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BIOSCIENCE ENGINEERING

DEPARTMENT - GREEN CHEMISTRY AND TECHNOLOGY
RESEARCH GROUP - THERMOCHEMICAL CONVERSION OF BIOMASS

PRODUCTION OF BIOCHAR AND ADVANCED CARBON MATERIALS BY TECHNICAL LIGNIN PYROLYSIS

Frederik Ronsse, Stef Ghysels

4th Asia Pacific Biochar Conference (APBC 2018): Advances in Biochar Research & Applications

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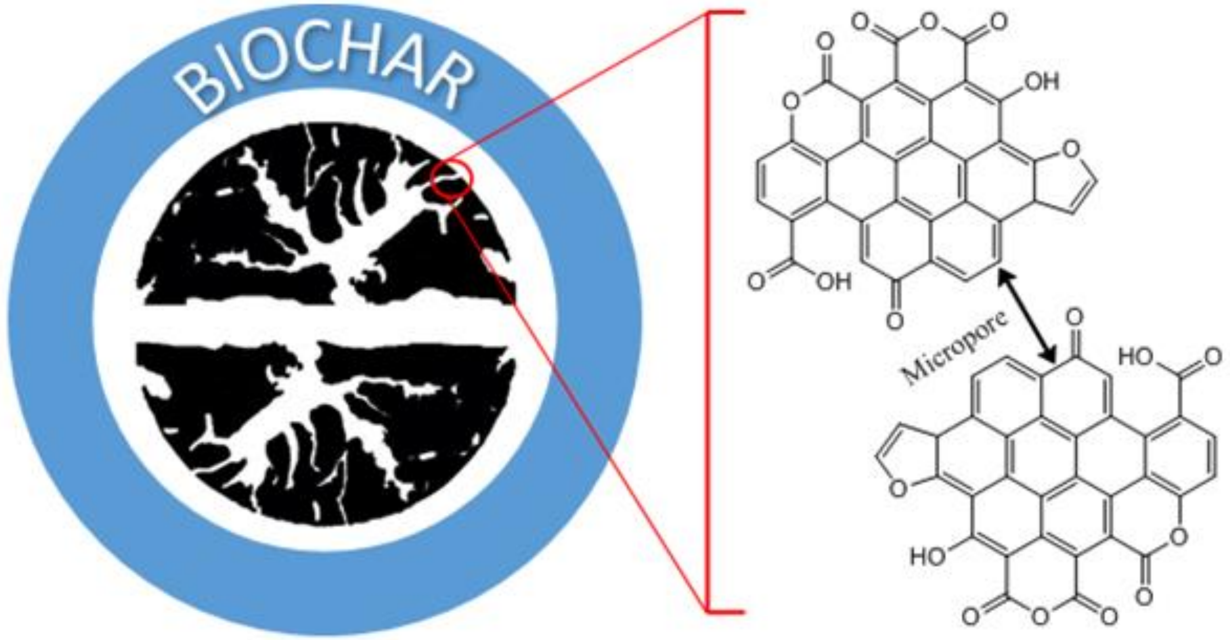
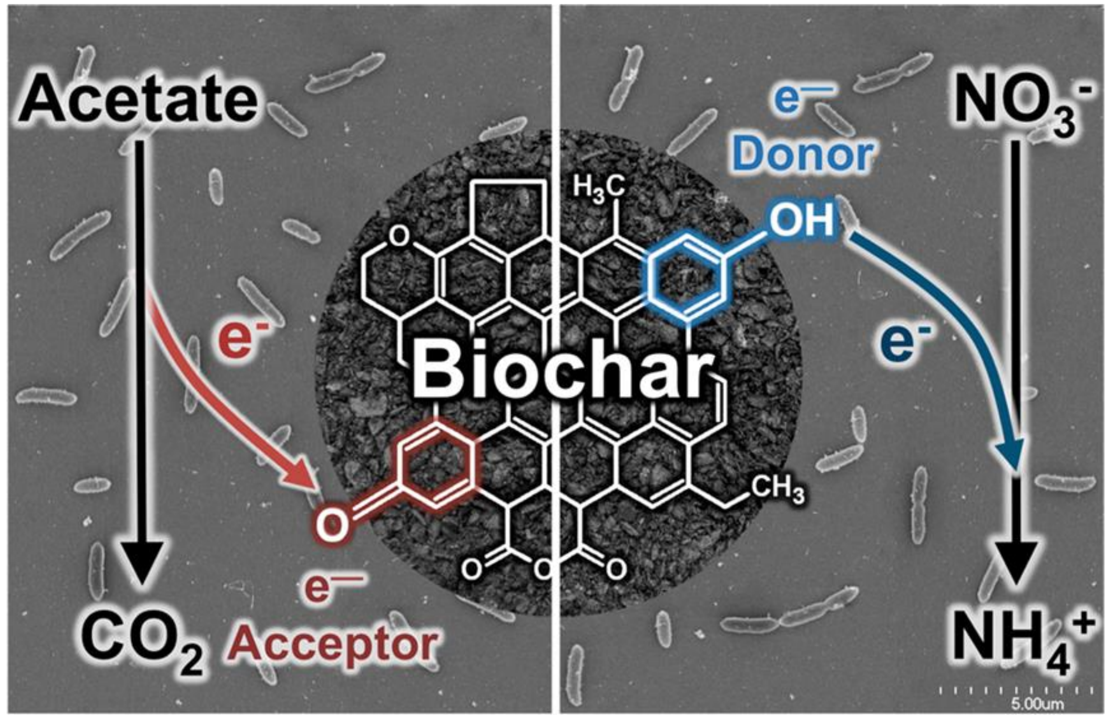
BIOCHAR AND ADVANCED CARBON MATERIALS

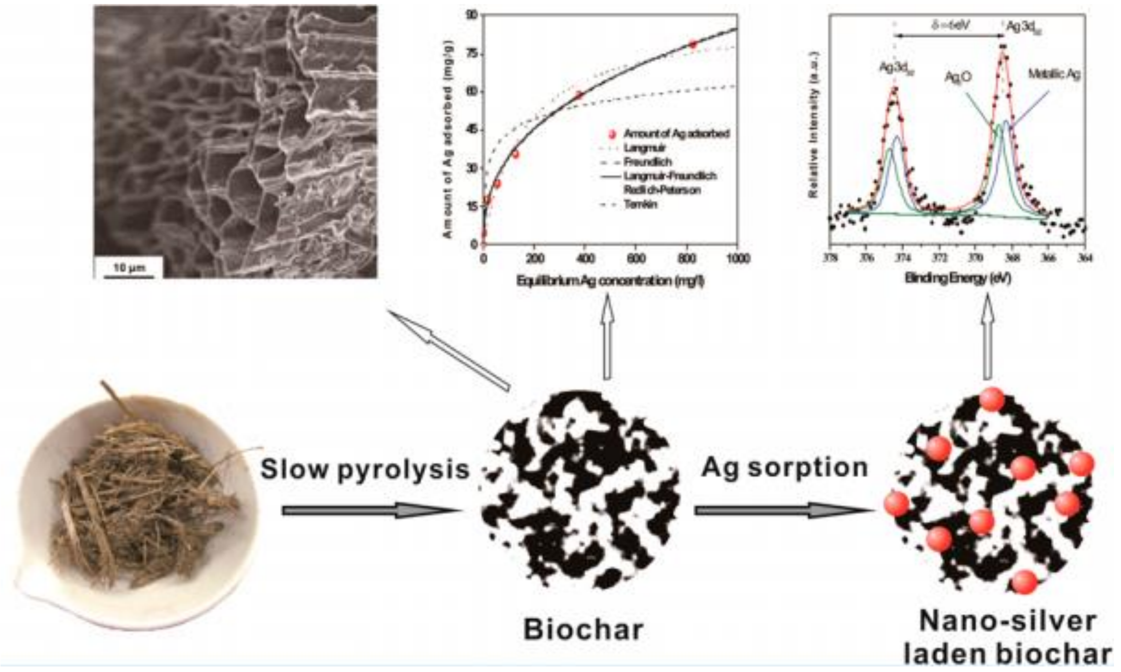
BIOCHAR IS A UNIQUE MATERIAL

- Highly porous
- Highly functional
- Biocompatible
- Redox-active
- (Photo)Catalytically active
- Has persistent free radicals

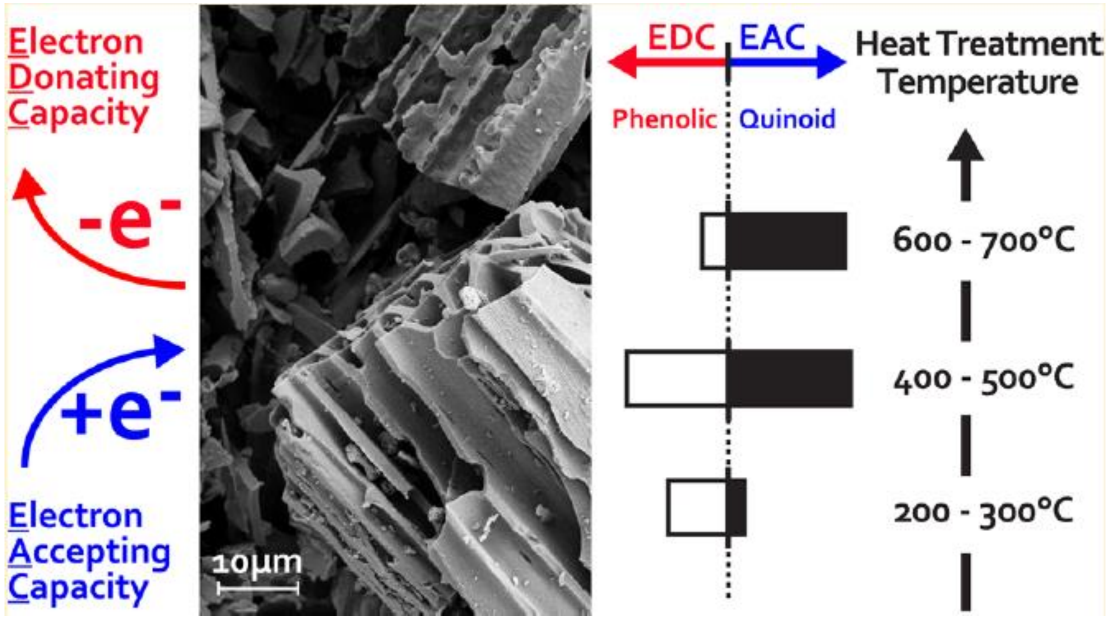




(Environ. Sci. Technol. Lett. 2016, 3, 62–66)



(ACS Appl. Mater. Interfaces 2015, 7, 10634−10640)



(Environ. Sci. Technol. 2014, 48, 5601–5611)

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OUR ONGOING BIOCHAR RESEARCH

- Advanced analysis of biochar chemistry:
  - Raman spectroscopy
  - XPS spectroscopy
- Electrochemical characterization of biochar
  - Electron donating/accepting capacity
- Development and validation of a comprehensive pyrolysis/carbonisation model
- Biochar stability testing

TECHNICAL LIGNIN

TECHNICAL LIGNIN: A BIOREFINERY SIDE STREAM

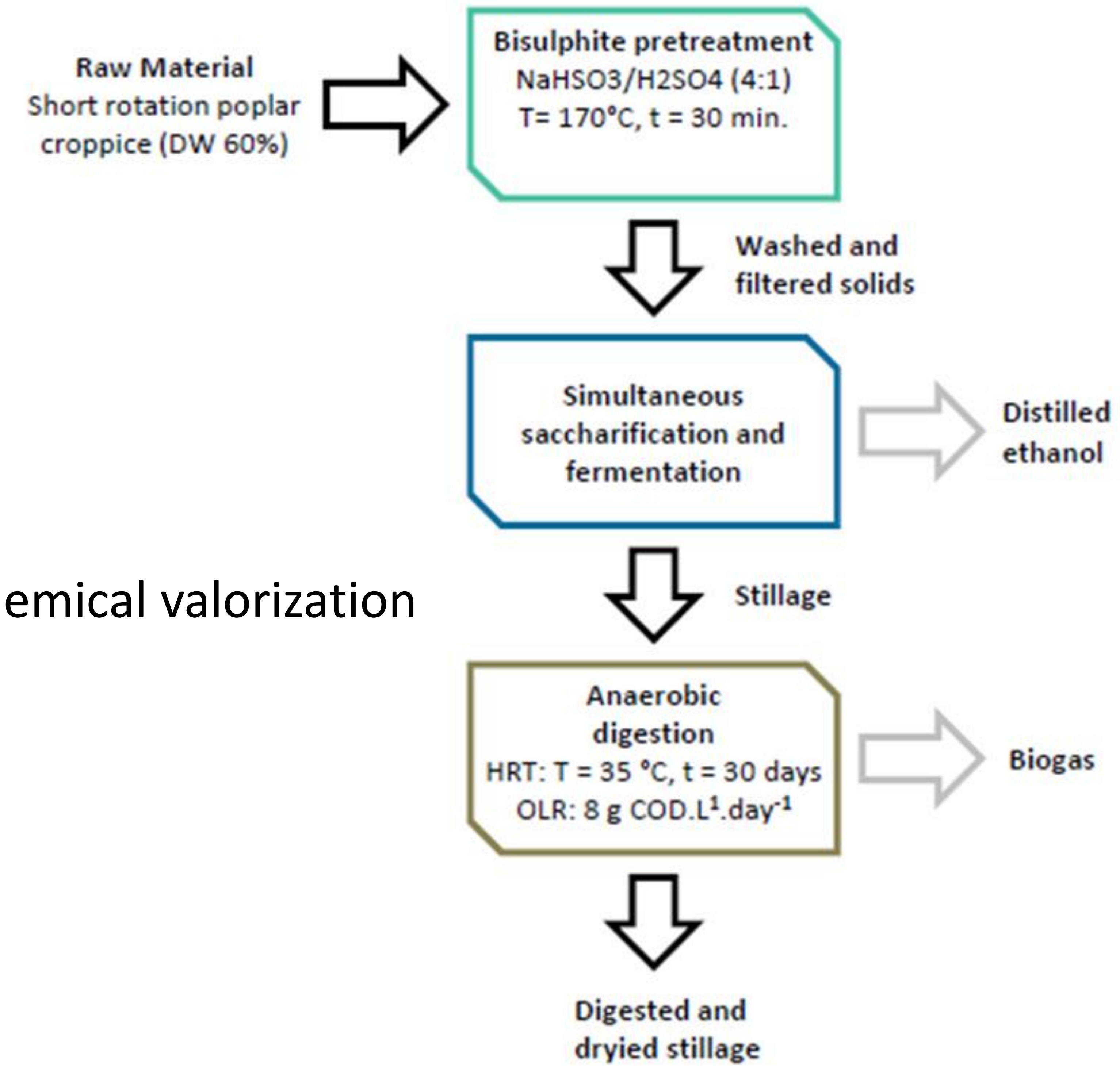
- Technical lignin evolves from any process in which the carbohydrate fraction of biomass is converted to value-added compounds
- In pursuing carbohydrate-valorization schemes, many biomass fractionations have been developed

Fractionation	Technical lignin
72% sulfuric acid	Klason lignin
Na_2S/NaOH	Kraft lignin
Extract lignin from waste liquor of the sulfate pulping process of soft wood.	Lignosulfonate
Using organic solvents to extract lignin.	Organosolv lignin
Hydrolysis of cellulose, leave lignin as a residue	Cellulolytic enzyme lignin

- Technical lignin is poorly valorized into value-added compounds, compared to the carbohydrate fraction

LIGNIN-RICH DIGESTED STILLAGE: A NOVEL TYPE OF TECHNICAL LIGNIN

- Lignin-rich digested stillage (LRDS) is a non-conventional form of technical lignin
- Integrated fractionation and valorization:
  - $Na_2S/NaOH$ pulping
  - Saccharification and fermentation
  - Digestion of the stillage residue
  - → Lignin-rich digested stillage
- Digested dried stillage (LRDS) as feedstock for thermochemical valorization



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LIGNIN-RICH DIGESTED STILLAGE: A NOVEL TYPE OF TECHNICAL LIGNIN

- Higher heating value is 20.06 $\pm$ 0.1 MJ/kg a.r.
- Klason lignin composition: 63.2 $\pm$ 0.7 wt% d.b.
- Compared to straw:
  - LRDS: ↑ C, N, S, ash and fixed carbon
  - LRDS: ↓ O, volatile matter
- S increased because bisulphate pretreatment
- N increased because microbial biomass
- C & O: lignin is richer in C, poorer in O
- Ash (nutrient) retain in the lignin fraction

Element	Conc. mg/kg	Element	Conc. mg/kg
Ag	<1	Ga	18
Al	1440	In	<1
B	6	K	150
Ba	30	Li	1
Bi	<1	Mg	1130
Ca	8230	Mn	62
Cd	<1	Na	24
Co	<1	Ni	13
Cr	7	Pb	7
Cu	2	Sr	23
Fe	3320	Tl	<1
		Zn	557

Feedstock characterization		
Feature	LRDS	Straw
Elemental analysis [wt% d.b.]		
Carbon	49.52	45.09
Hydrogen	5.43	5.31
Nitrogen	2.32	0.45
Sulfur	0.32	0.01
Oxygen	33.49	46.73
Proximate analysis [wt% d.b.]		
Moisture (on wet basis)	7.3	7.1
Volatile matter	58.32	83.11
Ash	8.19	2.41
Fixed carbon	25.57	7.38

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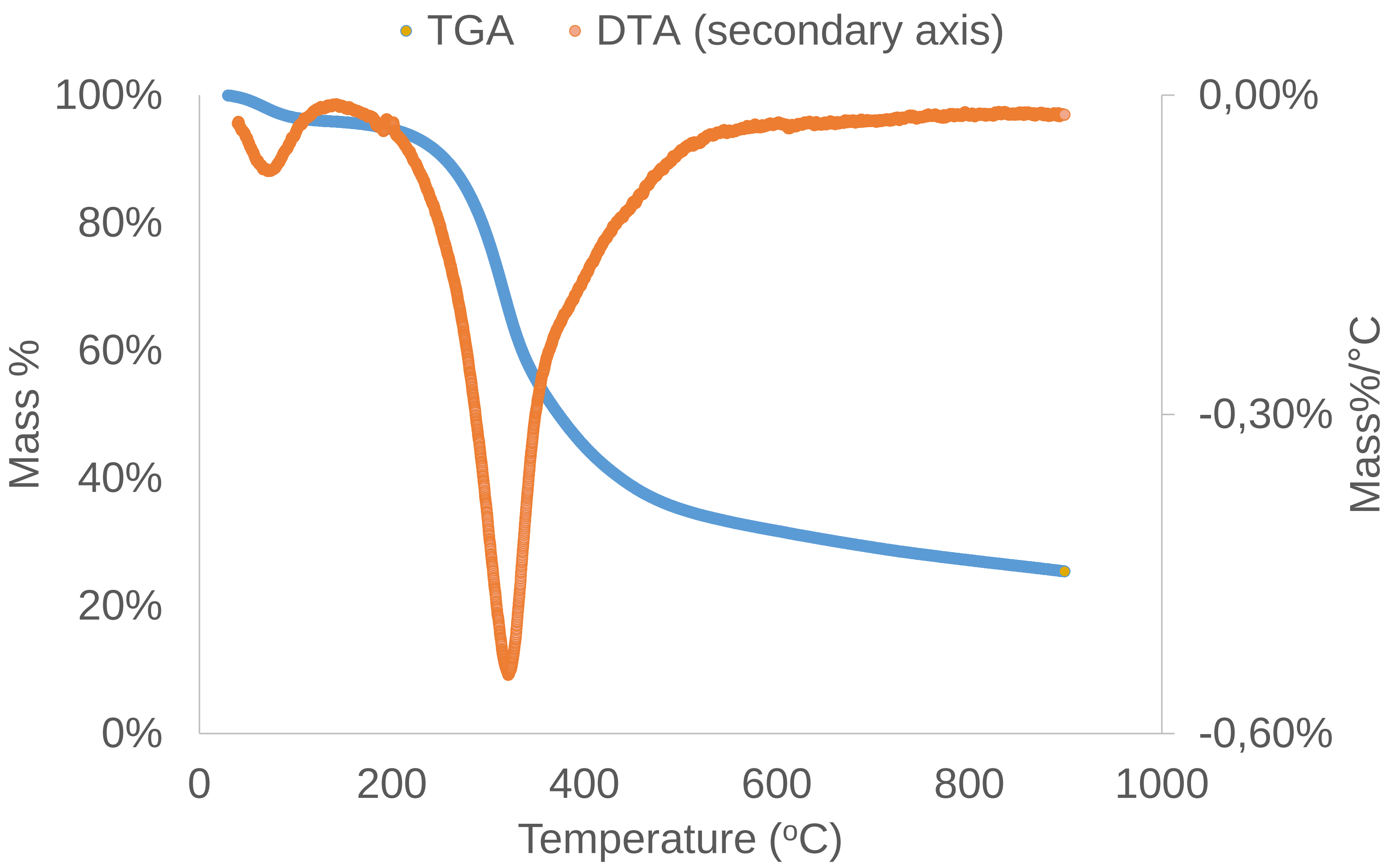
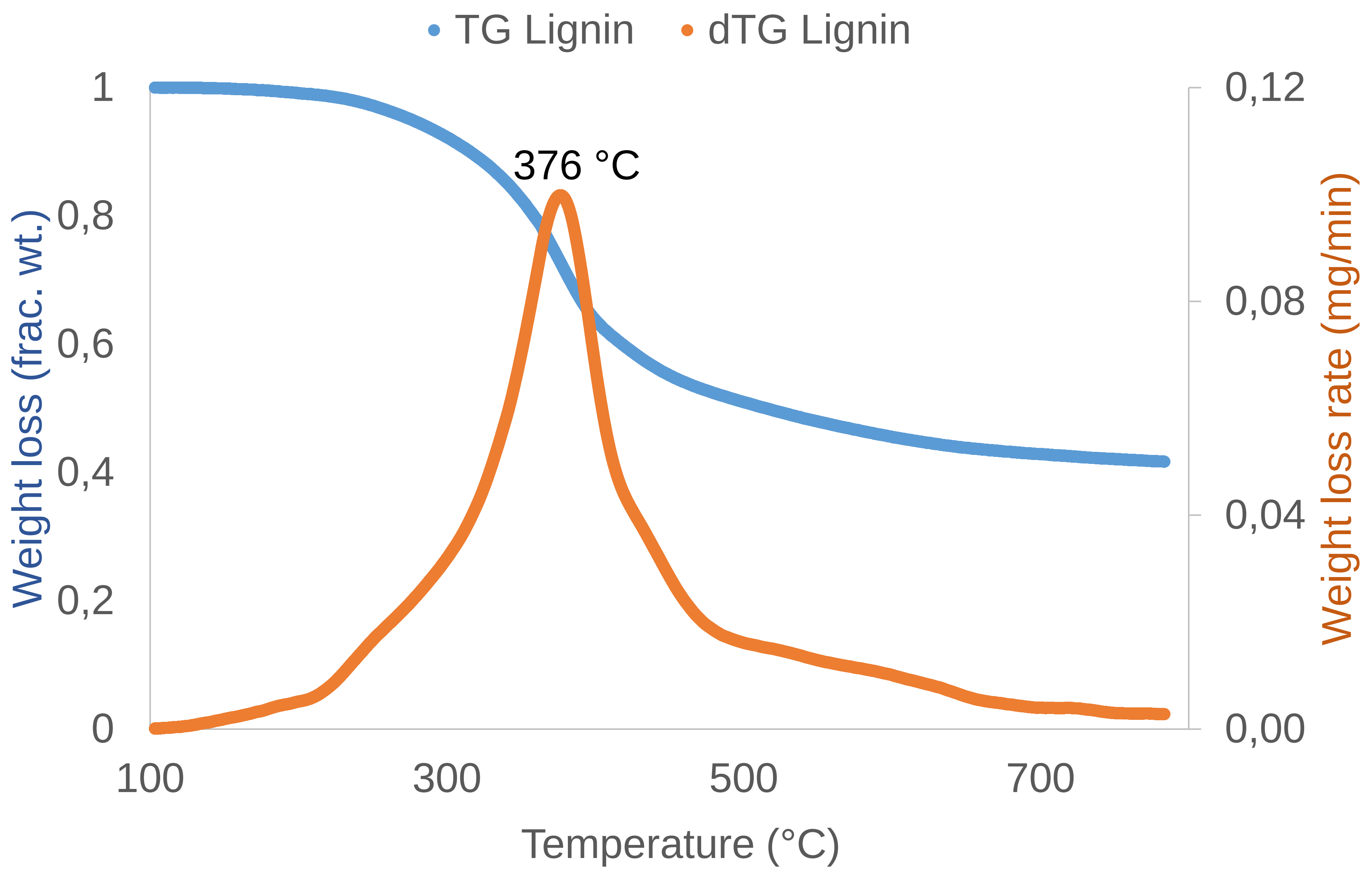
THERMOCHEMICAL VALORIZATION POTENTIAL OF LRDS

- Lignin-rich digested stillage reaches higher volatilization (less residual mass) compared to Organosolv lignin (closed to native lignin)





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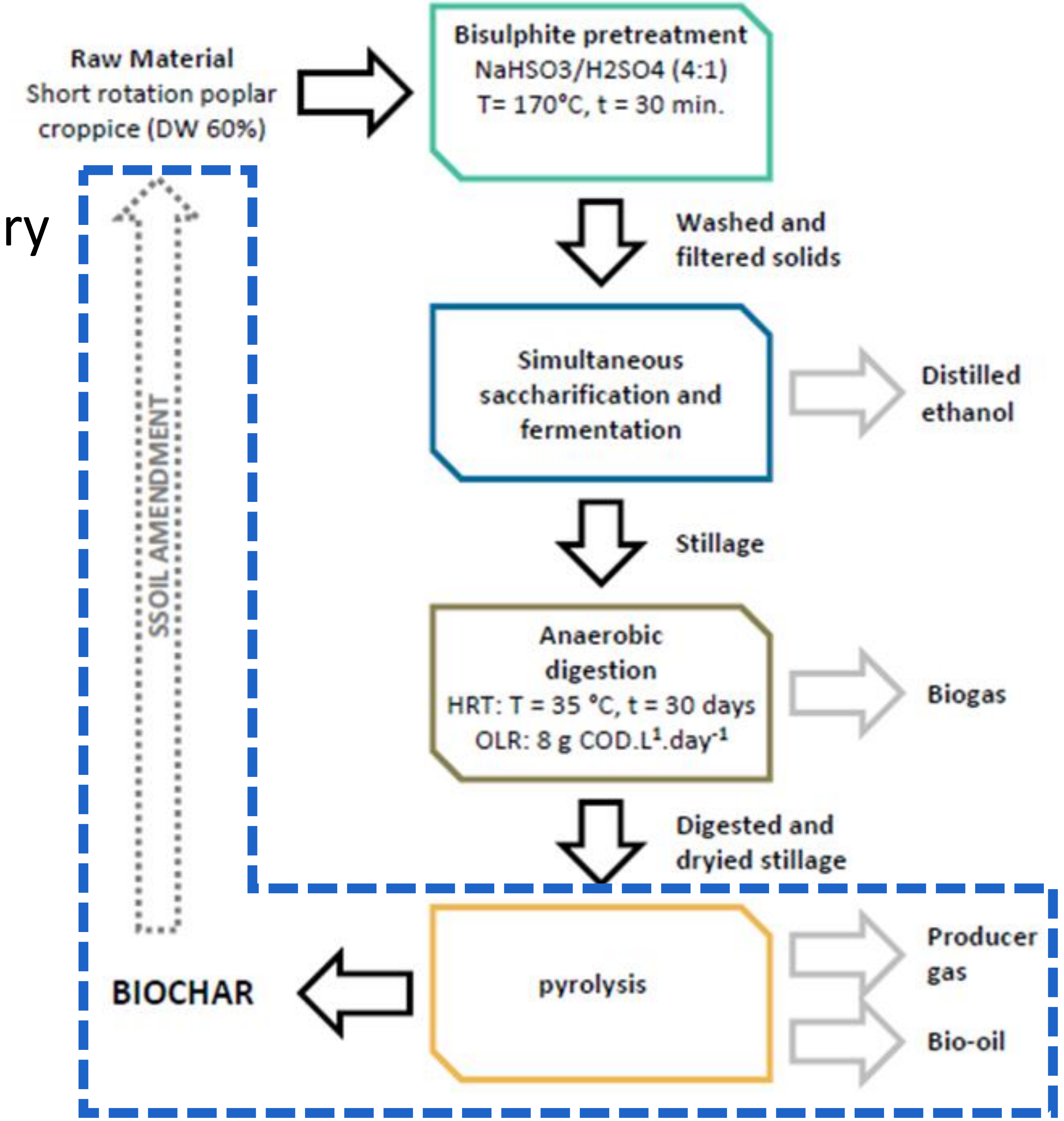
THERMOCHEMICAL VALORIZATION POTENTIAL OF LRDS

- Although LRDS achieves a higher volatilization, compared to Organosolv lignin, both lignin types tend to form relative high amount of solid residue
- Biochar production by fast pyrolysis and slow pyrolysis
- Mutual goal: nutrient recycling to sustain the proposed biorefinery
- Additional goal:
  - Fast pyrolysis: valuable phenolics
  - Slow pyrolysis: carbon sequestration, soil amendment



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FAST PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE

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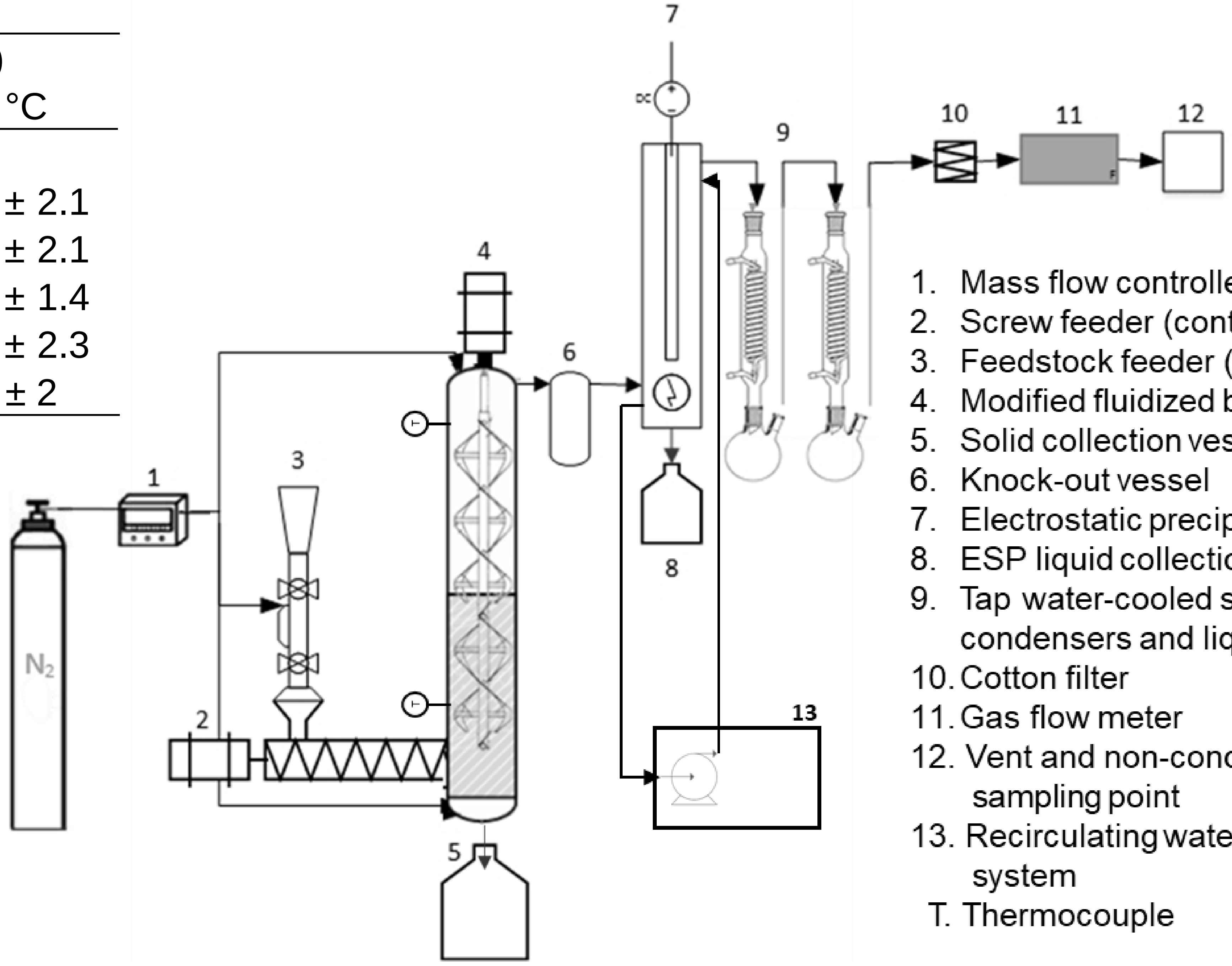
FAST PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – SET-UP & YIELDS

- Mechanically agitated bubbling bed reactor with fractionated condensation

Components	Yields (wt.% on feed basis) 430 °C	480 °C	530 °C
Pyrolytic-oil			
Heavy Phase	17.5 ±3.7	18.1 ± 2.6	15.1 ± 2.1
Aqueous Phase	9.7 ±3.7	9.9 ± 2.6	13.4 ± 2.1
Biochar	44.7 ±3.5	39.5 ± 2.8	37.1 ± 1.4
NCG	27.1 ±3.9	28.2 ± 2.1	31.5 ± 2.3
Total	99 ± 3.7	95.7 ± 2.5	97.1 ± 2

- Oil yield → ± 28%
- Biochar yield → ± 40%
- Biochar yield is high for fast pyrolysis



1. Mass flow controller
2. Screw feeder (continuous)
3. Feedstock feeder (batch)
4. Modified fluidized bed reactor
5. Solid collection vessel
6. Knock-out vessel
7. Electrostatic precipitator (ESP)
8. ESP liquid collection vessel
9. Tap water-cooled staged condensers and liquid collections
10. Cotton filter
11. Gas flow meter
12. Vent and non-condensable gas sampling point
13. Recirculating water cooling system

T. Thermocouple

(paper in preparation)

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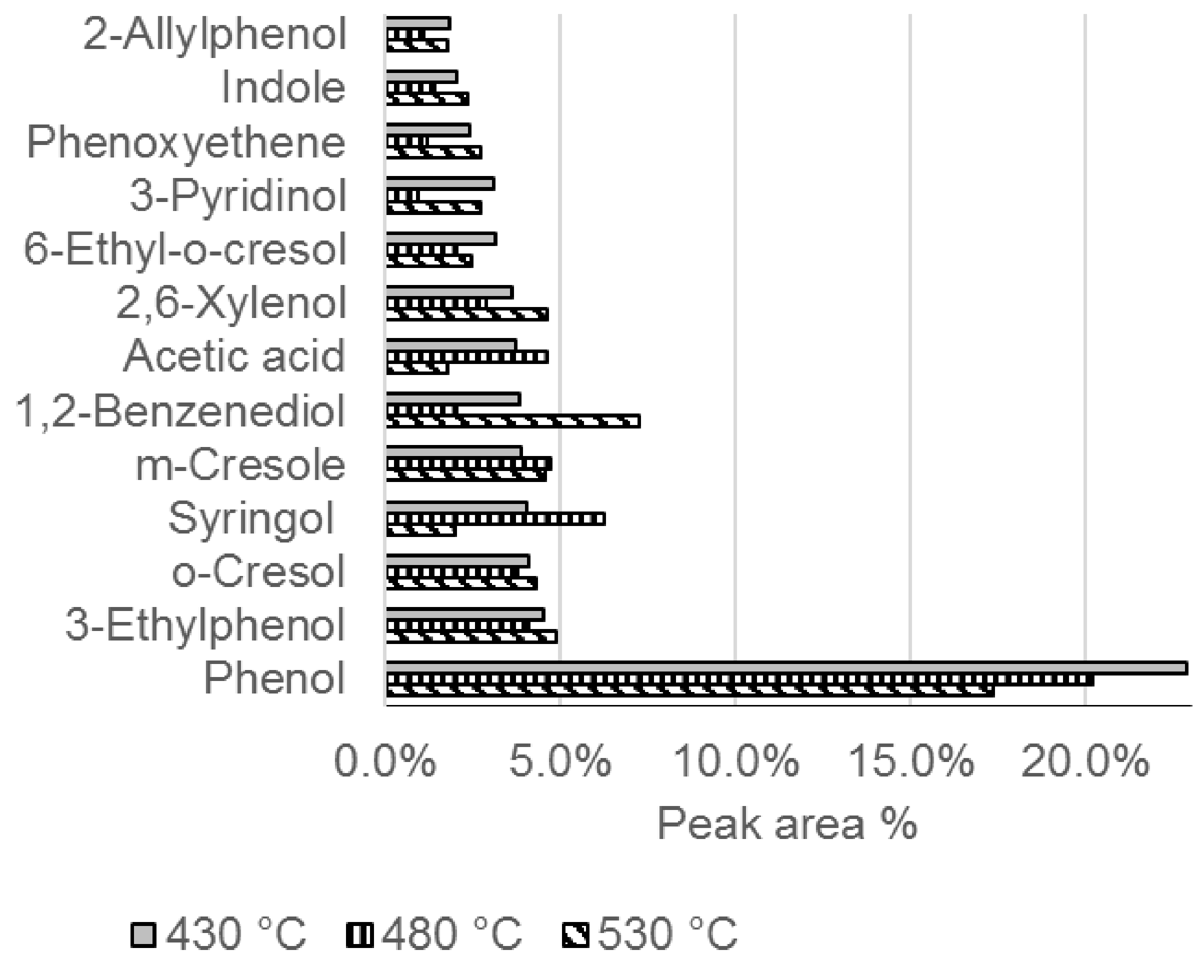
FAST PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – CHARACTERIZATION

- Heavy phase oil: many phenolics
- Biochar:
  - Ash recovery: 97.8% (430°C); 83.4% (480°C); 80.4% (530°C)
  - H/C: 0.60 (430°C) 0.56 (480 °C) 0.43 (530 °C)
  - O/C: 0.17 (430°C) 0.17 (480 °C) 0.13 (530 °C)
  - IBI and EBC complying: H/C < 0.7 and O/C < 0.4

	Char		
	430 ° C	480 ° C	530 ° C
N	1.95 ± 0.13	2.26 ± 0.06	1.99 ± 0.04
C	59.86 ± 1.25	63.69 ± 0.34	62.83 ± 0.63
H	2.97 ± 0.08	2.99 ± 0.09	2.24 ± 0.02
S	Below LOD	Below LOD	Below LOD
O	13.36 ± 1.14	9.93 ± 0.06	11.28 ± 0.20
Ash	21.87 ± 0.85	21.12 ± 0.18	21.66 ± 0.33



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FAST PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – CONCLUSION

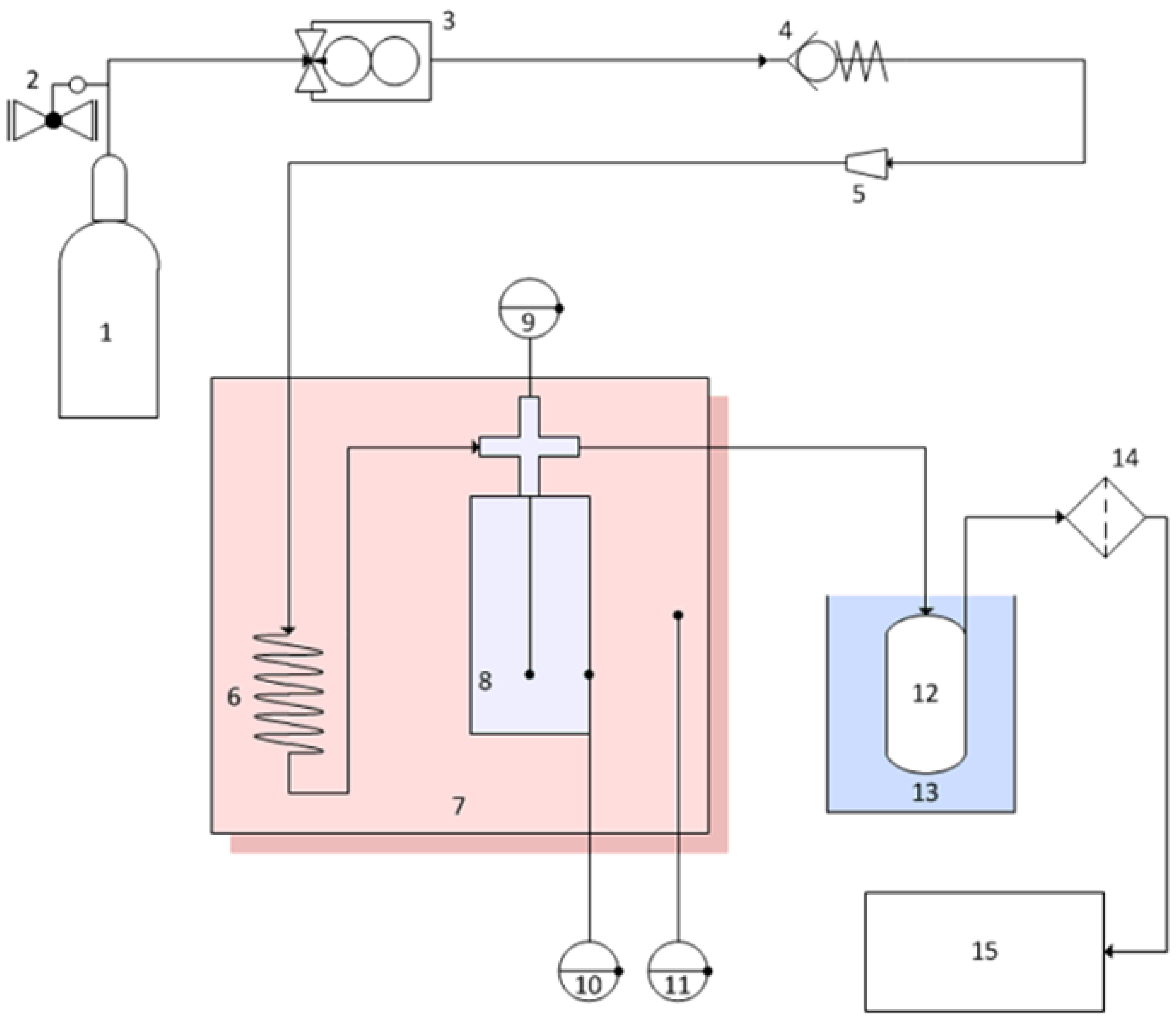
- Fast pyrolysis of LRDS achieves relatively high bio-oil yield, compared to other technical lignin
- Bio-oil is rich in phenolics
- Biochar is complying to IBI and EBC voluntary guidelines.
- Biochar retains the majority of the ash (nutrients): between

SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE

SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – SET-UP

- Bench-scale fixed bed slow pyrolysis
- Statistical analysis to optimize:
  - Optimize biochar yield
  - Optimize biochar quality (H/C & O/C ratio)
- Statistical analysis to quantify the effect of:
  - Highest treatment temperature (HTT)
  - Heating rate (HR)
  - Holding time (HT)

  on the biochar yield and quality



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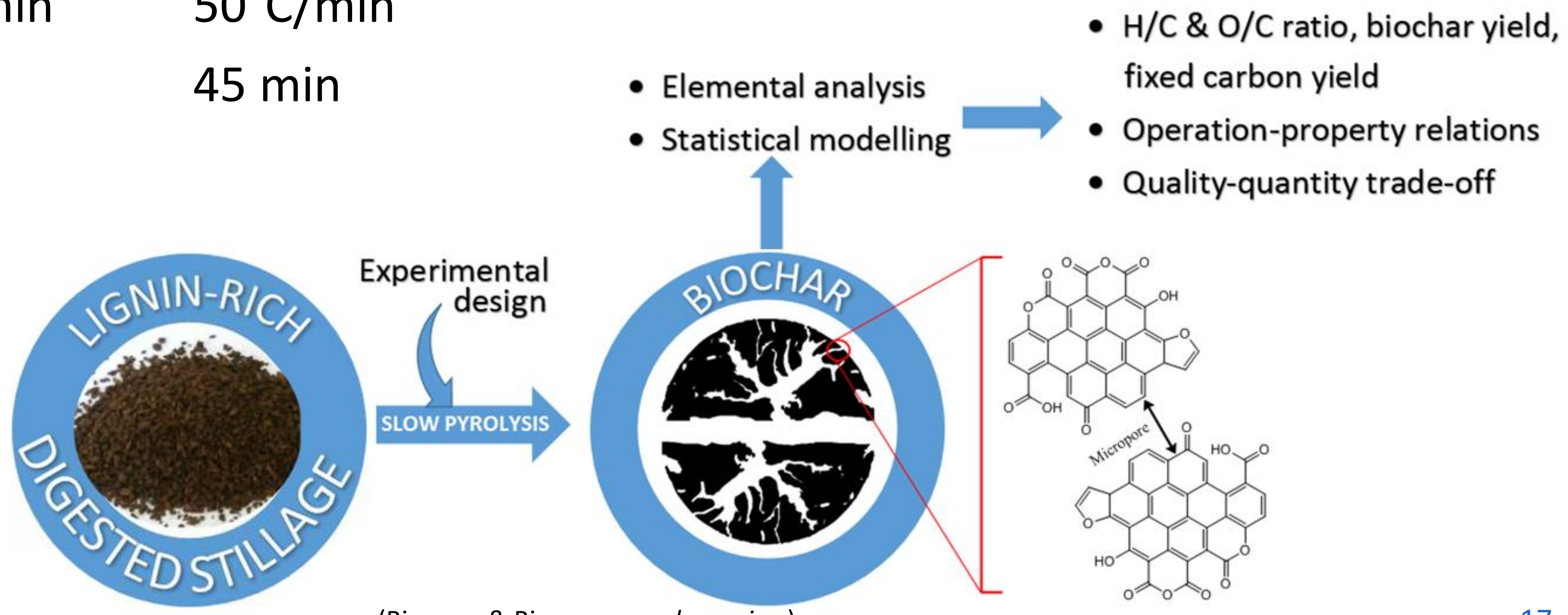
SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – EXP. DESIGN

- Experimental design:
  - Three factors: HTT, HR, HT
  - Three levels
  - 10 center runs
- → 3^3 factorial design with center runs
  - HTT: 370°C 410°C 450°C
  - HR: 5°C/min 20°C/min 50°C/min
  - HT: 5 min 15 min 45 min



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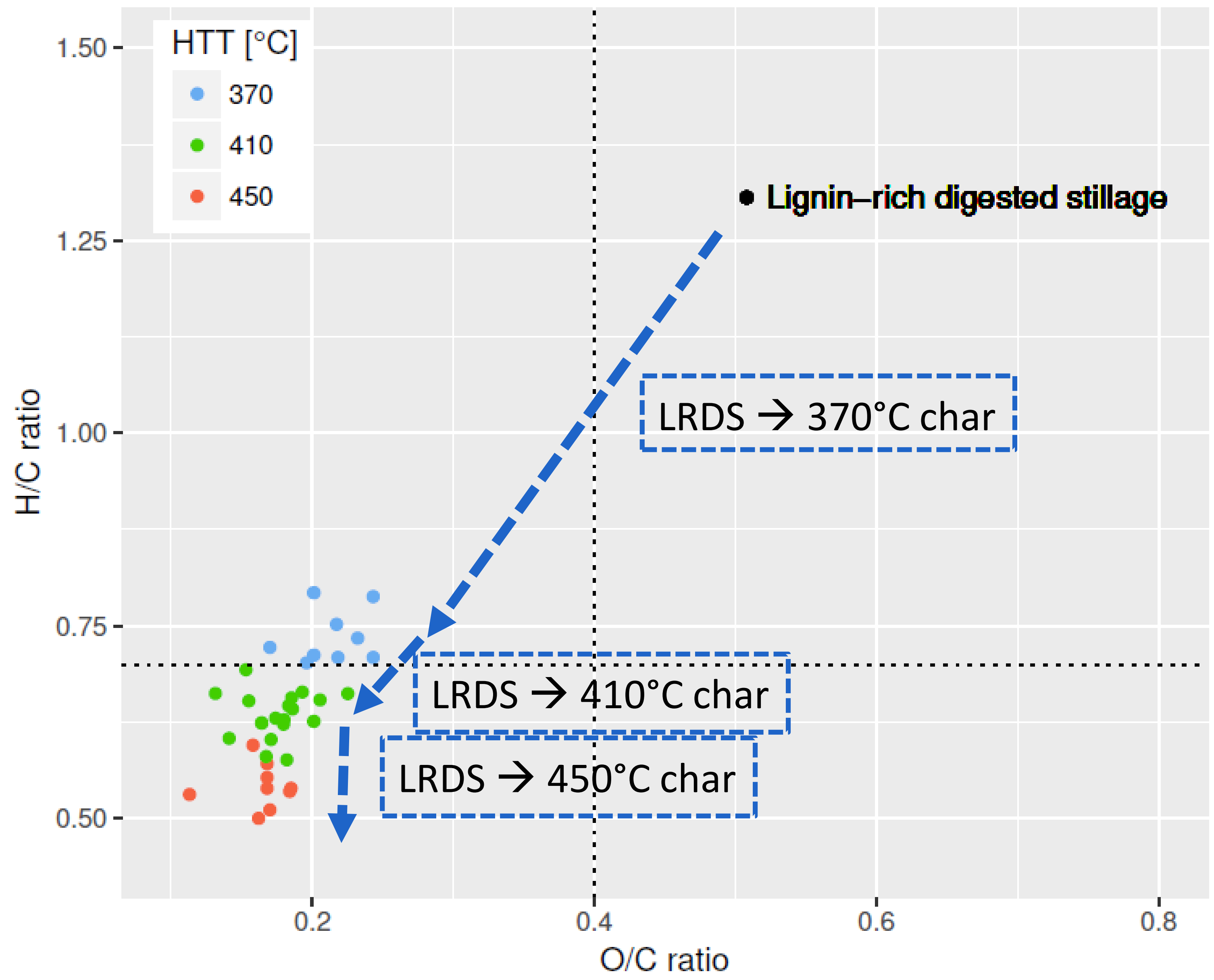
SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – RESULTS

- 2D and 3D Van Krevelen



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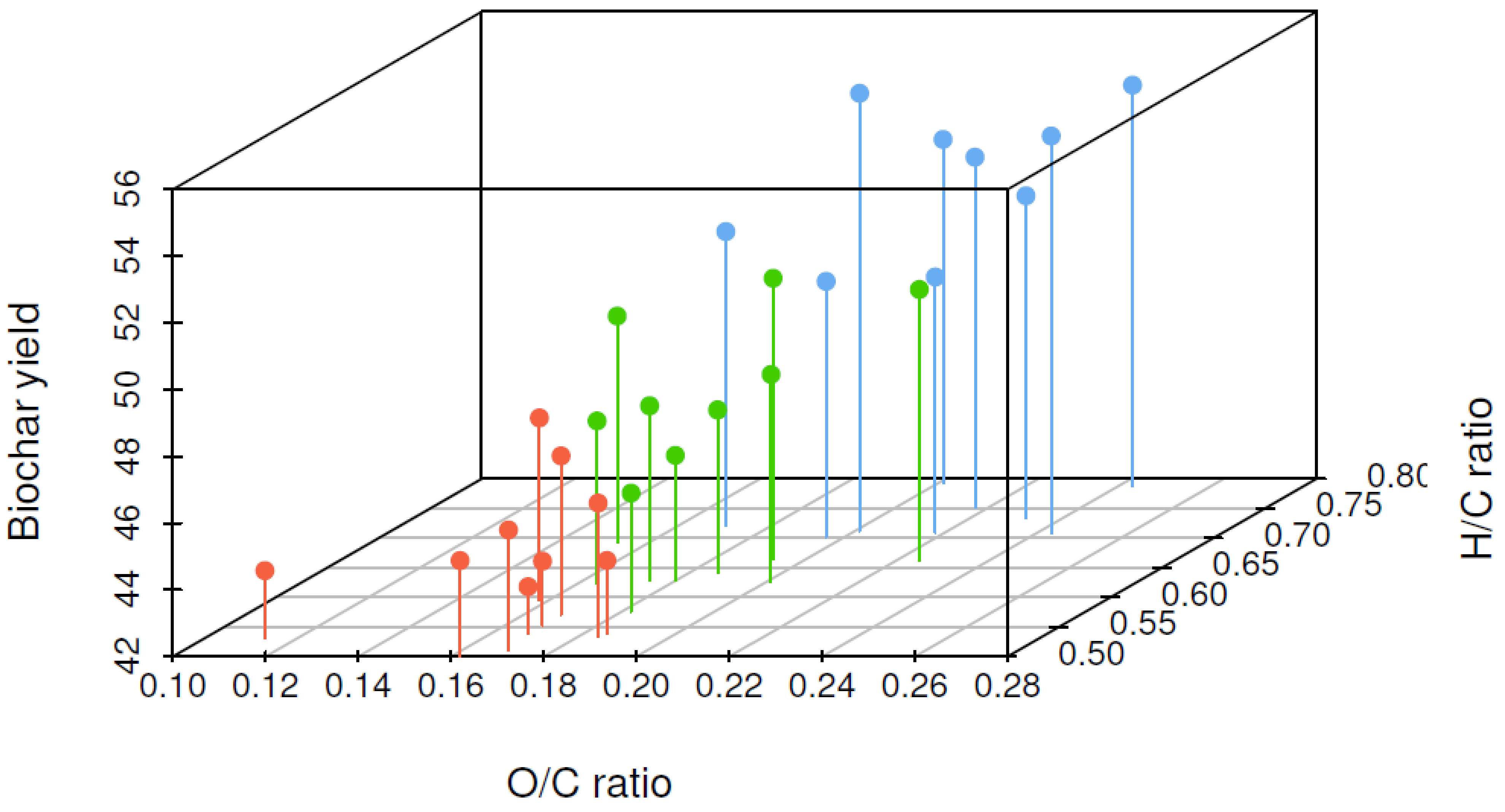

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SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – STATISTICS

- Influence of HTT, HR, HT (3^3 factorial design with center runs) assessed by
  - ANOVA
  - Kruskal-Wallis
  - Normality of Effects

Intersection: most influencing, conservative factor

Feedstock	Methods → / Response variables ↓	ANOVA	Kruskal-Wallis	Normality of Effects (985%)	Intersection
Lignin residue	Fixed carbon yield	HR	HR	none	none
	Biochar yield	HTT, HR, HT	HTT	HTT	HTT
	H/C ratio	HTT, HT	HTT	HTT, HT	HTT
	O/C ratio	HTT	HTT	HTT,HT	HTT
Straw	Fixed carbon yield	HR	HR	none	none
	Biochar yield	HTT, HR, HT, HTT:HR, HTT:HT	HTT, HR	none	none
	H/C ratio	HTT, HR, HT	HTT	HTT, HT	HTT
	O/C ratio	HTT	HTT	HTT	HTT

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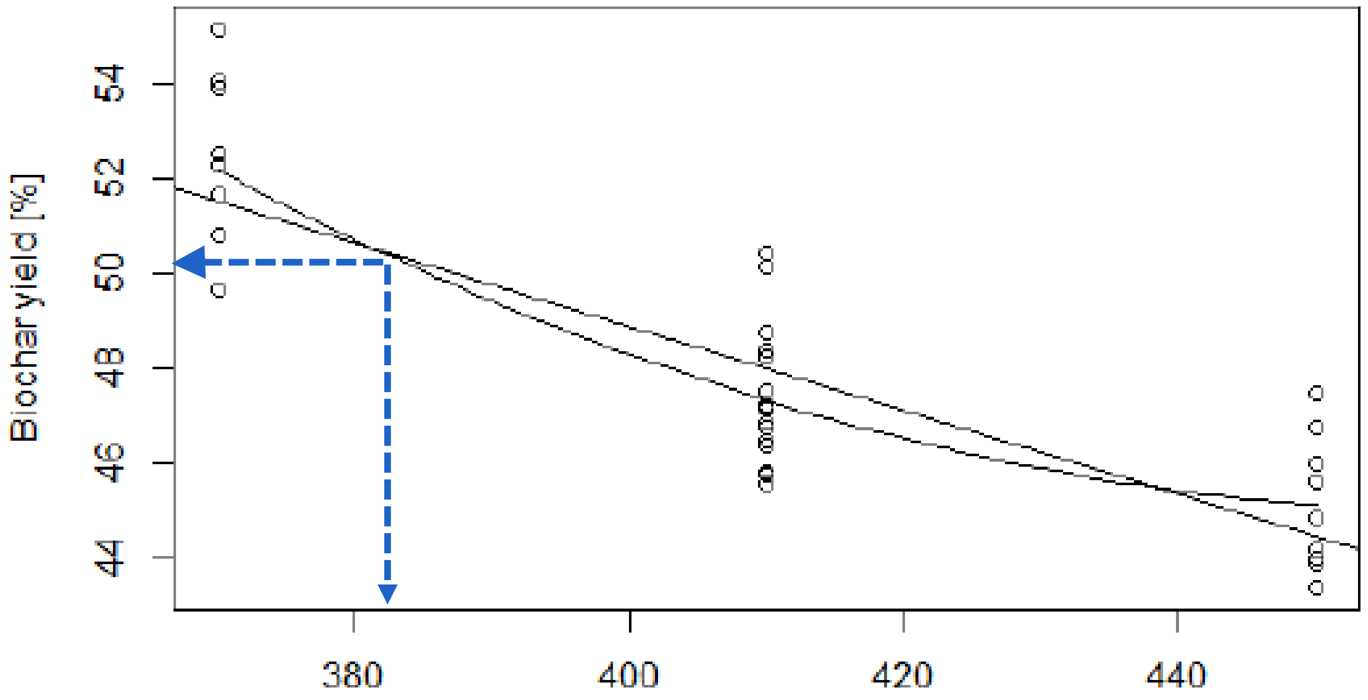
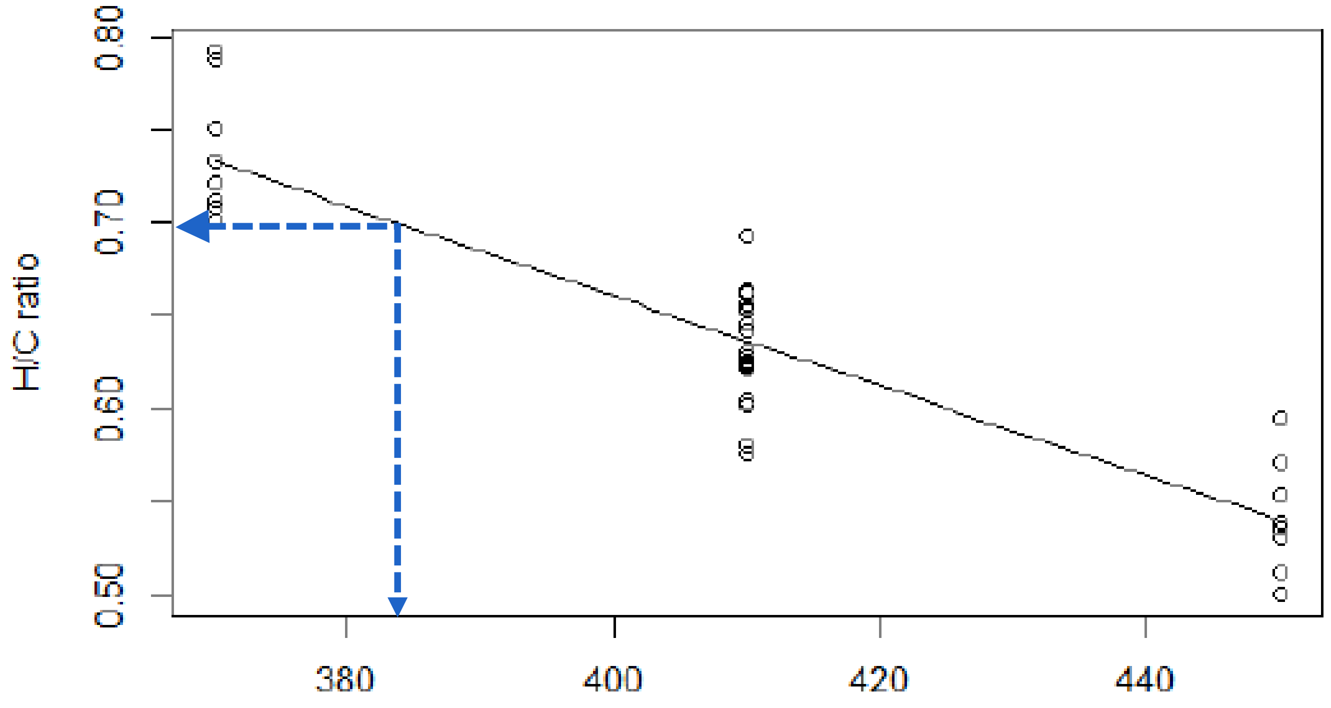
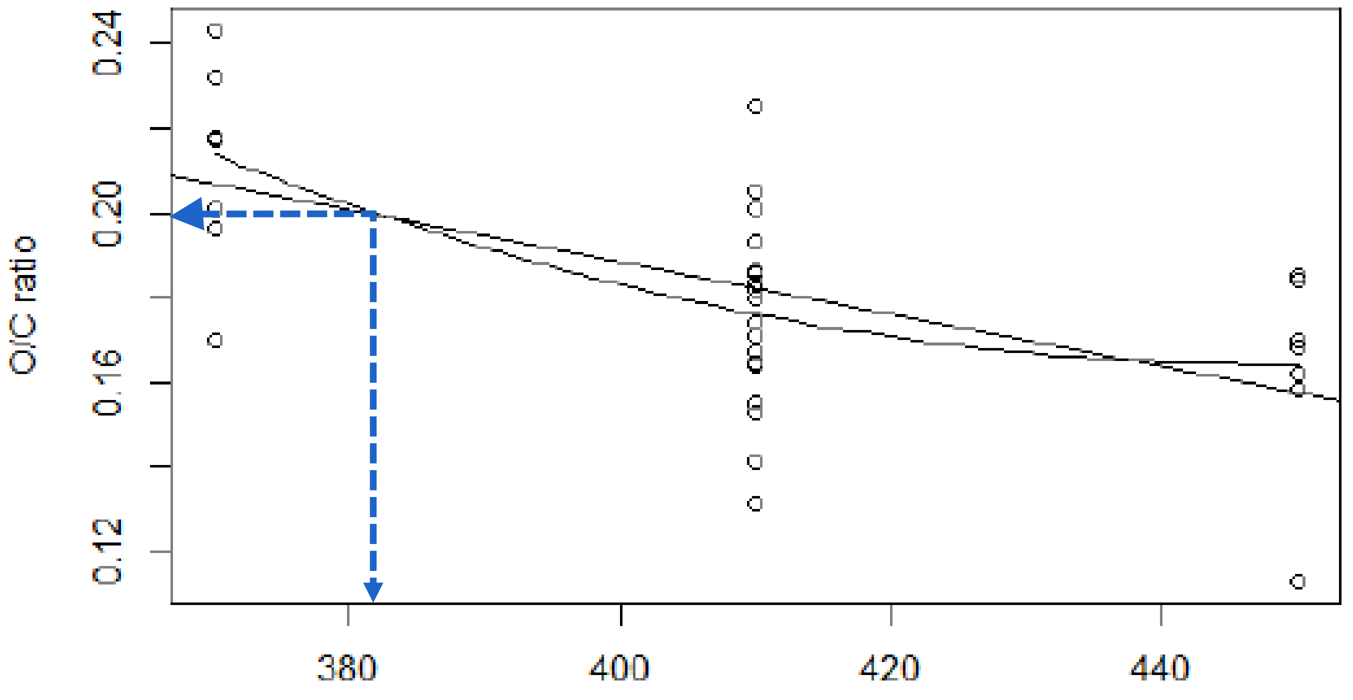
SLOW PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – MODELS

- Linear models were set up for biochar yield, H/C ratio and O/C ratio with HTT as factor
- Second order models were set up if curvature was significant
- Lignin-based biochar can be obtained with:
  - 50.7% yield
  - H/C ratio of 0.70
  - O/C ratio of 0.20
  - Already at 384°C







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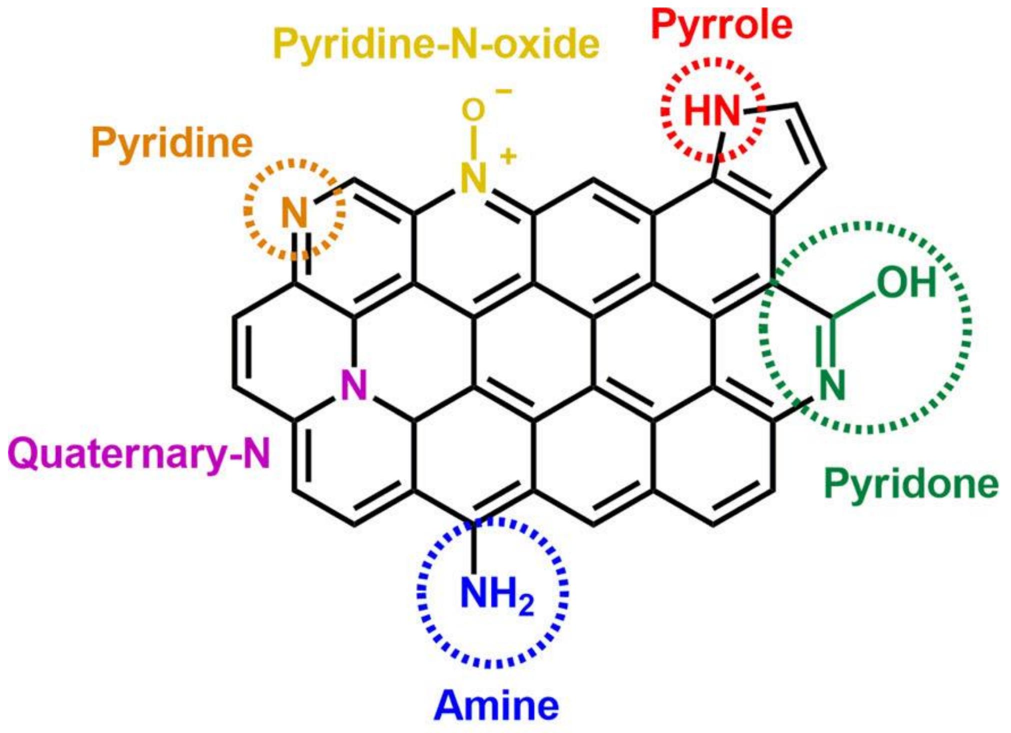
FAST PYROLYSIS OF LIGNIN-RICH DIGESTED STILLAGE – CONCLUSION

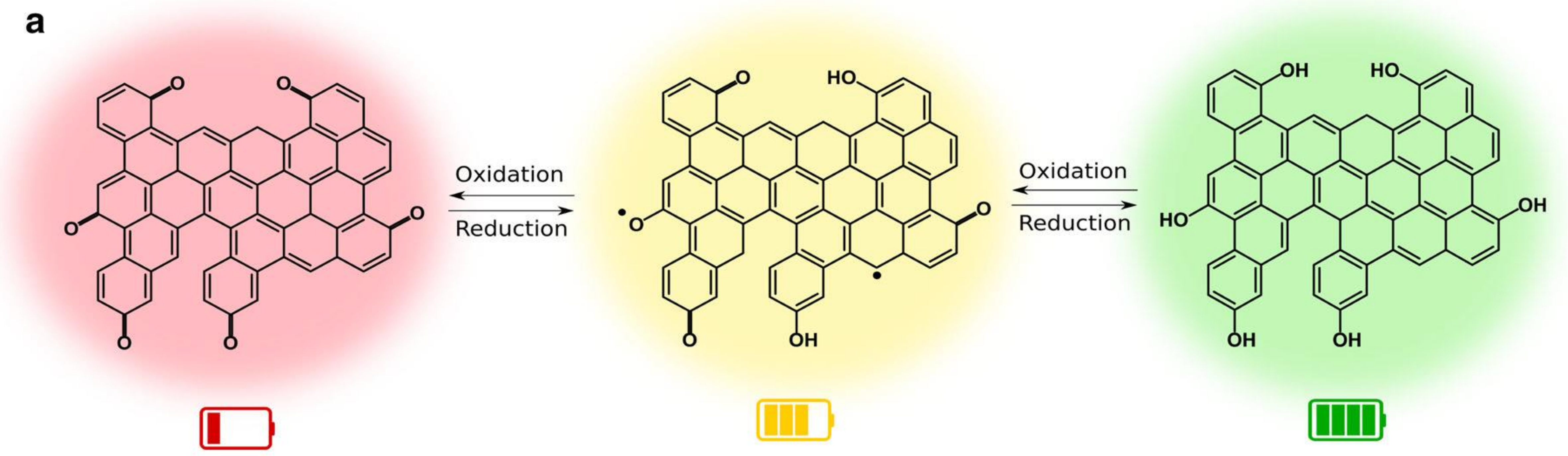
- Lignin-rich digested stillage has high biochar yield upon slow pyrolysis
- The HTT is the most influencing factor, determining yield, H/C and O/C ratio
- The fixed carbon yield is not influenced neither by HTT, nor by HR, nor by HT
- Less thermal energy is required to obtain IBI/EBC complying biochar

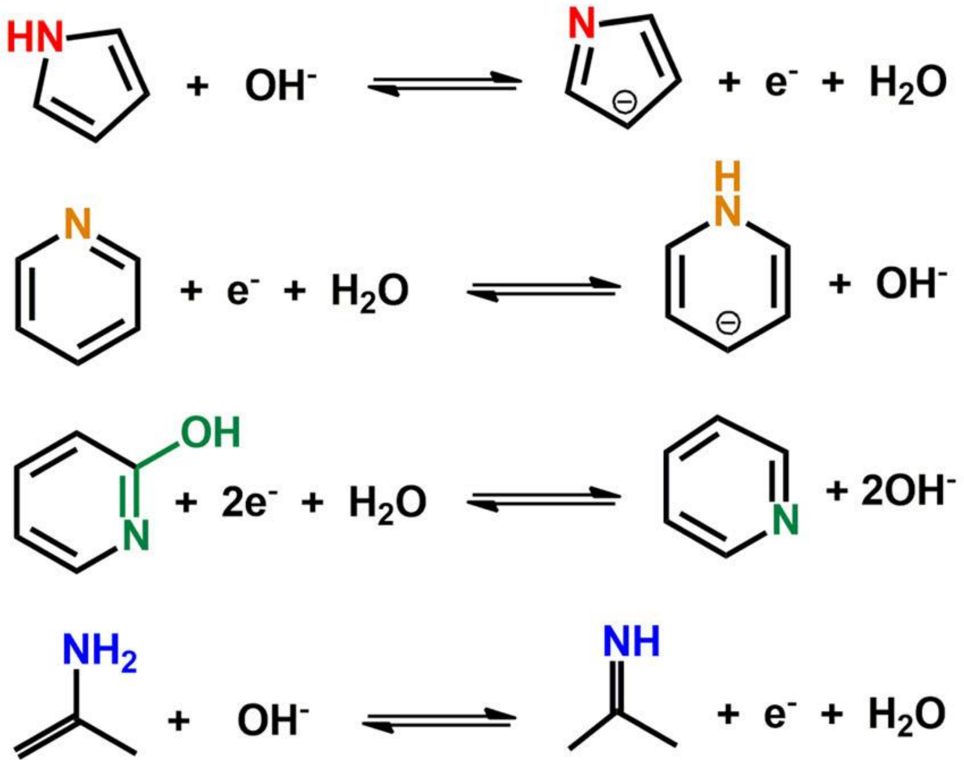
BIOCHAR ELECTROCHEMISTRY

ELECTROCHEMICAL PROPERTIES OF BIOCHAR

- Electron donating capacity (EDC)
- Electron accepting capacity (EAC)
  - Sum is electron exchange capacity (EEC)
- Role of oxygen and other heteroatoms







(Rev Environ Sci Biotechnol (2017) 16:695–715)

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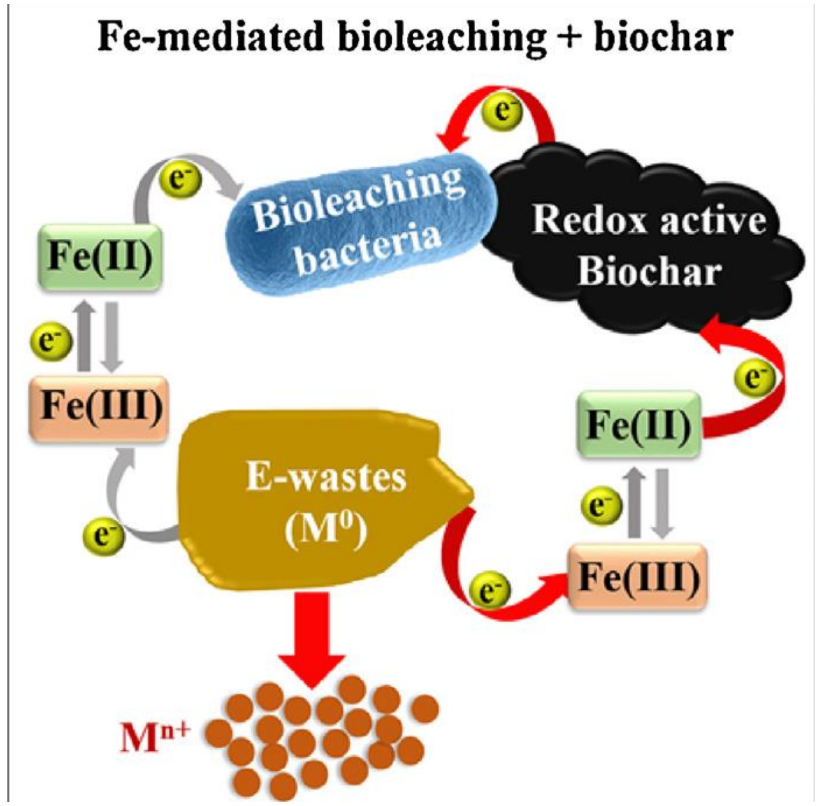
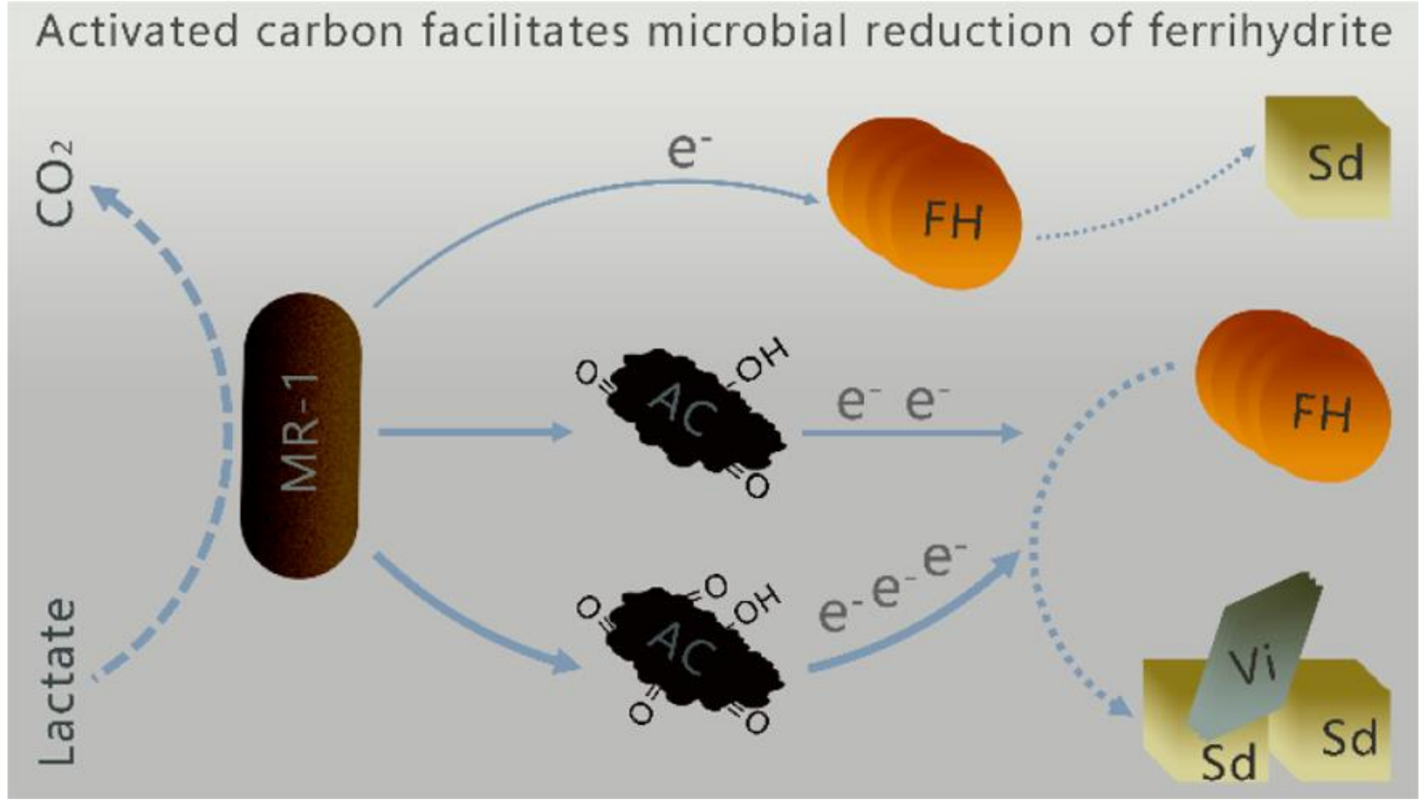
RELEVANCE OF ELECTRON EXCHANGE – SOLID REDOX MEDIA

- Extracellular sink/source of electrons for microbial communities
- A biochar “battery” which reversely accepts and donates electrons to the (a)biotic environment
- Degradation of micro pollutants
- Interfere with N-cycle in soil (denitrification)



(Jour. Haz. Mat. 320 (2016) 393–400)



(Environ. Sci. Technol. 2017, 51, 9709–9717)

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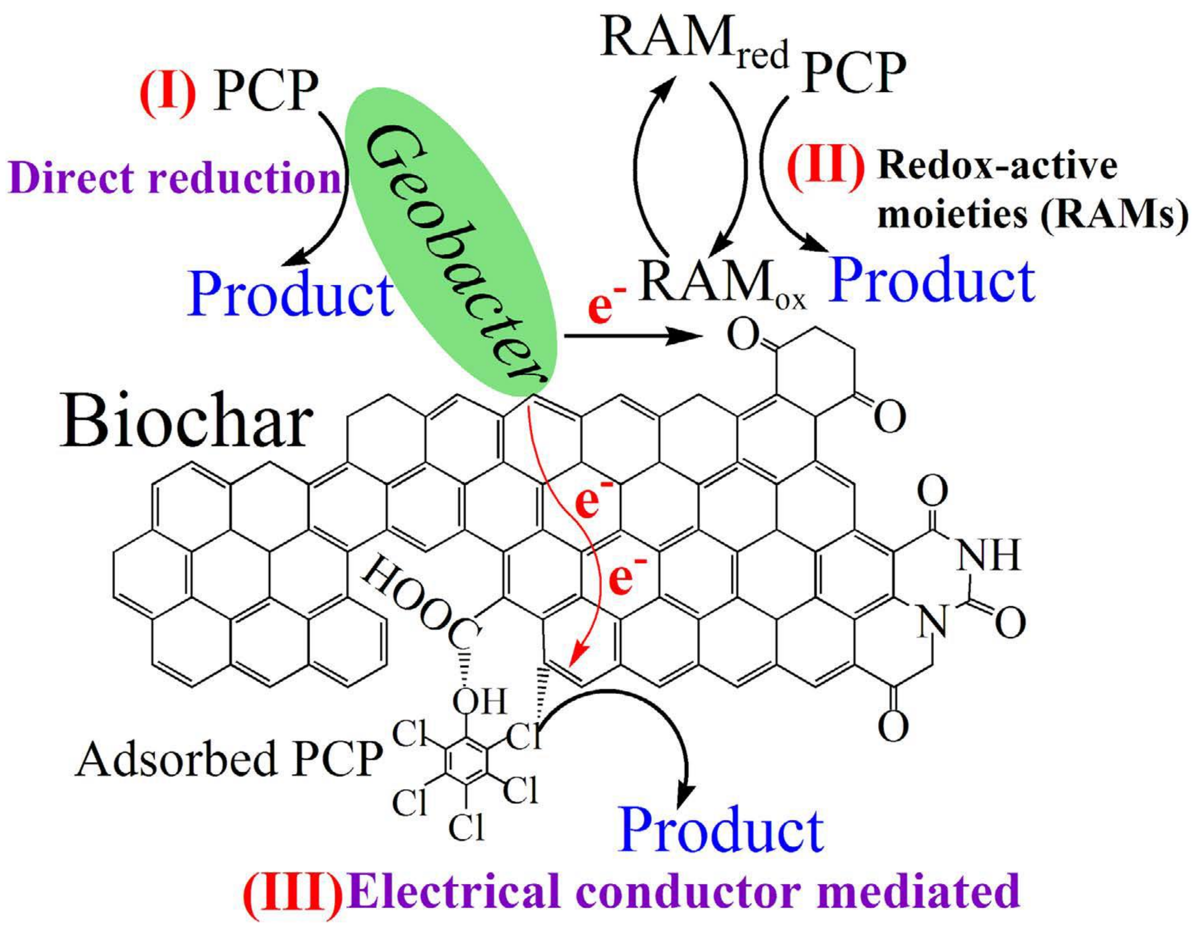
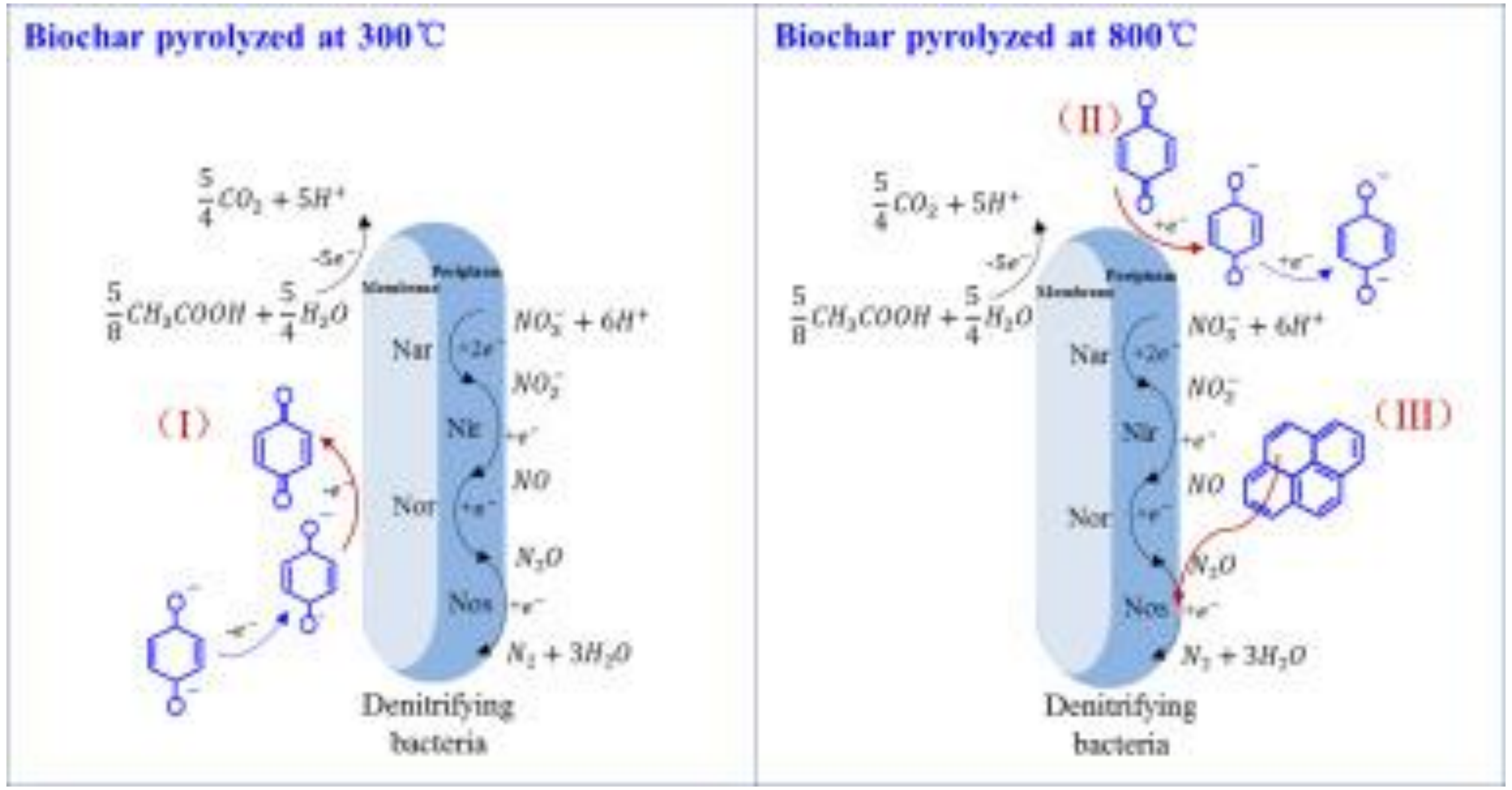
RELEVANCE OF ELECTRON EXCHANGE – SOLID REDOX MEDIA

- Degradation of micro pollutants (through conduction/electroactive moieties)
- Interfere with N-cycle in soil (denitrification); reduction of N_2O evolution



(Scientific **Reports** | 5:16221)



(j.scitotenv.2017.09.125)

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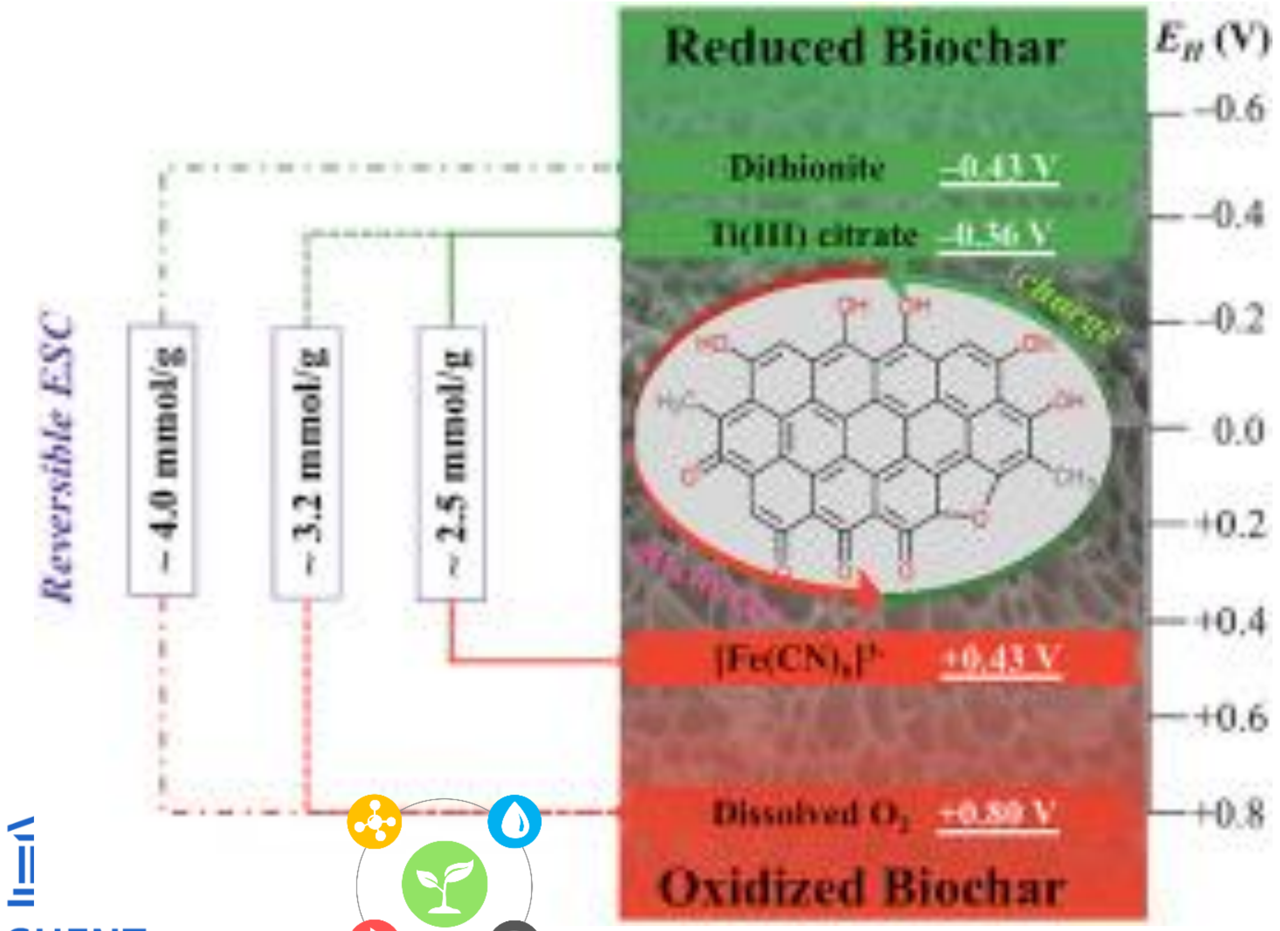
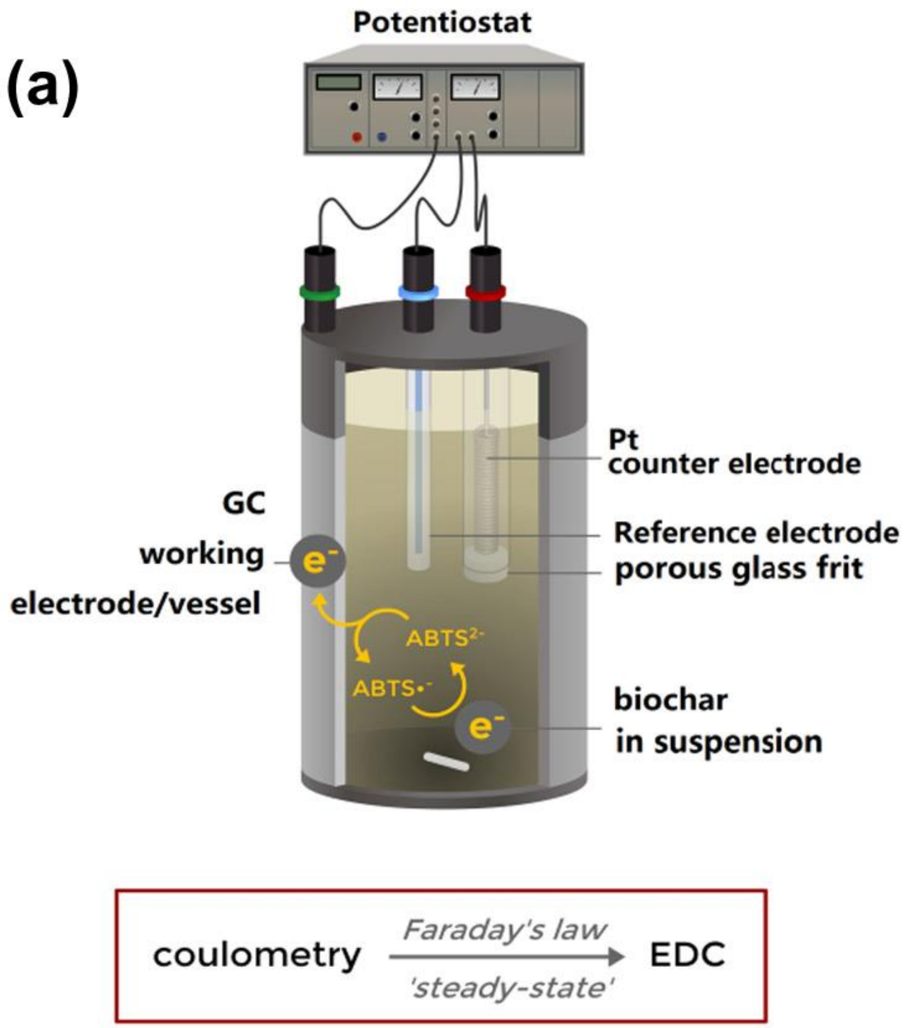
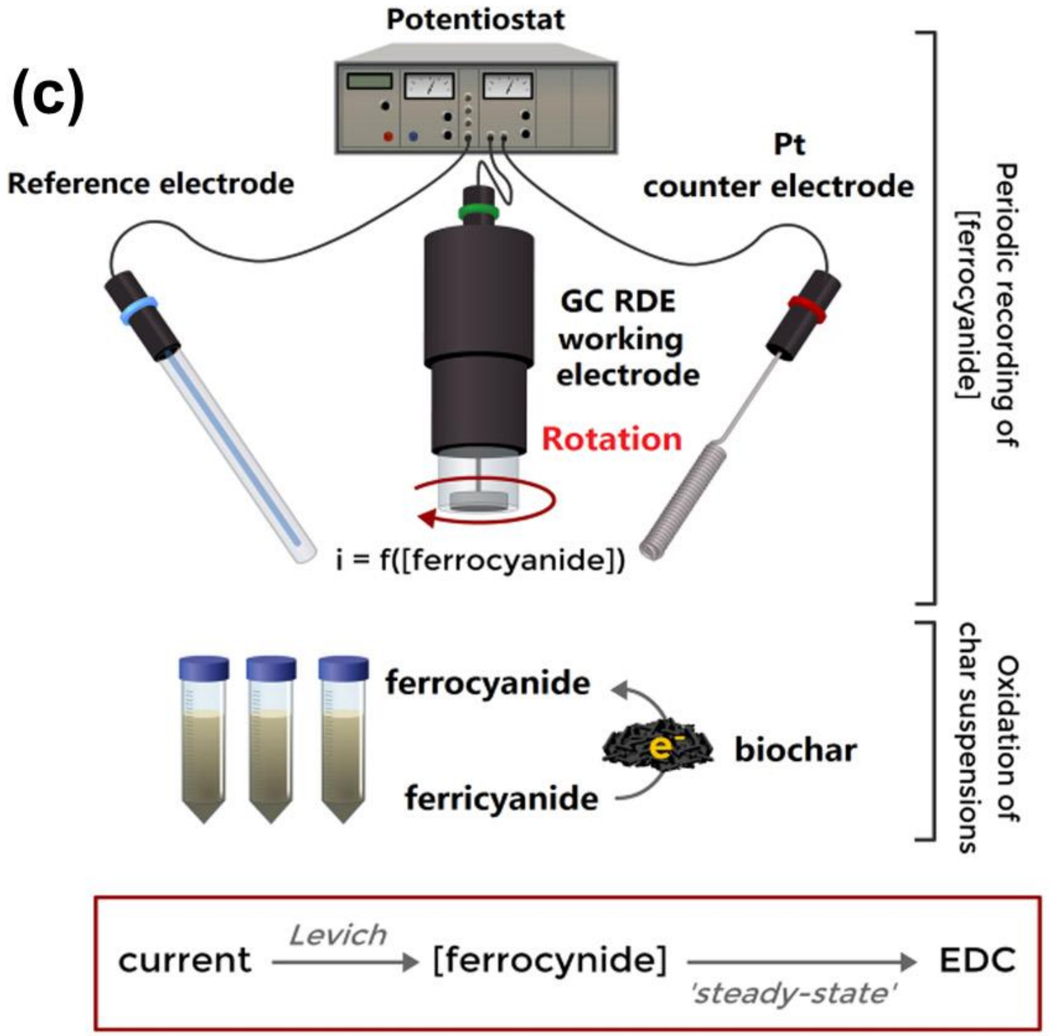
RELEVANCE OF ELECTRON EXCHANGE – EFFECT OF MEASURING

- EDC (and EAC) measurements:
  - Short VS long measurements
  - Electron donation is slow and underestimated if shortly measured
  - Mediator should be stabile for long measurements
  - Redox potential of mediator influences measurements







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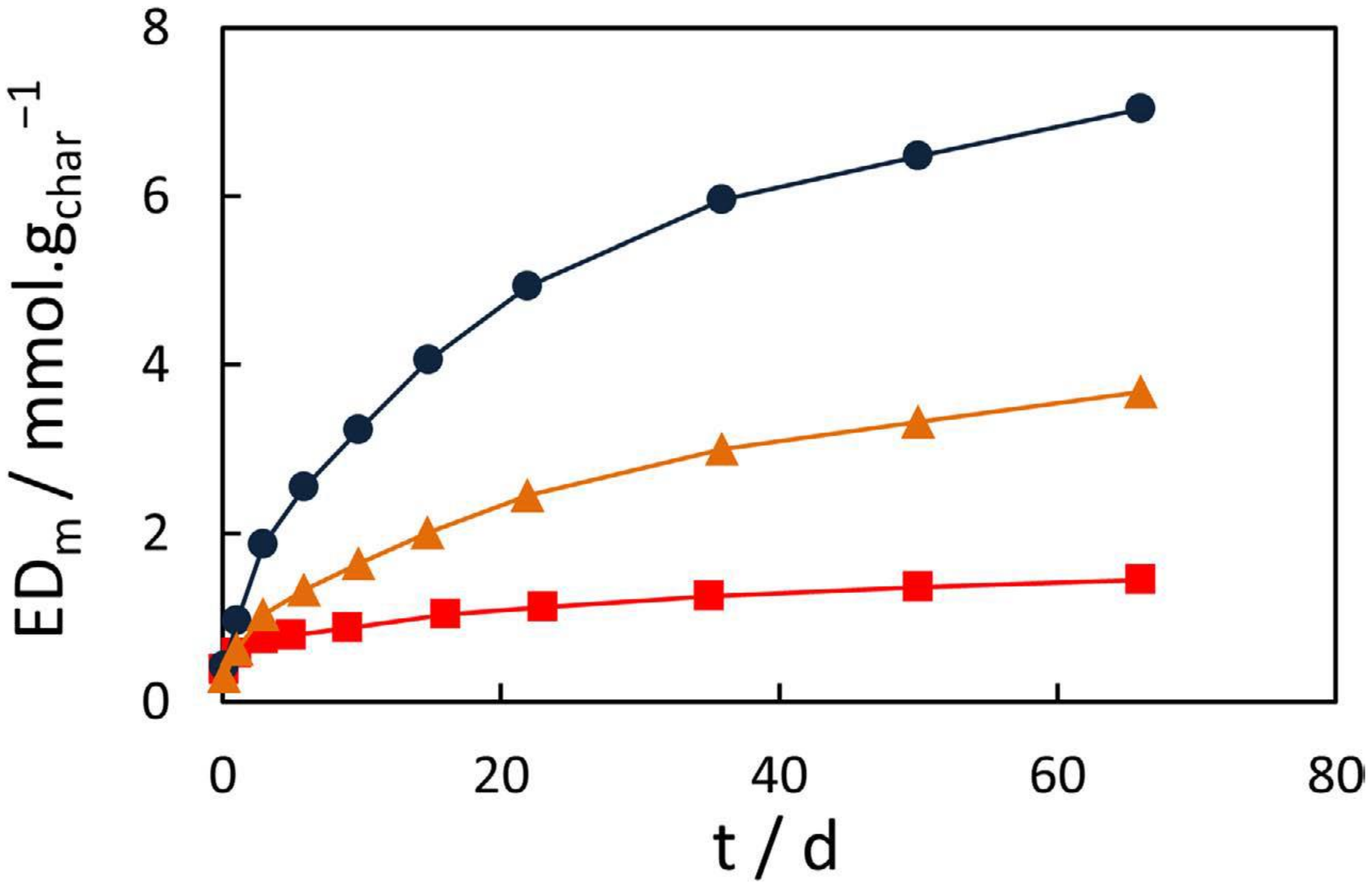
RELEVANCE OF ELECTRON EXCHANGE – EFFECT OF MEASURING

- EDC (and EAC) measurements:
  - Short VS long measurements (Prévoteau *et al.* 2016)
  - 400°C, 500°C, 600°C (t_R = 30 min) pine wood BC
  - Long term measurement of EDC via RDE electrode



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WHAT SHOULD WE TAKE HOME?

- Various technical lignin materials available
- Their chemical structure makes them ideal for highly aromatic biochars
- Valuable chemicals from fast pyrolysis of technical lignin (receiving lot of attention) → difficult
- High char yields possible
- Favorable electrochemical properties of the char → high value applications

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PYRO 2020

23rd International Symposium

on Analytical and Applied Pyrolysis

PYRO 2020 will be held in Ghent, Belgium

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