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Slow pyrolysis of lignin rich residue from lignocellulosic biorefining operations

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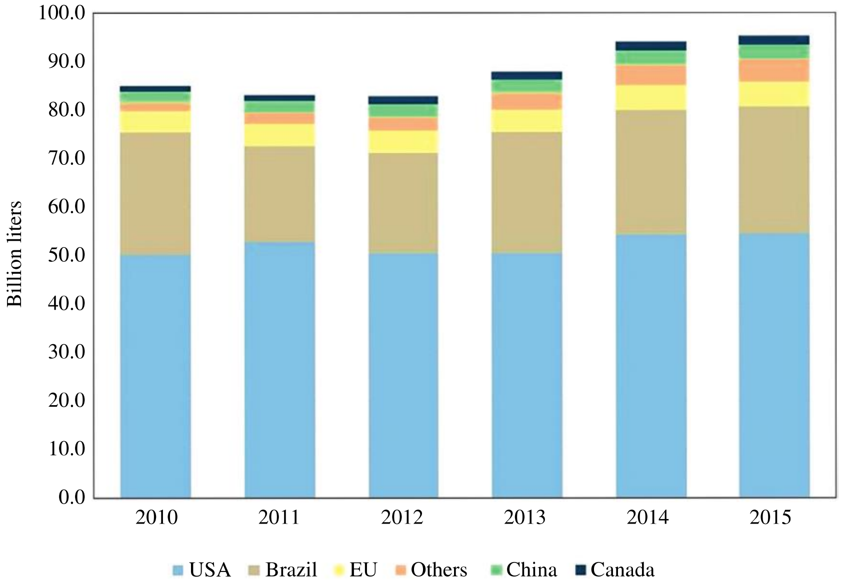
Lignin rich residue from bioethanol production

World 1st generation fuel ethanol producion

(ISO, 2014)



Research projects in EU

15 research project have been selected for EU funding and have signed a grant agreement with INEA by 30 June 2017.

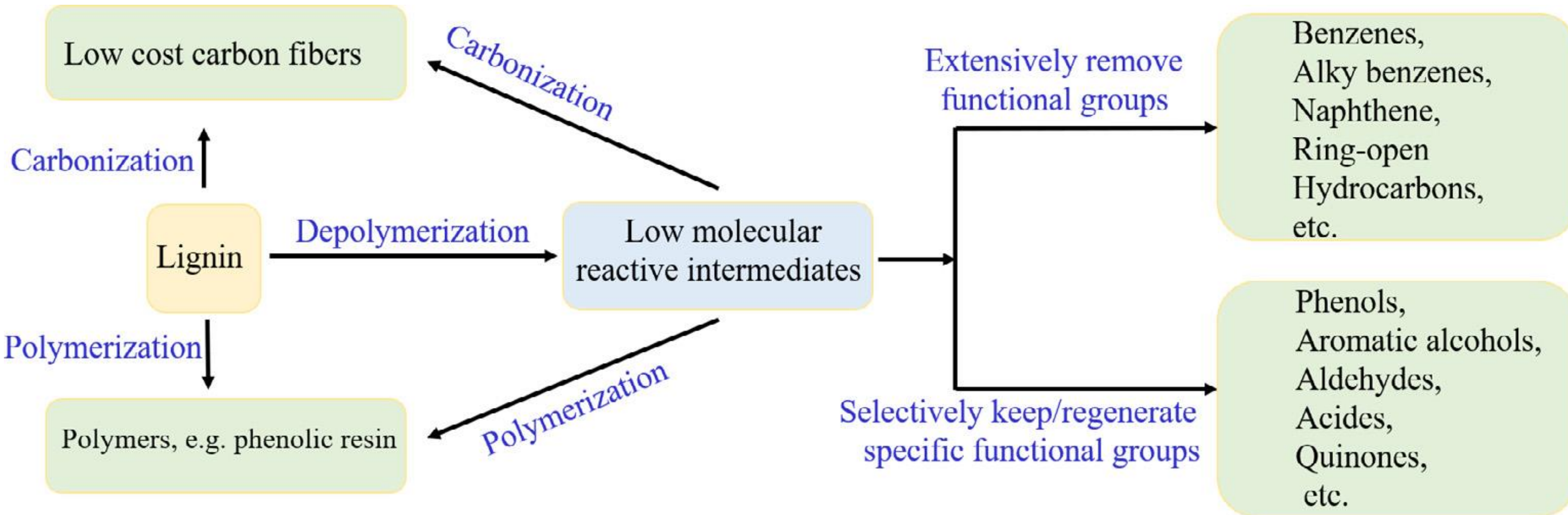
Commercial-Scale Cellulosic Ethanol Projects Using Sugar Platform *(AEC, 2012.)*

Location	Opening Year	Capacity/ Year Million Gallons (in Liters)	Feedstock
USA	2014	25 (95)	Corn stover, wheat straw and grasses
Italy	2014	20 (76)	Wheat straw
Brazil	2014	22 (83)	Sugarcane, straw
USA	2014	20 (76)	Corn stover and cobs
Brazil	2015	10 (38)	Sugarcane bagasse
USA	2015	25 (95)	Corn stover
USA	2015	10 (38)	Wheat straw
Canada	delayed	20 (76)	Hardwood and pulpwood
Denmark	2016	20 (76)	Wheat straw
USA	2016	20 (76)	Energy grass
USA	2017	25 (95)	Energy cane
Slovakia	2017	16.5 (62)	Wheat and rapeseed straw
Brazil	2017	16.9 (64)	Sugarcane bagasse

In 2018, with the acquisition of the production site of Crescentino, ENI consolidated the plan of producing bioethanol from biomass residues

ISO, 2014. Ethanol Year Book 2014. International Sugar Organization, London,

Strategies for lignin rich residue conversion



Wang et al., 2019. Bioresource Technology 271 (2019) 449–461

The ideal lignin isolation procedure requires

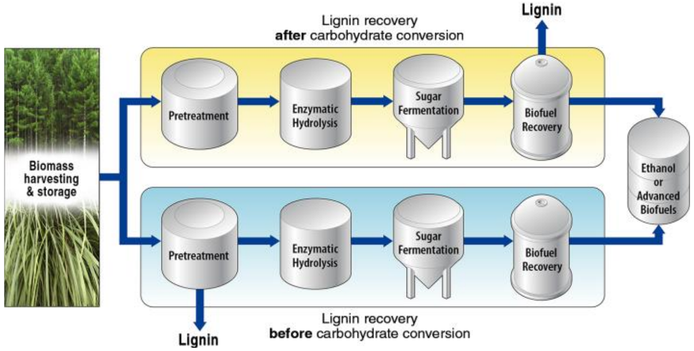
- high purity,
- high yield,
- low condensation of lignin structures.

High revenues but…high costs

The identification of catalysts that allow selective degradation/conversion of lignin under mild conditions is the most promising but still most challenging approach

Relaxing the lignin purity constrain

Lignin rich residue



Lignin rich residue

(Ragauskas et al., 2014)

Slow pyrolysis →

Liquid

Gas
(CO_2 , CO, CH_4, H_2)

CHAR

Agronomic application as nutrients source and carbon sequestration

Adsorbent of undesired species in fluid streams

Catalyst in AOP for wastewater treatment and anaerobic digestion process

Filler in polymer composites

…

‘**Char**’ stands for a wide range of carbonaceous products from biomass pyrolysis.

For some applications different biochars satisfying certain characteristics can produce similar effects.

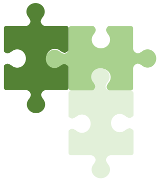
Literature background

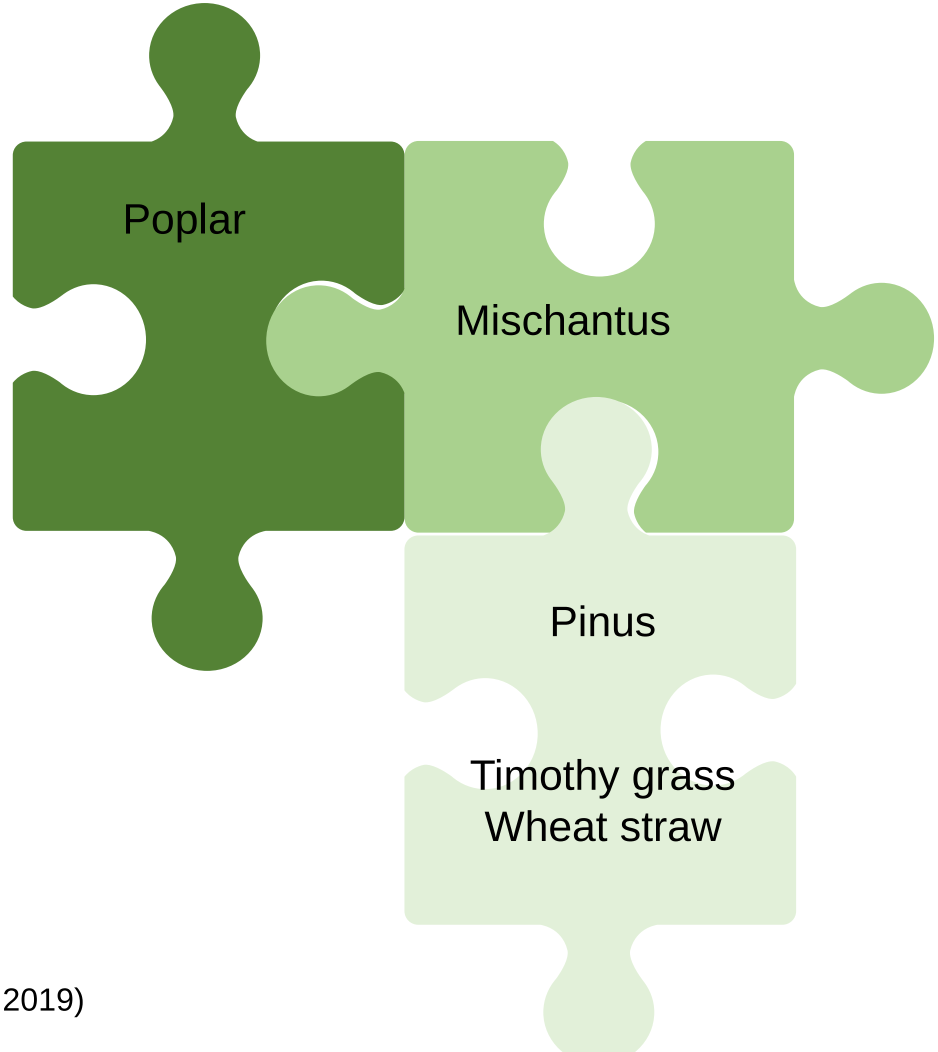
Fast pyrolysis of lignin/lignin rich residues for phenols recovery were widely studied.

Less work has been done on slow pyrolysis of lignin rich residue from bioethanol production

Few data are available referring to:

- **different raw biomasses**





(F. Melligan et al., 2012; Nanda et al., 2014; Ghysels et al., 2019)

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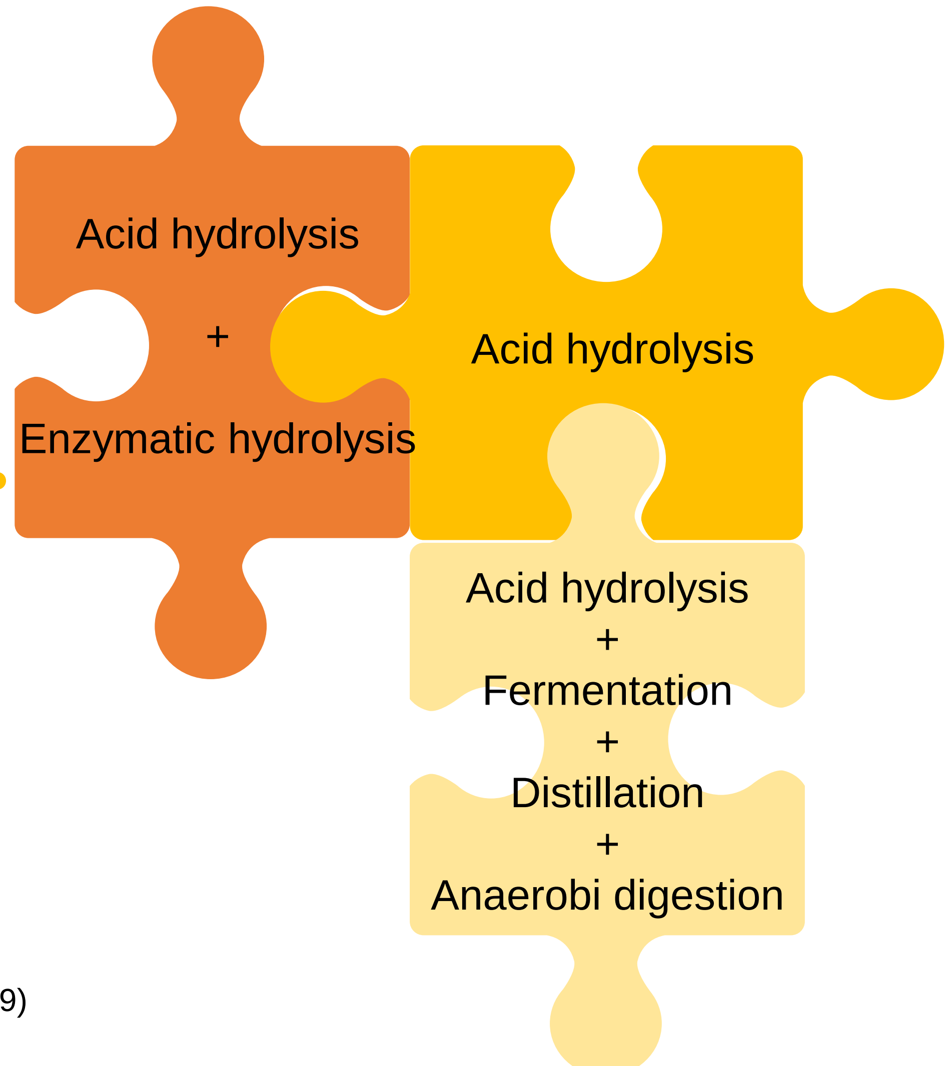

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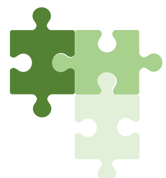
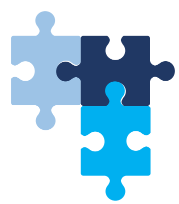
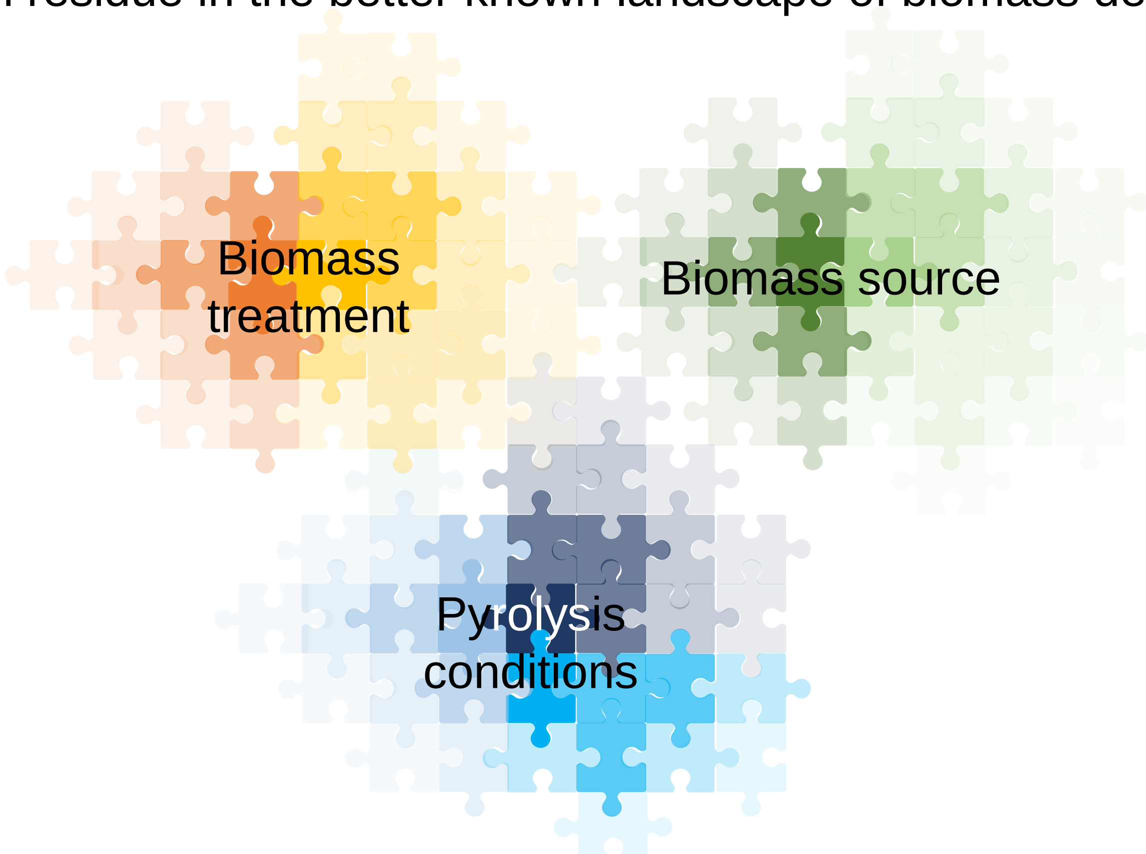
- **different raw biomasses** 
- **different bioethanol production processes** 
- **different pyrolysis conditions** 

(F. Melligan et al., 2012; Nanda et al., 2014; Ghysels et al., 2019)

Aim of the work

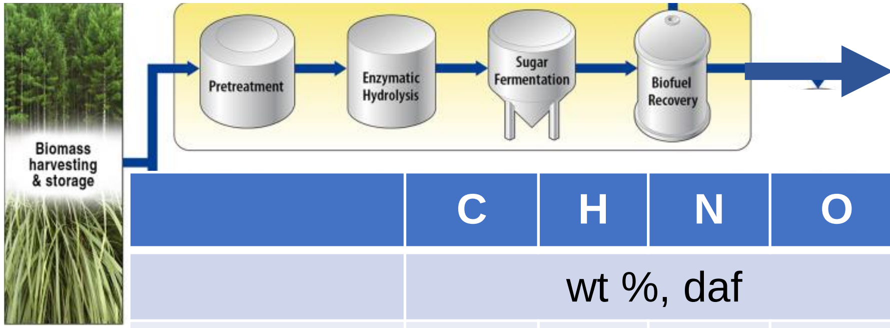
To expand the knowledge on the characteristics of the chars from the slow pyrolysis of lignin rich residue in the better known landscape of biomass derived chars



- The feedstock was characterized and the effect of different pyrolysis temperatures on the char quality and quantity was analyzed and quantified

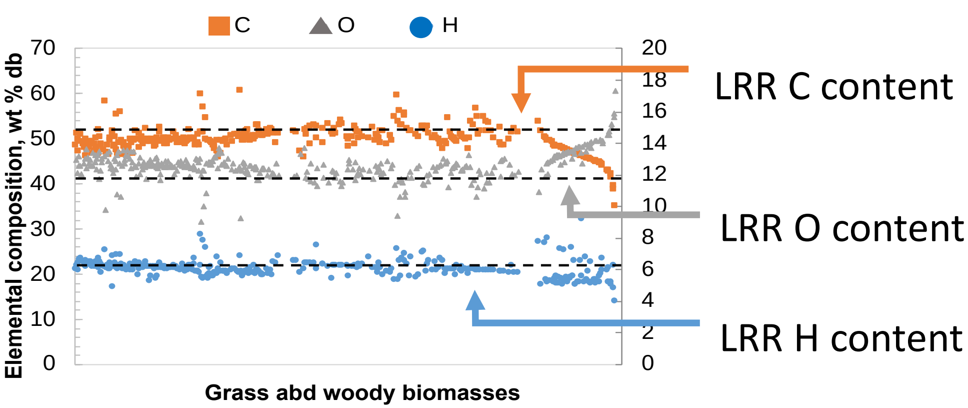
- Comparison with chars obtained in the same conditions from raw biomasses

Feedstock



Lignin Rich Residue

	C	H	N	O	Volatiles	Fixed carbon	Ash
	wt %, daf				wt %, db		
LRR	52.1	6.2	0.3	41.3	69.6	22.4	8
Alkali lignin	65.0	5.9	n.d.	29.1	49.9	40.1	10
Arundo donax	47.6	5.8	0.1	46.1	75.8	17.4	6.8



	LRR	Arundo donax
Extractives, wt%, db (H_2O, EtOH)	31.8	6.5
Klason lignin, wt%, db	56.0	19.7

Na	K	Ca	Mg	P
ppm, db				
142	6875	1791	302	804

Experimental set-up

Thermogravimetric analysis

Final temperature: **700 °C**

Heating rate: **5 °C/min**

Carrier gas: **N_2**

Operating conditions in the pyrolysis tests

Final temperature: **300-700 °C**

Heating rate: **5 °C/min**

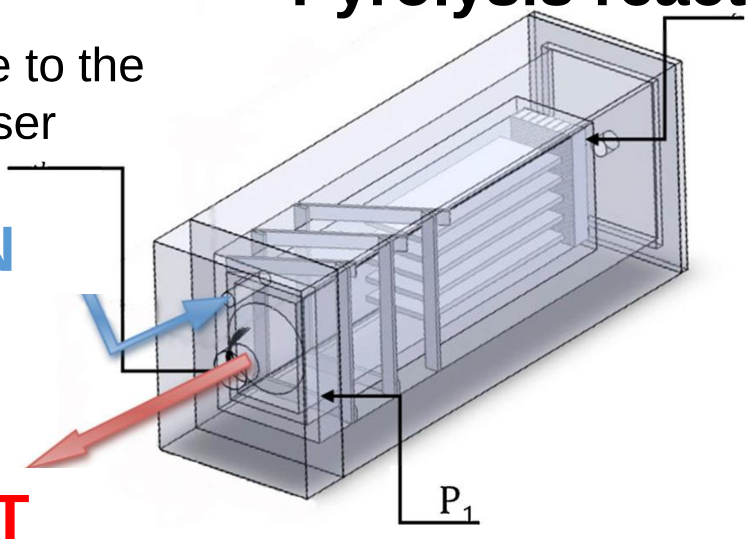
Carrier gas: **N_2**

Gas sampling
Online GC/TCD analysis

Vapor phase to the condenser

Pyrolysis reactor

Carrier gas IN



Carrier gas OUT

Feedstock characteristics

Amount: 6 g

Size: <600 μm

Sample height on the tray = 0.1 cm

IN

OUT

Experimental procedures

Determination of products yields and composition

Gas: construction of releasing rate curves starting from micro GC/TCD analysis performed every 120 s

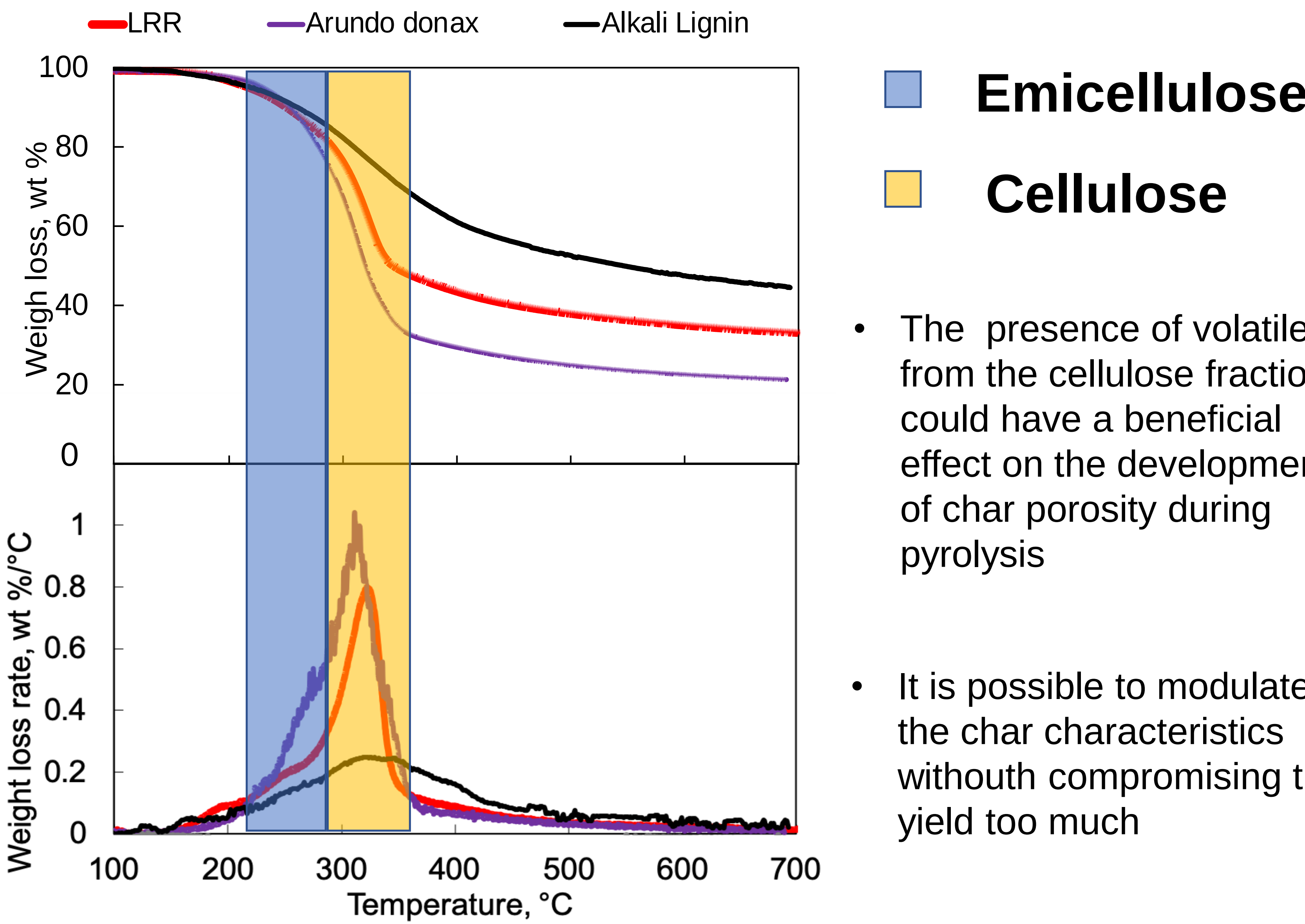
- Column 1: Molsieve 5A to detect H_2, O_2, N_2, CO, CH_4.
- Column 2: Plot U to detect CO_2, C_2H_4, C_2H_6.

Char: gravimetrically with respect to the feedstock.

- pH (deionized water 1:20 wt/wt - ASTM D4972-13)
- N_2 adsorption porosimetry
- Elemental analysis (CEN/TS 15104)
- Proximate analysis (ASTM E870)
- ICP/MS analysis
- Scanning Electron Microscopy

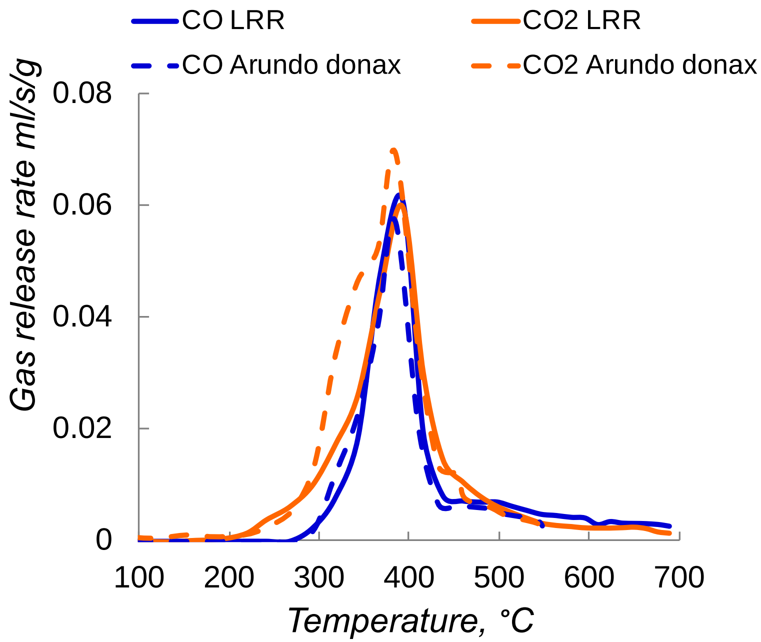
Liquid: amount needed to complete the mass balance.

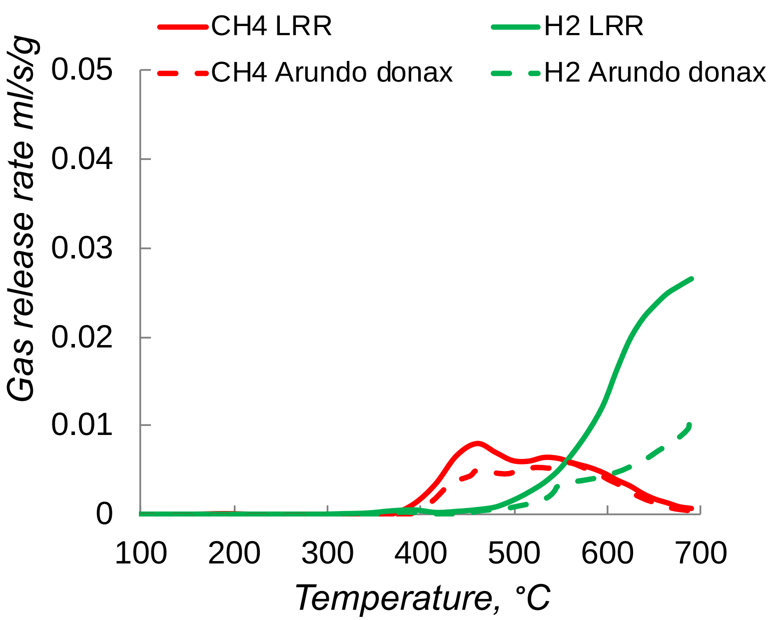
Understanding the thermal behavior of LRR

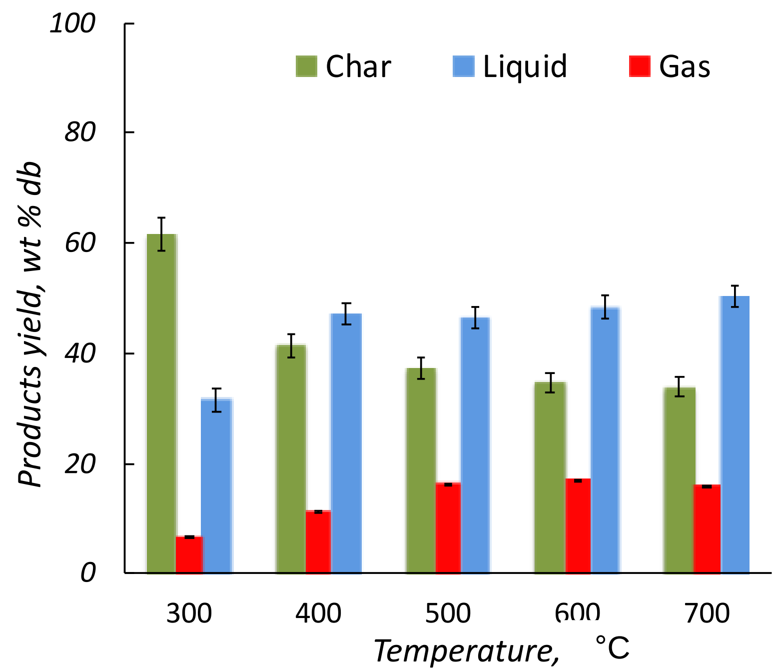


- The presence of volatiles from the cellulose fraction could have a beneficial effect on the development of char porosity during pyrolysis
- It is possible to modulate the char characteristics withouth compromising the yield too much

Products yield and gas release rate







Differently from the majority of the biomasses CO and CO_2 are produced in similar amounts because of the low amount of hemicellulose in LRR sample

Char composition: *Elemetal and proximate analysis*

	Temperature, °C				
	300	**400**	**500**	**600**	**700**
C, wt % db	58.5	63.6	69.4	69.8	71.6
H, wt % db	4.6	3.2	2.4	1.7	0.9
N, wt % db	0.5	0.4	0.4	0.4	0.4
O, wt % db	23.6	15.1	6.5	6.0	4.5
H/C	0.94	0.60	0.41	0.29	0.15
O/C	0.30	0.18	0.07	0.06	0.05
Moisture, wt%	2.4	4.2	4.3	3.1	3.6
Volatiles, wt%	47.4	26.9	17.2	13.7	10.6
Fixed Carbon, wt%	37.8	51.8	58.1	61.7	64.1
Ash, wt%	12.5	17.0	20.4	21.5	21.8

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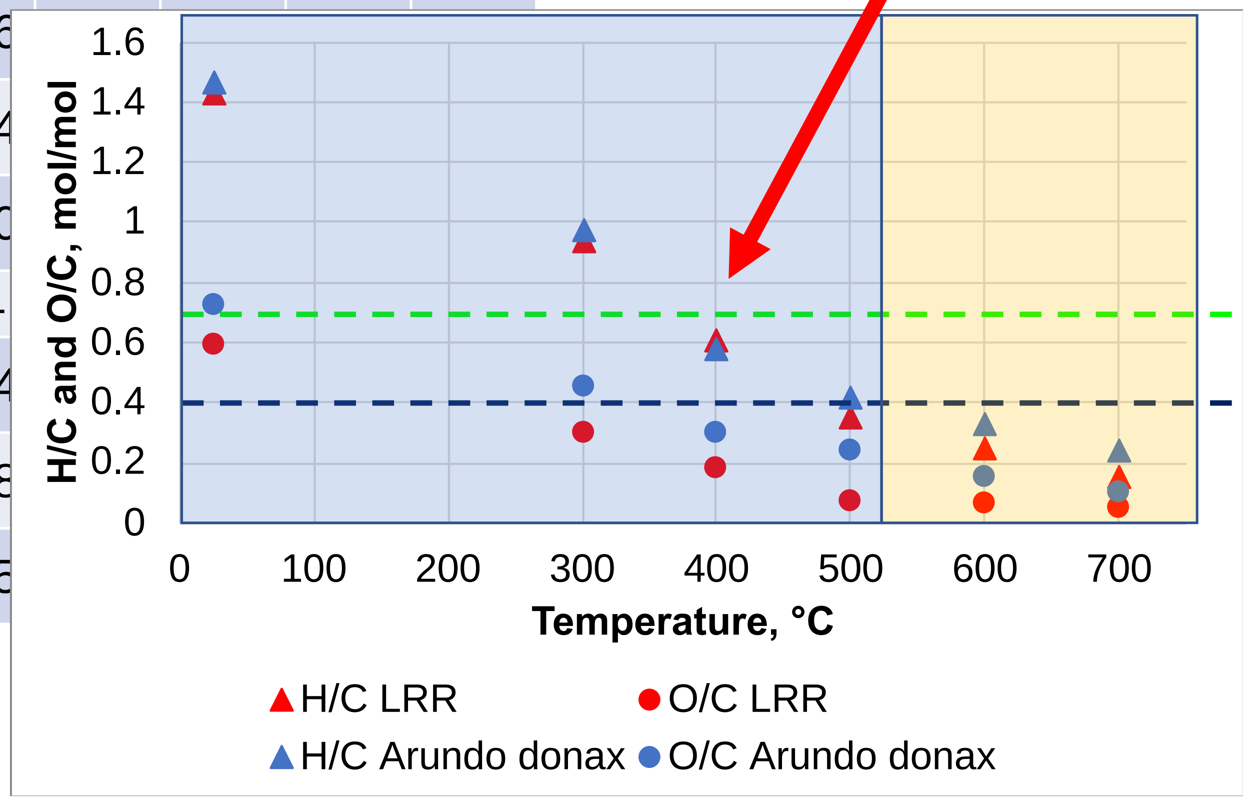
Moisture, wt%	2.4				
Volatiles, wt%	47.4				
Fixed Carbon, wt%	37.8				
Ash, wt%	12.5				

H/C

O/C

Limits for the application of biochar in soils
(IBI and EBC standards)



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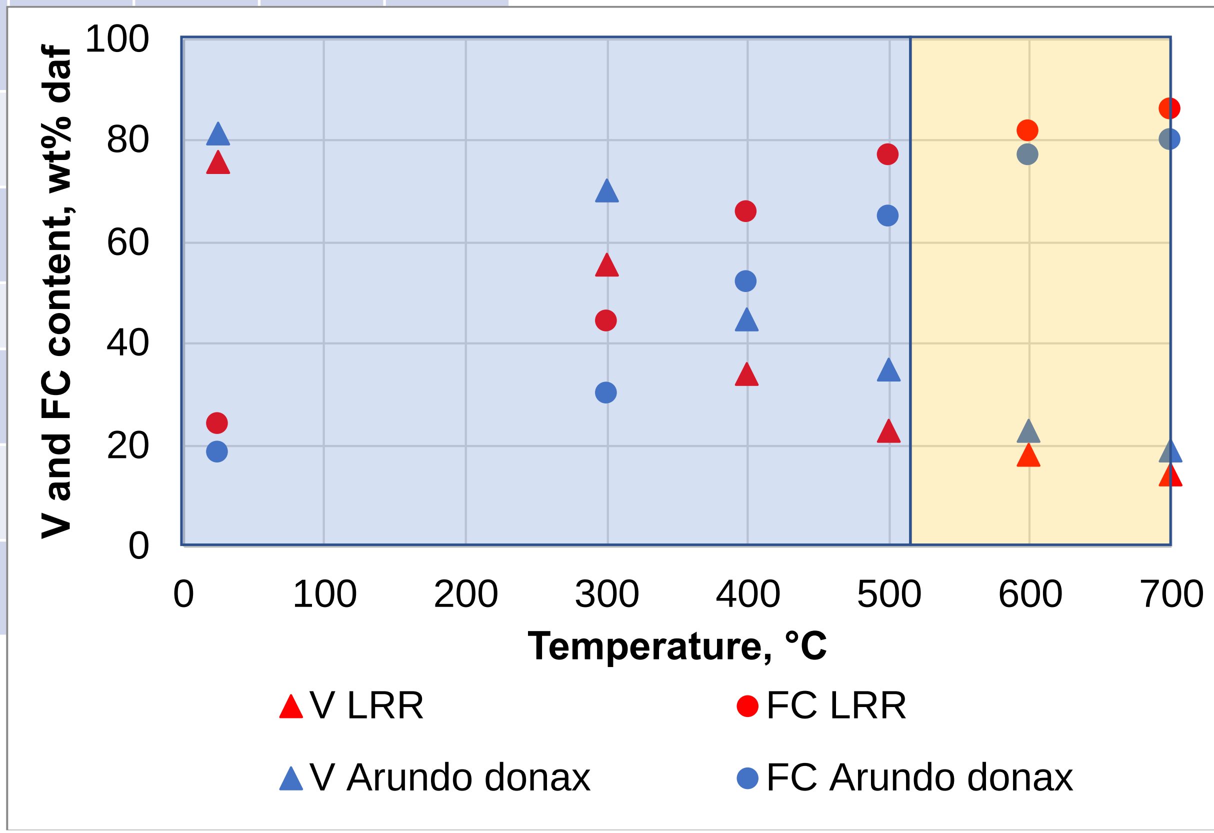
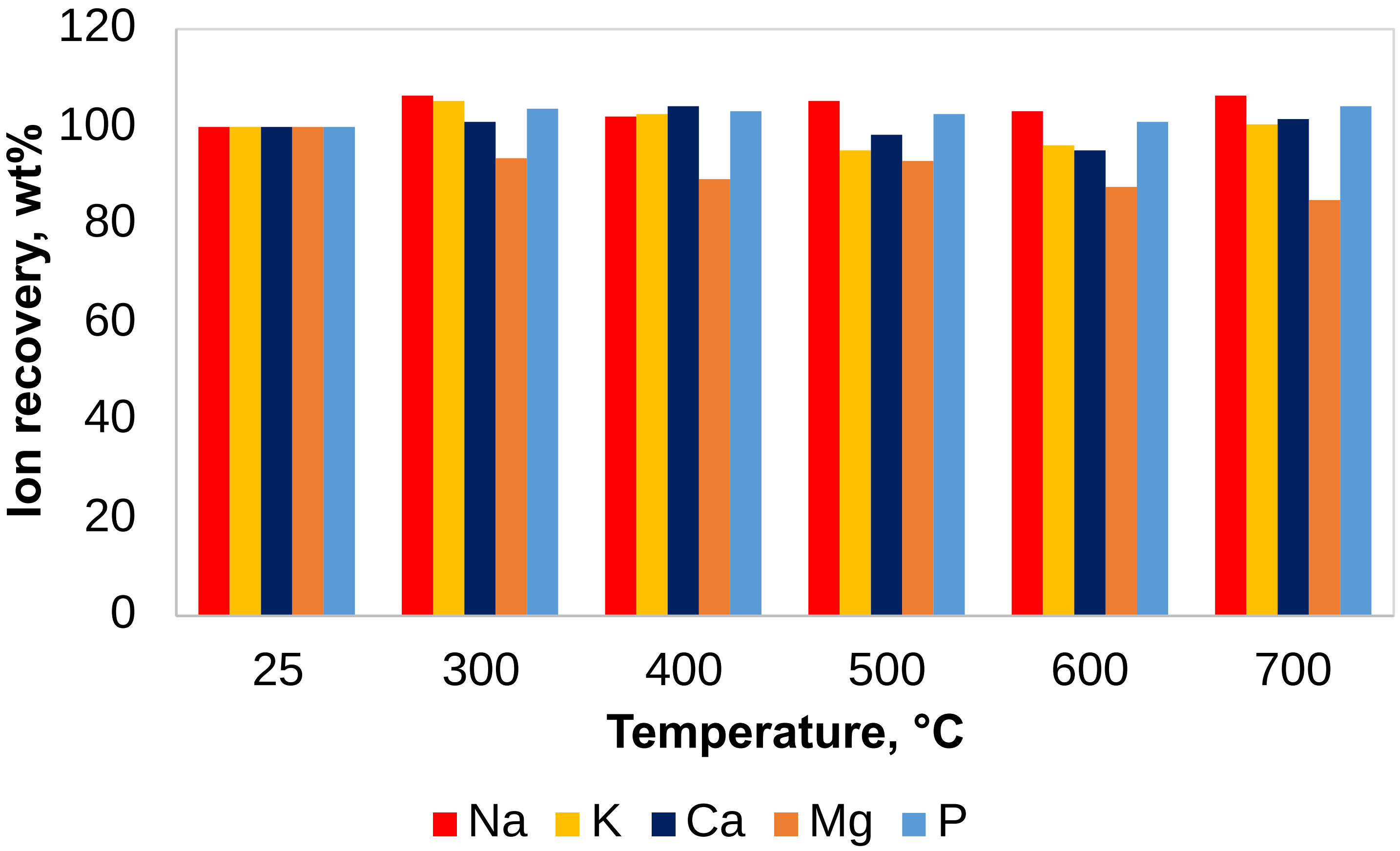
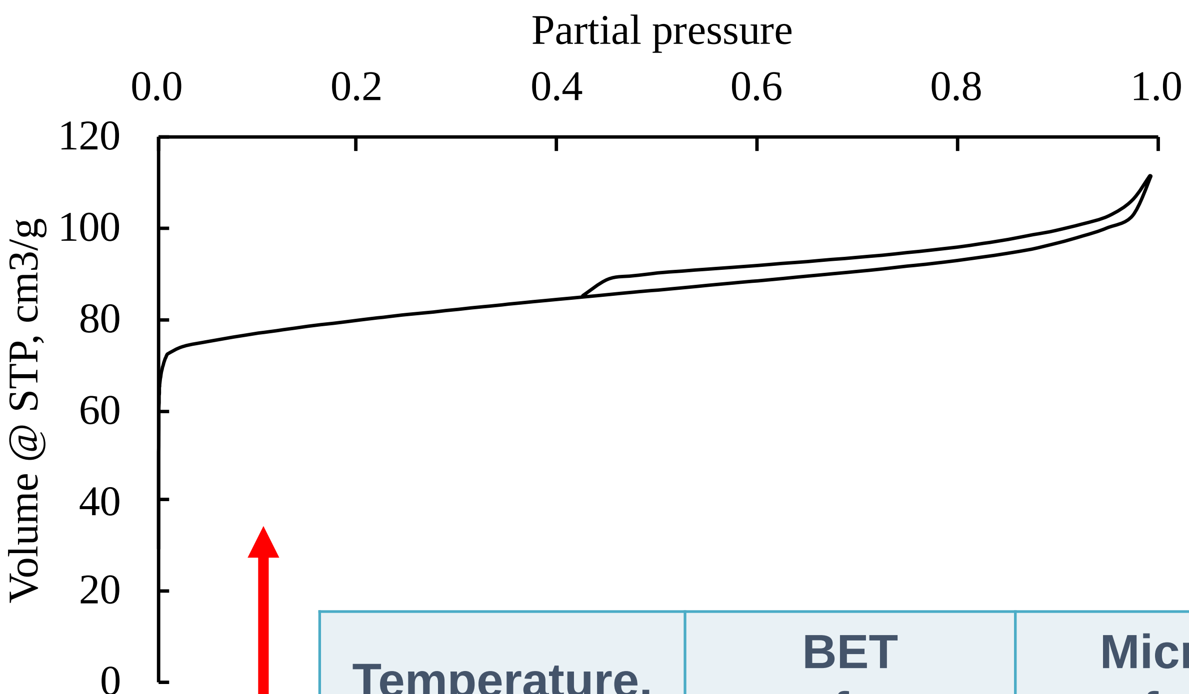


Char composition: *inorganics distribution and pH*



	Temperature, °C					
	25	**300**	**400**	**500**	**600**	**700**
pH	5.9	7.8	9.9	9.9	10.0	10.1

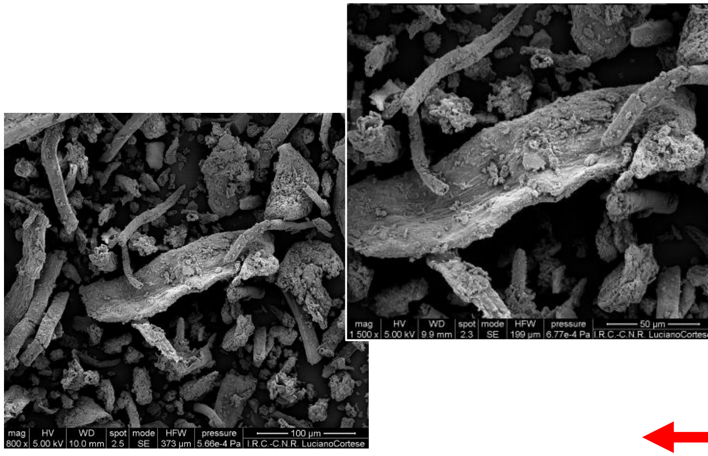
Char structure: *porosimetry*



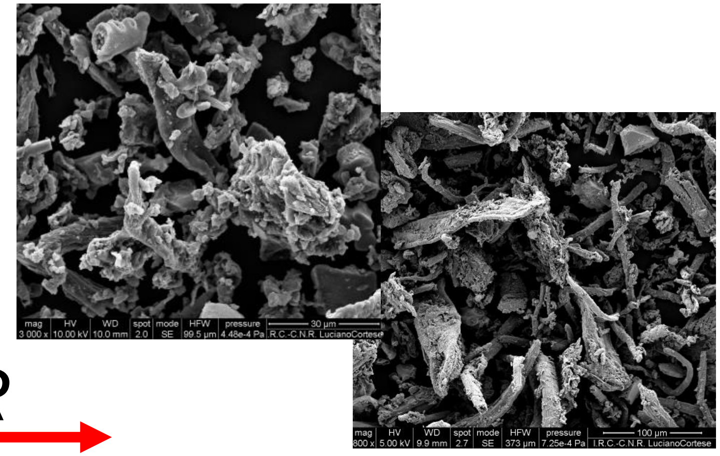
Temperature, °C	BET surface, m^2/g	Micropore surface area, m^2/g	Total pore volume, cm^3/g
300	2.5	0.2	0.010
400	5.5	2.1	0.032
500	126.7	91.4	0.044
600	289.6	135.2	0.170
700	124.3	77.8	0.172

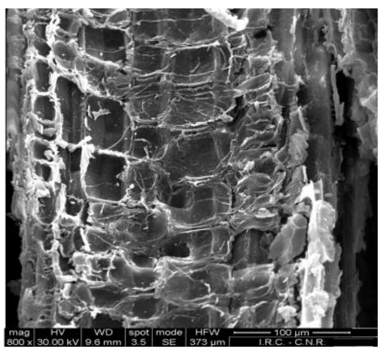
Char structure: *SEM*

Raw biomass | *Char at 600 ° C*

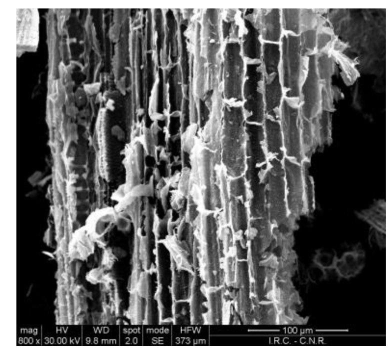


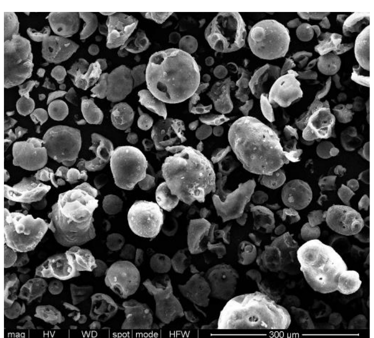
LRR



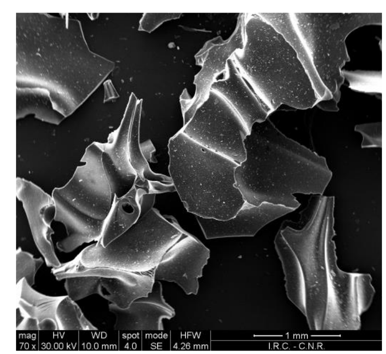


Arundo donax





alkali lignin



Conclusions and perspectives

LRR still contains high amounts of cellulose and ash

The thermal behaviour of LRR residues is very different from the one of alkali lignin typically used as reference compound for biomass lignin.

The produced chars meet the International Biochar Initiative and European Biochar Certificate standards ($H/C_{org}<0.7$ and $O/C_{org}<0.4$), even at low temperature when biochar yield is still high

pH cannot be easily modulated by increasing the pyrolysis temperature

The main inorganics are retained in the chars even at high pyrolysis temperature but their bioavailability should be assessed

The porous character of the chars encourages to test their potential in applications involving surface phenomena: we are currently testing the chars for the synthesis of polymer composite with electrical properties