Characterization of biochars by nuclear magnetic resonance

Yann LE  
_BRECH CNRS-University of Lorraine, LRP, 54000 Nancy, France_

Roger GADIOU  
_CNRS-University of Haute-Alsace, IS2M 68100 Mulhouse, France_

Luc DELMOTTE  
_CNRS-University of Haute-Alsace, IS2M 68100 Mulhouse, France_

Jésus RAYA  
_CNRS-University of Strasbourg, ICS, 67100, Strasbourg, France_

Younes BOUIZI  
_University of Lorraine, CRM2, 54000 Nancy, France_

See next page for additional authors

Follow this and additional works at: https://dc.engconfintl.org/biochar_iii

Recommended Citation

Yann LE, Roger GADIOU, Luc DELMOTTE, Jésus RAYA, Younes BOUIZI, Gwendal KERVERN, Sebastien LECLERC, Sabine BOUGUET-BONNET, and Anthony DUFOUR, "Characterization of biochars by nuclear magnetic resonance" in "Bio-Char III: Production, Characterization and Applications", Franco Berruti (Western University, London, Ontario, Canada); David Chiaramonti (Politecnico di Torino, Italy); Silvia Fiore (Politecnico di Torino, Italy); Manuel Garcia-Perez (Washington State University, USA); Ondrej Masek (University of Edinburgh, Edinburgh, UK) Eds, ECI Symposium Series, (2023). https://dc.engconfintl.org/biochar_iii/46

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in Bio-Char III: Production, Characterization and Applications by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
Authors
Yann LE, Roger GADIOU, Luc DELMOTTE, Jésus RAYA, Younes BOUIZI, Gwendal KERVERN, Sebastien LECLERC, Sabine BOUGUET-BONNET, and Anthony DUFOUR

This abstract and presentation is available at ECI Digital Archives: https://dc.engconfintl.org/biochar_iii/46
Characterization of biochars by Nuclear Magnetic Resonance


*yann.le-brech@univ-lorraine.fr
Solid state $^{13}$C NMR analysis have been widely used to investigate the structure of aromatic materials (Freitas_2012, Baccile_2014, Brewer_2014):

- Non destructive method
- Not limited by sample insolubility
- Provide detailed and quantitative structural information
Characterization of biochars by Nuclear Magnetic Resonance
$^{13}$C ssNMR analysis of chars are quantitatives?

$^{13}$C Direct-Polarization (DP/MAS): Simple experiment and provide quantitative data
Incon. long time acquisition (long relaxation times) and low isotopic abund. of $^{13}$C

$^{13}$C Cross-Polarization (CP/MAS): Transfer energy thought $^1$H to $^{13}$C
Adv. $^1$H have short relaxation times (~s)
Incon. $^{13}$C Magnetization dynamics will depends on $^1$H location in material
Solution. Design specifics CP/MAS methods to mimic the DP conditions
  Multiple CP with $^1$H repolarization (R.Johnson_JMR_2014)
  APHH CP method (M. Hervé_Biochim_1994)
  Correct integrals by a factor, “build up” method (Mehring_1983)
\[ ^{13}\text{C} \text{ ssNMR CP/APHH biomass and biochars} \]

Comparison between \[ ^{13}\text{C} \text{ DP/MAS} \] and \[ ^{13}\text{C} \text{ CP/MAS APHH} \] at 125 MHz and 18 kHz spinning for native Miscanthus and biochars produced by slow pyrolysis (5°C/min)

Evolution of Miscanthus carbon structure as function of temperature by CP/MAS APHH
$^{13}$C ssNMR CP/APHH biomass and biochars

All spectra deconvoluted, the quantification of main moieties have been established as function of temperature

Y. Le Brech, Carbon, 2016
Improve biochar structural information from ssNMR

1 Dimensional $^{13}$C ssNMR method are limited by poor resolution and overlapping caused by complex structure of biomasses and biochars

2 Dimensional $^1$H-$^{13}$C ssNMR methods can provide more structural information


2D $^1$H-$^{13}$C HETCOR methods combined with high field (750MHz) and with FSLG irradiation to improve $^1$H resolution

$^1$H-$^{13}$C HETCOR 750MHz of native Miscanthus
Improve biochar structural information from ssNMR

1 Dimensional $^{13}$C ssNMR method are limited by poor resolution and overlapping caused by complex structure of biomasses and biochars

2 Dimensional $^1$H-$^{13}$C ssNMR methods can provide more structural information


2D $^1$H-$^{13}$C HETCOR methods combined with high field (750MHz) and with FSLG irradiation to improve $^1$H resolution

$^1$H-$^{13}$C HETCOR 750MHz of native Miscanthus
Improve biochar structural information from ssNMR

Comparison between native Miscanthus and biochar 300°C by 2D $^1$H-$^{13}$C HETCOR

$^1$H-$^{13}$C HETCOR 750MHz of native Miscanthus and biochar
In-situ NMR during biomass pyrolysis

Specific In-situ $^1$H NMR probe was adapted from commercial probe (Bruker®)

$^1$H NMR spectra were deconvoluted into Gaussian (solid-like) and Lorentzian (liquid-like) distribution functions
In-situ NMR during biomass pyrolysis

Specific In-situ $^1$H NMR probe was adapted from commercial probe (Bruker®)
Surface affinity of \( \text{H}_2\text{O} \) with biochars

\(^1\text{H} \) Fast Field Cycling (FFC) NMR relaxometry has been applied in order to recognize the molecular dynamics of \( \text{H}_2\text{O} \) on biochar surface. (Bubici_MRC_2015)

\(^1\text{H} \) FFC NMR relaxometry applied on cylindrical samples of pyrolysed Douglas wood (500°C to 1000°C)
Perspectives

➢ Reduce analytical time for biochar investigation by NMR by using Ultra-fast $^1$H NMR (100 kHz) at 750 MHz Magn. Field

Ultra-Fast $^1$H NMR
*Alyssum Murale*

$^1$H chemical shift (ppm)
Thanks for your attention