Rambabu et al. 2015).

Reference	Precursor	Activation agent	S_BET (m2/g)	Vo (cm3/g)	Conversion (%)
THIS STUDY	**Barley**	**CO2**	**788**	**0.3495**	**13.86**
Savova et al. 2001	Almond shell	H_2O	998	0.4	17.8
Savova et al. 2001	Cherry bones	H_2O	875	0.28	11.2
Savova et al. 2001	Nut shell	H_2O	743	0.21	17.9
Lua et al. 2004	Pistachio shell	CO2	778	0.466	-
Girgis et al. 2002	Peanut shell	H_2O	253	0.079	27.0
Marciall et al. 2000	Almond shell	CO2 / H_2O	1005.7 - 1315.4	-	15.84 – 6.34
Fan et al. 2004	Corn	H_2O	311- 442	-	-
El-Hendawy et al. 2001	Corn	H_2O	607 - 786	0.296	8.7
Okutucu et al. 2001	Pistachio shell	CO2	588.6 – 708.6	0.293	-
Rambabu et al. 2015	Rape	H_2O	240 - 384	-	15.5 – 19.3
Rambabu et al. 2015	"	CO2	320 ± 8	-	-
Aworn et al. 2008	Corn	H_2O	423-651	-	-
Aworn et al. 2008	"	CO2	732-836	-	-

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THANK YOU VERY MUCH FOR YOUR ATTENTION

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