Lignocellulose Feedstock (LCF) for Material Development

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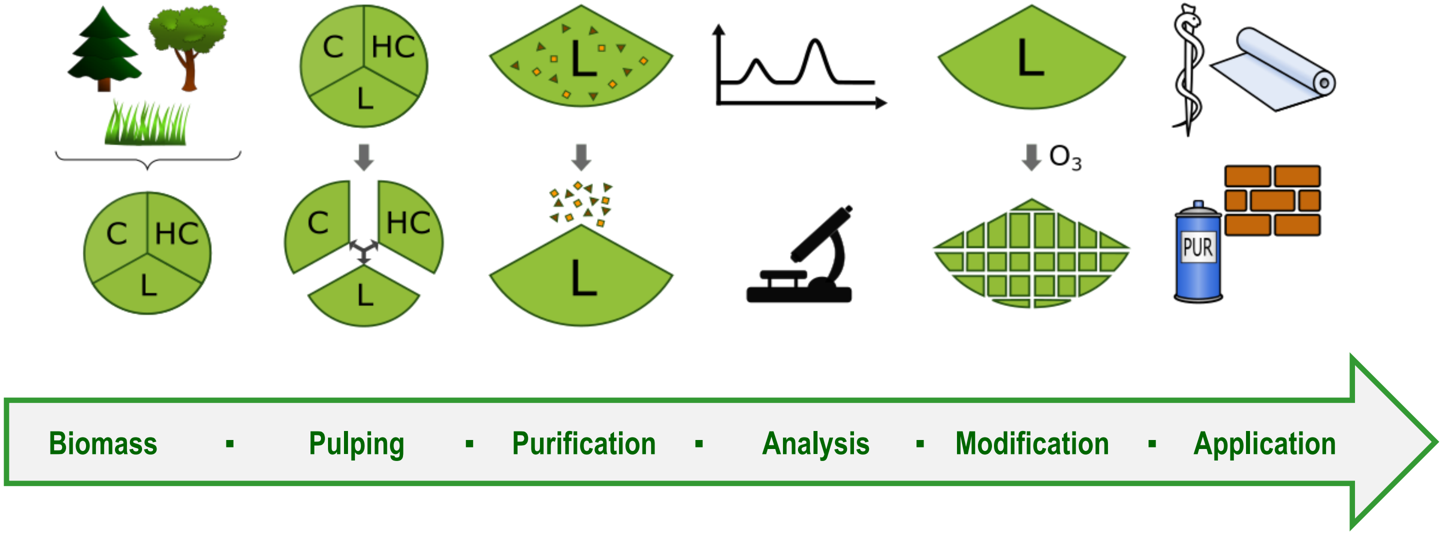
NRW GI/FG Ressourcen ▪ Leverkusen ▪ November 6, 2018

Lignocellulose Feedstock (LCF) – a Renewable Resource for Energy and Material Development

Cellulose (C), Hemicellulose (HC), Lignin (L)



Biomass ▪ **Pulping** ▪ **Purification** ▪ **Analysis** ▪ **Modification** ▪ **Application**

- Wood
- Grass

- Kraft
- Organosolv

- SEC, NMR
- SAXS/WAXS, CT-EM

- Demethylation
- Depolymerisation

Kamm, *et al.* (**2006**) In: **Biorefineries – Industrial Processes and Products**.Wiley-VCH
El Khaldi-Hansen *et al.* (**2016**) In: **Analytical Techniques and Methods for Biomass**.Springer.
Alzagameem et al. (**2018**) In: **Biomass and Green Chemistry**. Springer

Biobased Polymers for Construction and Packaging

- **Lignin-based Polymers for Construction Applictions**
  BMBF (2014-18) University Bonn, Innovatec GmbH, DLR Köln
  Henkel AG&CoKG, Dynea Erkner GmbH

- **Miscanthus Cascade Utilization**.
  BioSC / SEED (2015/16) University Bonn/CKA, RWTH Aachen

- **Biobased Materials** EFRE Programme (EU/NRW 2017-20)
  Coordination: University Bonn/CKA (> 25 regional SME)

- *Submitted to*: BMBF FHprofUnt. (Spectral Service AG, Uni Wellington/NZ)
  Polymer Analysis via 2D NMR & Multivariate Analysis

- *Submitted to*: BMBF Bioeconomy. (RWTH Aachen, DLR Cologne, WOOD Kplus Linz)
  Lignin Depolymerization to Tailored Components

Biocompatible Polymers for Drug Release and Tissue Regeneration

- **Optimization of Optimaix® for Tissue Engineering**
  EU/Ziel2NRW (2012-16) Matricel GmbH Herzogenrath, University Heidelberg

- **Personalised Cell-based Implantates for Bone Defects of Critical Size**
  BMBF (2015-19) Uni Düsseldorf, DKFZ/Uni Heidelberg, Uni Jena, Uniklinikum Münster
  Zellwerk GmbH Berlin, botiss biomaterials GmbH Berlin (straumann group)

- **Hybrid-Materials for Bone Regeneration**
  BMBF (2019-22) Uni Jena, Uni Bonn, Artoss GmbH, Spectral Service AG

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für Polymerforschung
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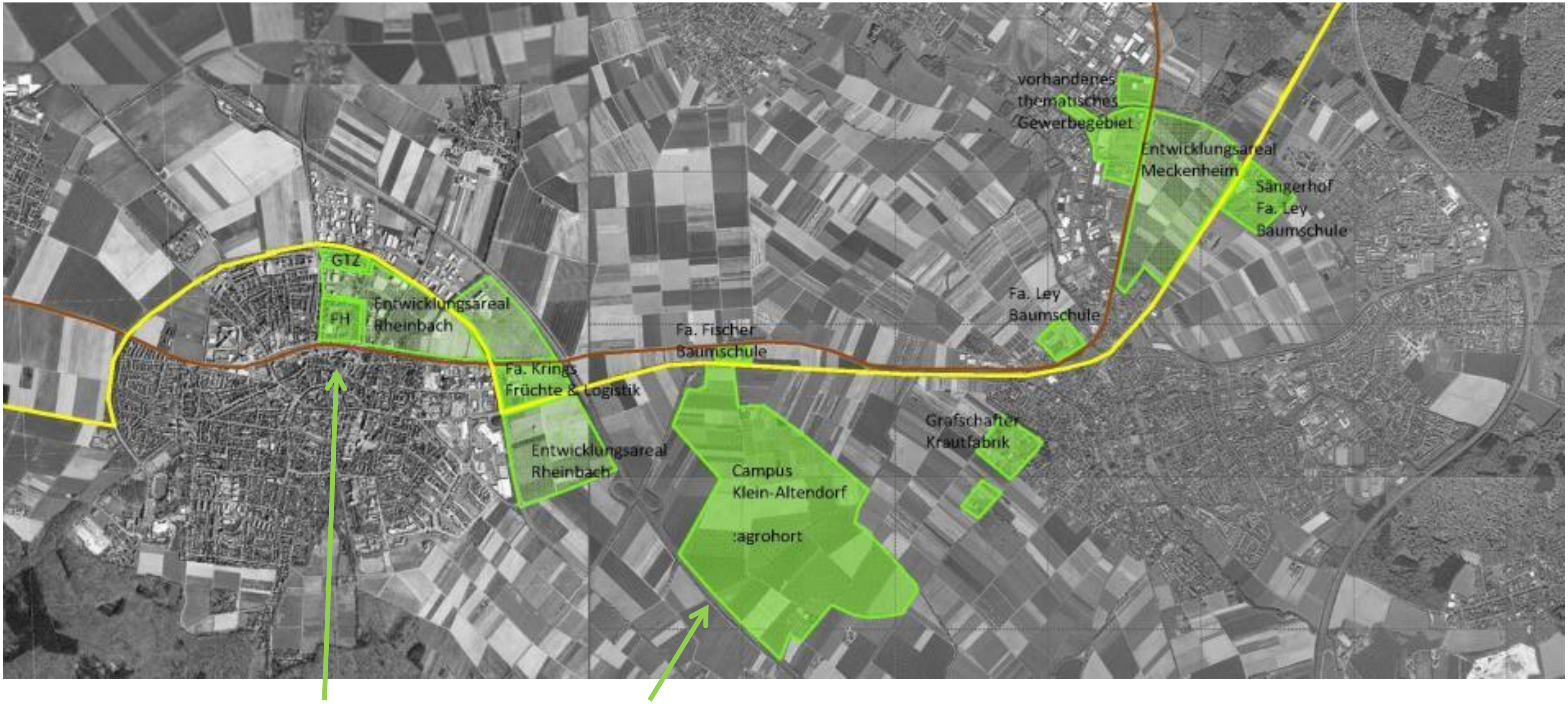
UNIVERSITÄT DÜSSELDORF



H-BRS and **University Bonn/Campus Klein-Altendorf** (180 ha)
City of **Rheinbach**

Lignocellulose Feedstock

Miscanthus

- ***low input* crop**: recycles nutrients stored in roots
  little to no fertilizer after being established

- **C4 plant:** ca. 5% of earth's plant biomass
  30 % of terrestrial carbon fixation
  (oxaloacetates versus D-3-phosphoglycerat)

- **high photosynthesis yield** at arid condition
  assisting CO_2 sequestration

- **perennial plant**: saving production costs
  decreasing environmental impact
  no tillage, less soil compaction/erosion

- ***Miscanthus* cascade utilization project**

Pude R *et al.* GCB Bioenergy (2017) 9, 274–279.

Campus Klein-Altendorf , Field Lab University Bonn

Cultivation of > 30 *Miscanthus* genotypes

Miscanthus sachariflorus

Miscanthus sinensis

Miscanthus *versus* Wood Pellets

	Lignin **%**	**Calorific value** kWh/kg	**Ash** **%**	**Moisture** **%**	**Density** kg/m³
Miscanthus X giganteus	19	4.9	1.5-3.5	**< 20**	**120**
Wood pellet (spruce)	22	5.1	2-3	**> 32**	**250**

Miscanthus x giganteus originally cultivated in Asia
hybrid of *Miscanthus sachariflorus / sinensis*

2013: ca. 67.500 t *Miscanthus* in Germany
ca. 4.500 ha (15 t / ha)
85 % energy recovery (wood chips, pellets)

Harvesting in: Sept, Jan and/or April
Variation of plant constitution/water content

Kraska T *et al*. (2018) Scientia Horticulturae 235: 205–213.

Lignocellulose Feedstock

Company	**Pulping Process**	**Capacity** (t/a)
Alfeld (SAPPI)	Mg sulphite	130.000
Ehingen (SAPPI)	Mg sulphite	130.000
Mannheim (SCA)	Mg sulphite	220.000
Stockstadt (SAPPI)	Mg sulphite	140.000
Blankenstein (Mercer)	**Kraft**	**300.000**
Stendal (Mercer)	**Kraft**	**600.000**

- Global annual availability ca. 70 Mio t ▪ Annual growth rate of 2 % until 2023.
- Increasing total market size: US$ 904 Mio in 2017 to US$ 1021 Mio in 2023.

Benchmark: energetic use of blak liquor.

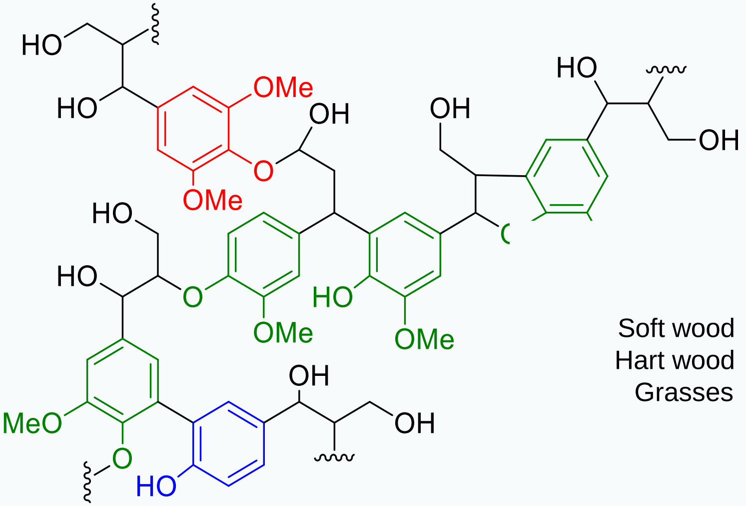
Lignin Market - Forecasts from 2018 to 2023. ID: 4479455. Report February 2018.

Lignin Composition & 3D Structure

Approaches in lignin research:

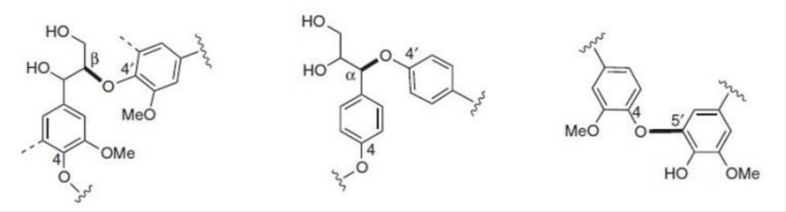
1. **Exploitation of unmodified lignin**
   and improve access to functional group
   (via optimizing the isolation process)

2. **Chemical modification of lignin**
   functionalization versus depolymerization

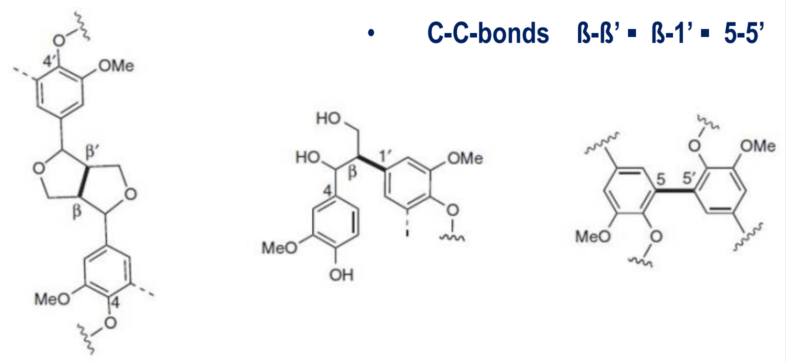


Soft wood	G units
Hart wood	GS units
Grasses	HGS units

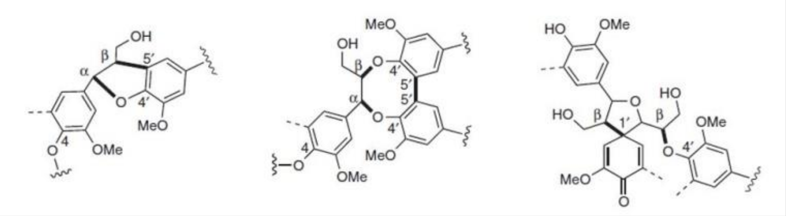
- **ether bonds ß-O-4' ▪ α-O-4' ▪ 4-O-5'**



- **C-C-bonds ß-ß' ▪ ß-1' ▪ 5-5'**



- **more complex linkages**

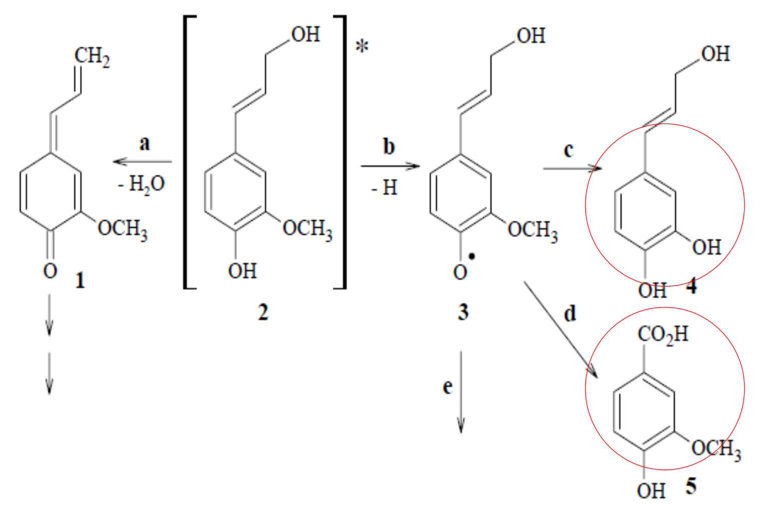


Alzagameem A *et al.* (**2018**) Molecules 23, 2664.
doi:10.3390/molecules23102664

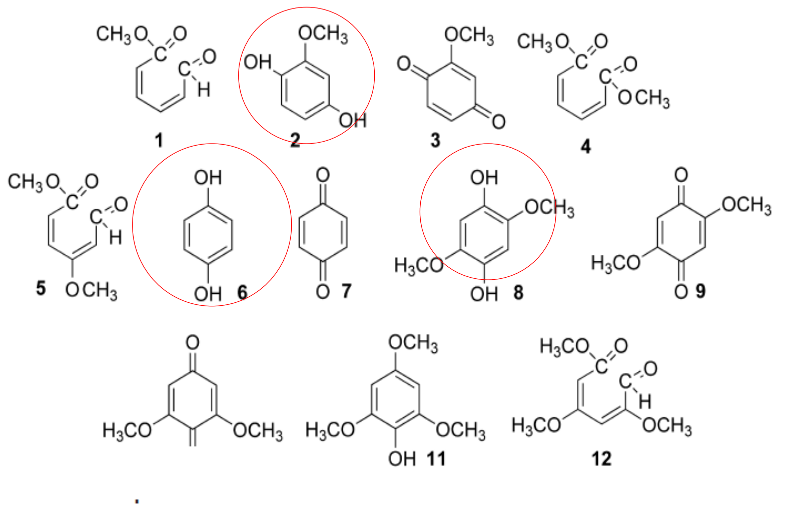
Lignin Depolymerization

photofragmentation via $^1O_2$

oxidative fragmentation via O_3



Photolysis of lignin model compounds (Kansal, 2008)



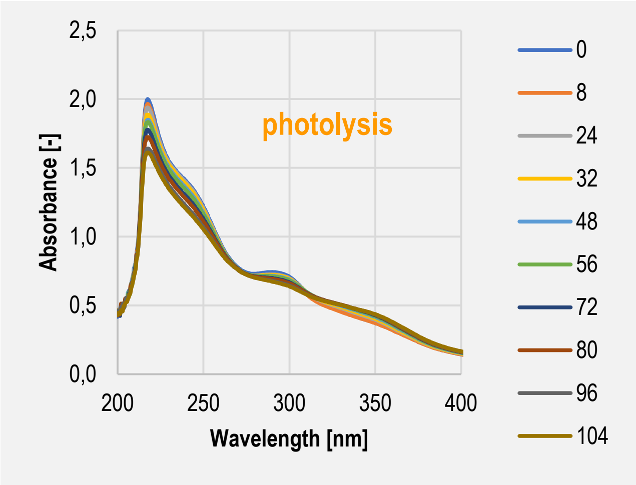
Ozonolysis of lignin model compounds (Sonntag, 2009)

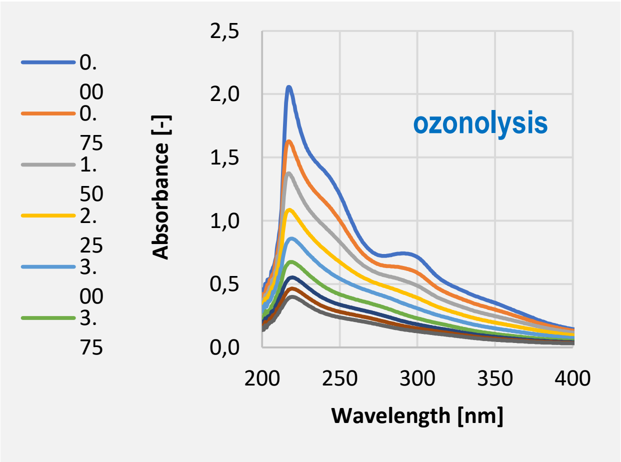
Do *et al.* Preprints **2017**, 2017100128, doi:10.20944/preprints201710.0128.v1)

Target: monomers and/or oligomers of low polydispersity and appropriate functionality for polymer synthesis

Parameter: temperature ▪,pH ▪ reaction time ▪ catalyst ▪ ozon concentration / flow rate ▪ light source / intensity

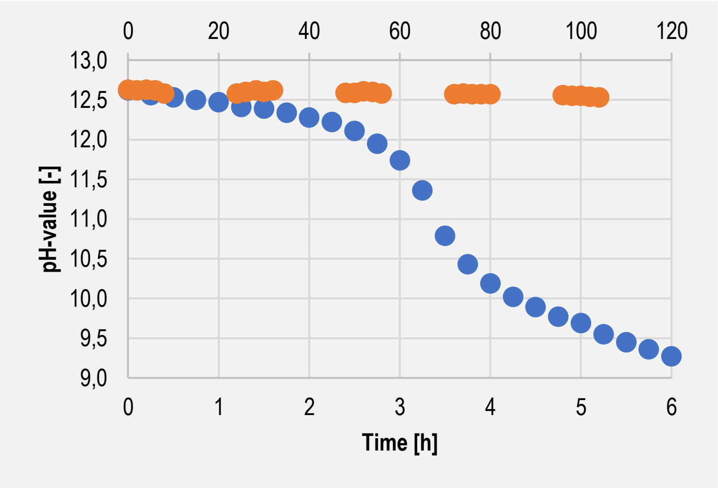
Lignin for Energy Storage





UV absorbance at **280 nm**
decreases during **ozonolysis** but
stays approximately constant in **photolysis**

ozonolysis versus **photolysis**
pH decrease indicating mineralization for **ozonolysis**



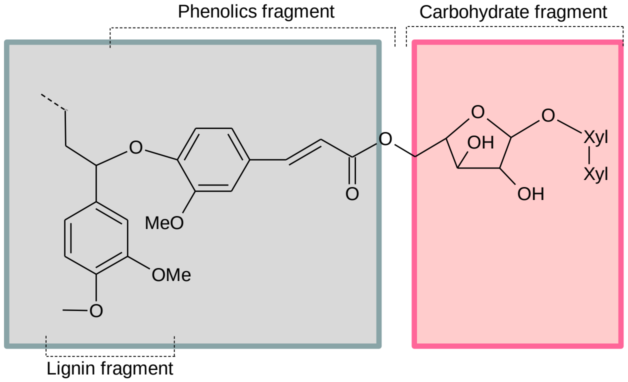
Pulping Process and Lignin Structure

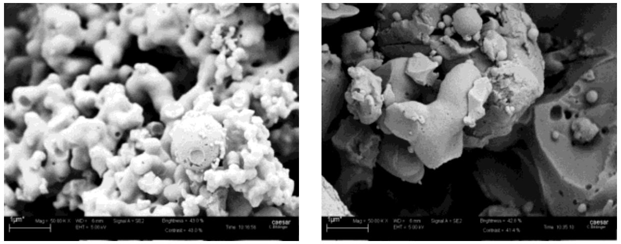
Lignin structure as function of:

- plant type (cultivation / harvesting conditions)
- pulping process (solvent, temperature, pressure, catalysts)

Pulping process	AFEX NH_3	H_2O steam explosion	**Organosolv** methanol	Sulfonate
Lignin % w/w	25	52	94	71
Sugar % w/w	5	21	none	12
Solubility	low	low	high	low
T_g (°C, DSC)	87	75	123	113
T_d (°C, DSC)	341	367	346	374
M_W (SEC) g/mol	≈ 1.500	≈ 2.000	≈ 2.000	≈ 15.000
H / G / S unit	**20/70/10**	**13/42/45**	**32/49/19**	**17/75/8**

Pulping process with influences on: ▪ monolignol ratio ▪ linkages
▪ number/nature of functional groups ▪ morphology ▪ molecular weight
▪ polydispersity ▪ surface polarity and topography





Lignin surface: pulping with / without acidic catalysts

Hansen *et al.* (**2016**) J Polym Environ 24, 85-95
doi:10.1007/s10924-015-0746-3.

Biomass Influence on Lignin Amount and Structure

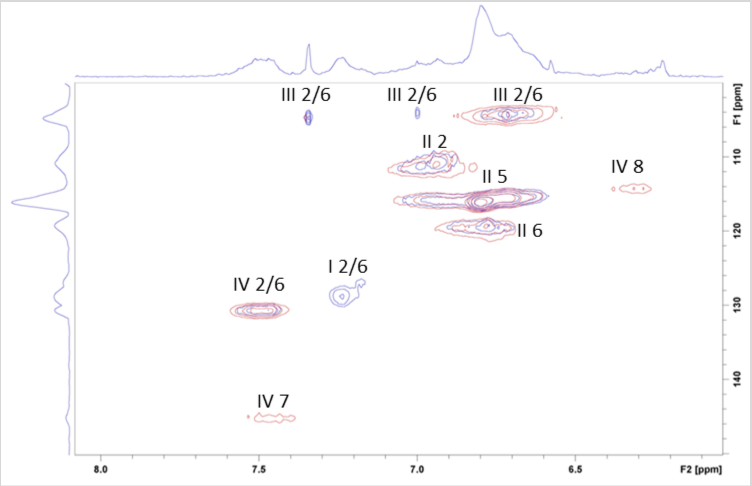
	Beech	*M. giganteus* 2012	*M. giganteus* 2014	*M. robustus*	*M. sinensis*
M_w [g/mol]	1553	1075	1004	943	934
M_n [g/mol]	533	700	675	646	637
PDI	**2,92**	**1,54**	**1,49**	**1,46**	**1,47**

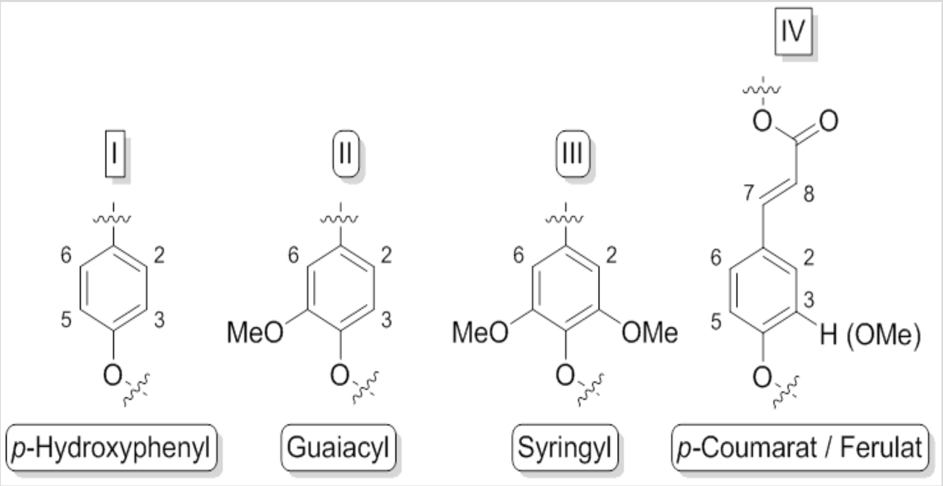
- **Lignin MW and Polydispersity**
- Biomass source beech *versus* miscanthus

- **Monolignol content via HSQC NMR**

Miscanthus X giganteus

- **H** highest in leaves and early harvest
- **S** highest in stem and late harvest





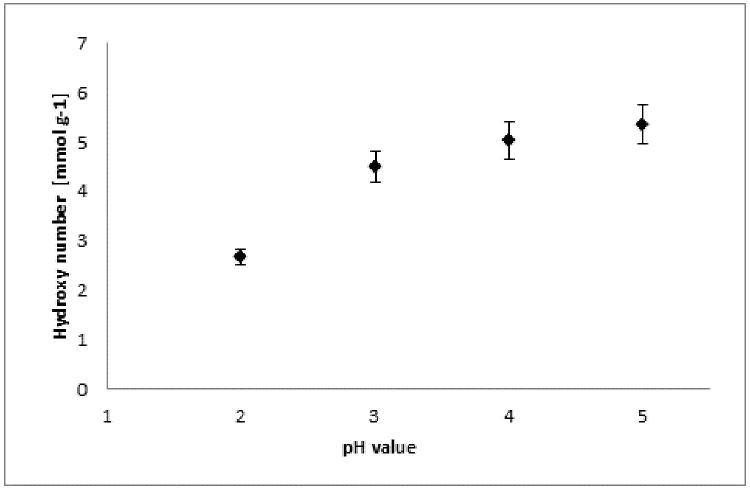
Witzler *et al.* (**2018**) Molecules 23:1885. doi:10.3390/molecules23081885

OH Number of Lignins

ISO 14900:2001(E)

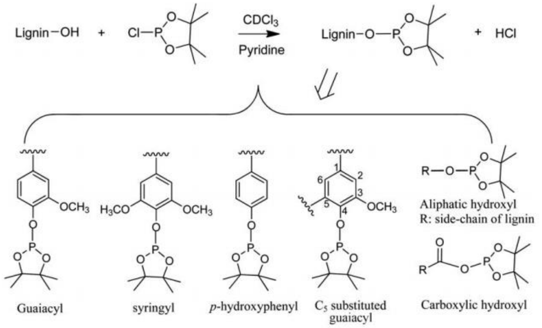
Acetylation

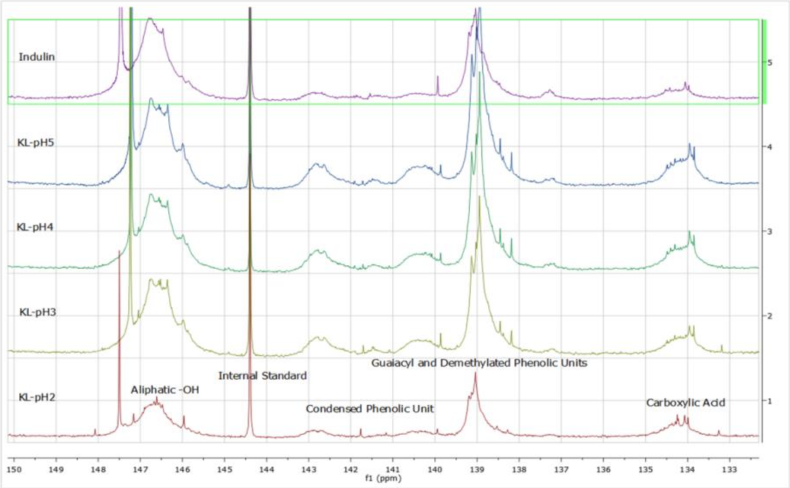
Kraft lignin	**Yield** [g/100 g black liq]	**Mw** [g/mol]	**OH number** [mmol/g]	**Tg** [°C]
pH 2	21.40	1885	**4.81**	147.9
pH 3	14.65	1797	**5.02**	147.2
pH 4	13.53	1731	**5.65**	142.5
pH 5	12.95	1504	**6.00**	134.0



^{31}P NMR

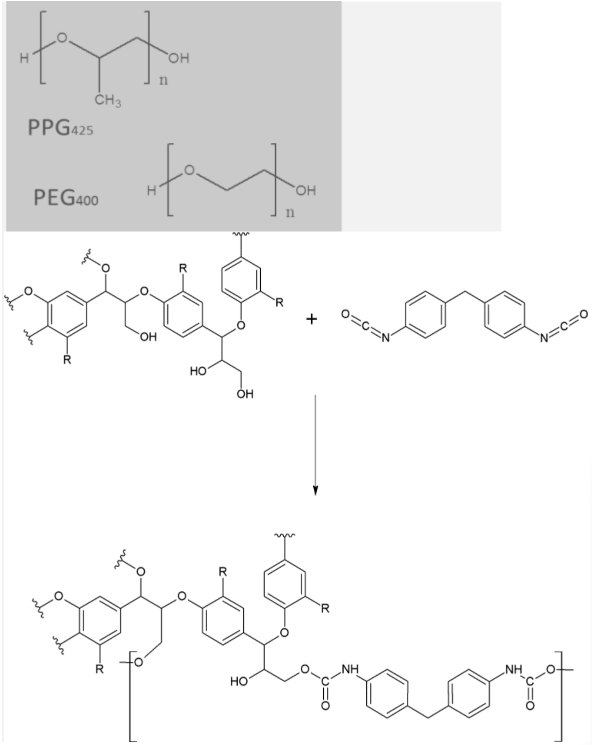
Phosphorylation



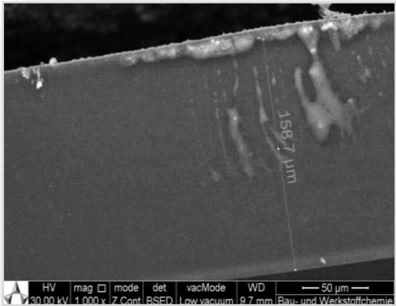


Klein *et al.* (**2018**).
Manuscript ID: RA-ART-10-2018-008579.

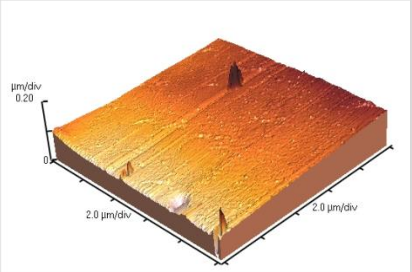
Lignin-based PU Coatings



homogeneous ▪ transparent
flexible spin coat films



average thickness 160 µm

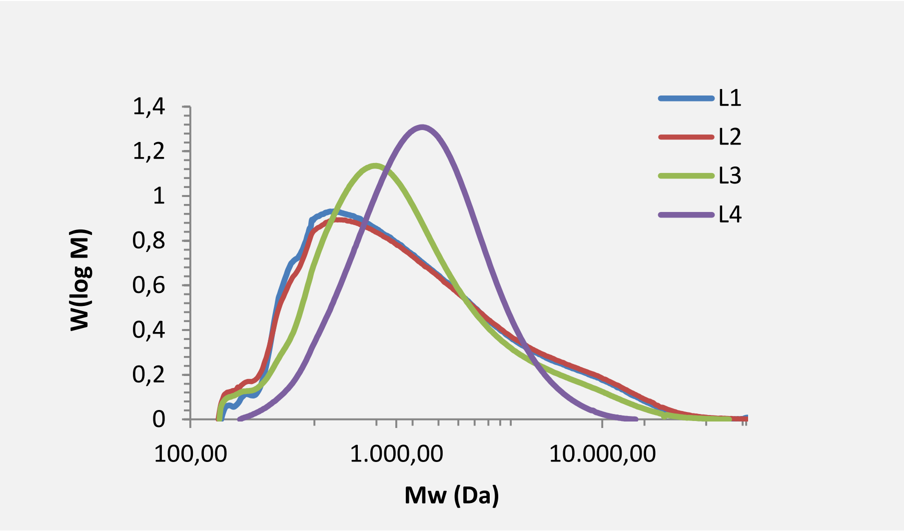


color modification (dyes, carbon).

lignin content increased up to 80 %

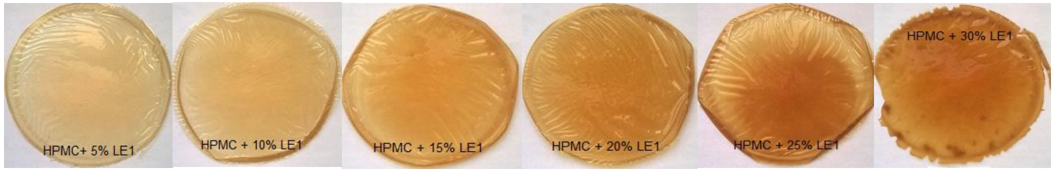
Klein *et al*. (**2018**).
Manuscript ID: RA-ART-10-2018-008579.

Lignin-based Drug Release



SEC of Kráft Lignin Fractions L1 to L4.

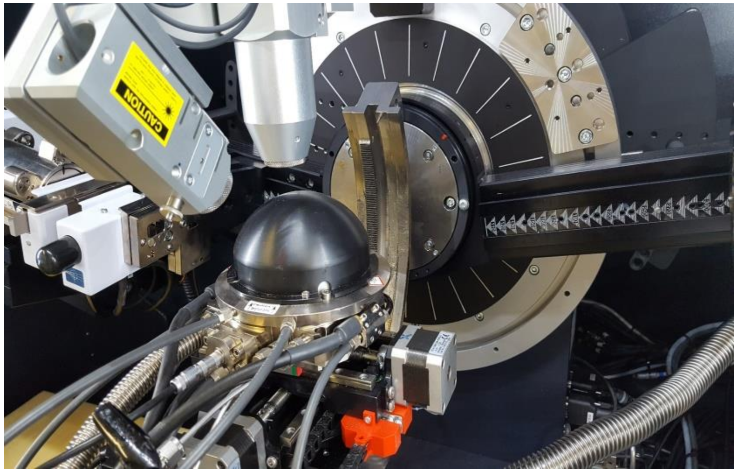
Fraction	Mn (g mol $^{-1}$)	Mw (g·mol^{-1})	PD
L1	720	2108	2.9
L2	706	2226	3.2
L3	757	1816	2.4
L4	1043	1690	1.6



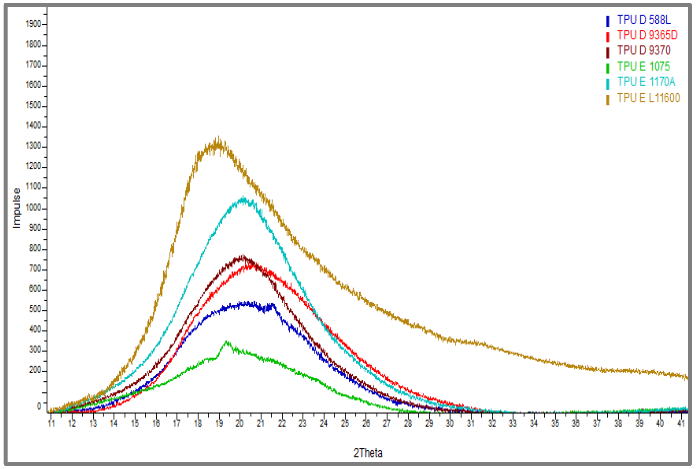
Lignin-based films with hydroxypropyl methylcellulose (HPMC):
From left to right 5, 10, 15, 20, 25 and 30 weight % lignin

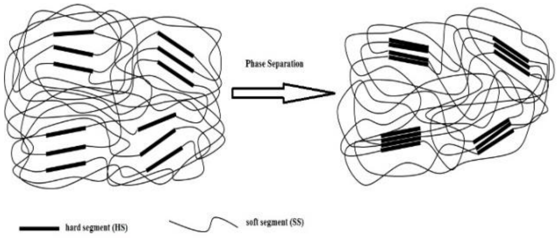
Alzagameem *et al.* (**2018**), Molecules 23:2664.
doi:10.3390/molecules23102664.

Morphology Analysis via Xray Diffraction



- Bruker D8 diffractometer
- 2 D detector Vantec 500
- µ-source Incoatec Microsource IµS
- Anton-Paar DHS 1100 Temperature Dome





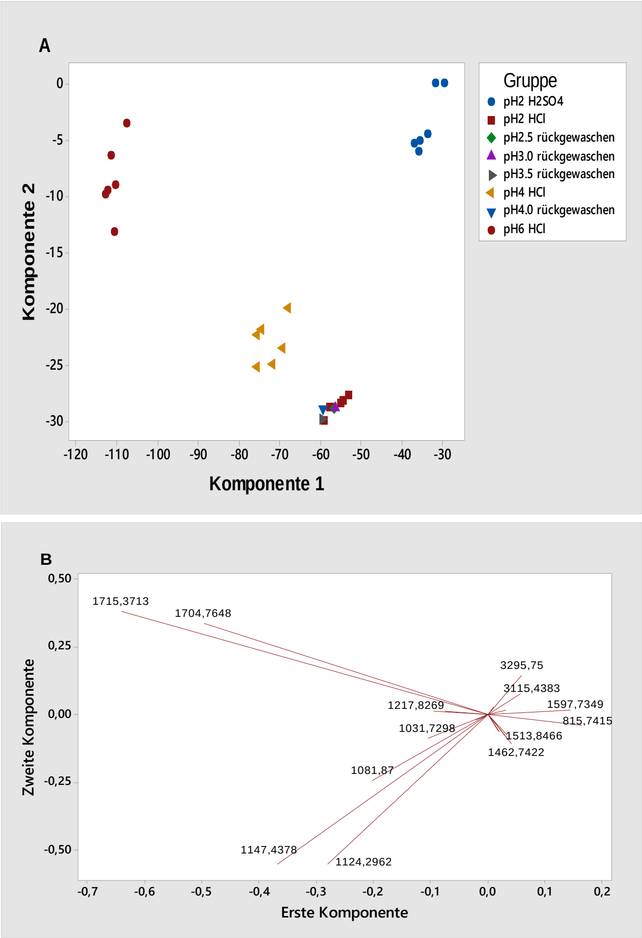
WAXS / SAXS morphology analysis of lignin-based PU

- decreasing size of crystalline domains
- significant temperature dependency (T 30-130°C)

Witzleben *et al.* ST (**2015**) J Chem Chem Eng 9:494-499.
doi: 10.17265/1934-7375/2015.08.002

Hochschule
Bonn-Rhein-Sieg
University of Applied Sciences

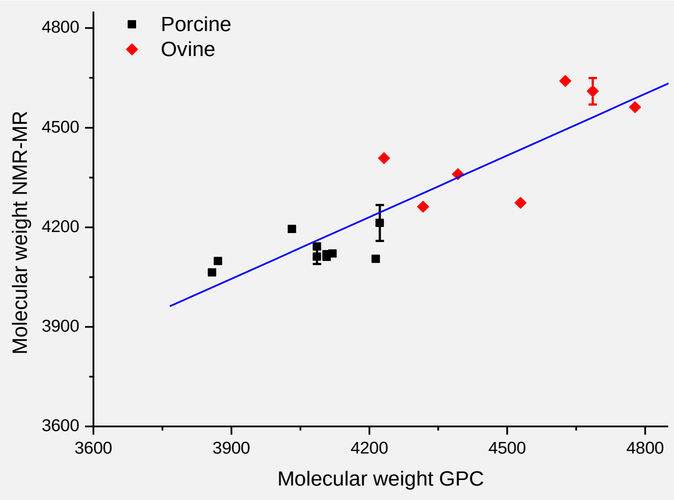
Multivariate Data Analysis
Principal Component Analysis



Principal Component Aanalysis of FTIR data.
Above: Groups of precipitated lignins at different pH.
Below: FTIR wavenumber of corresponding signals.

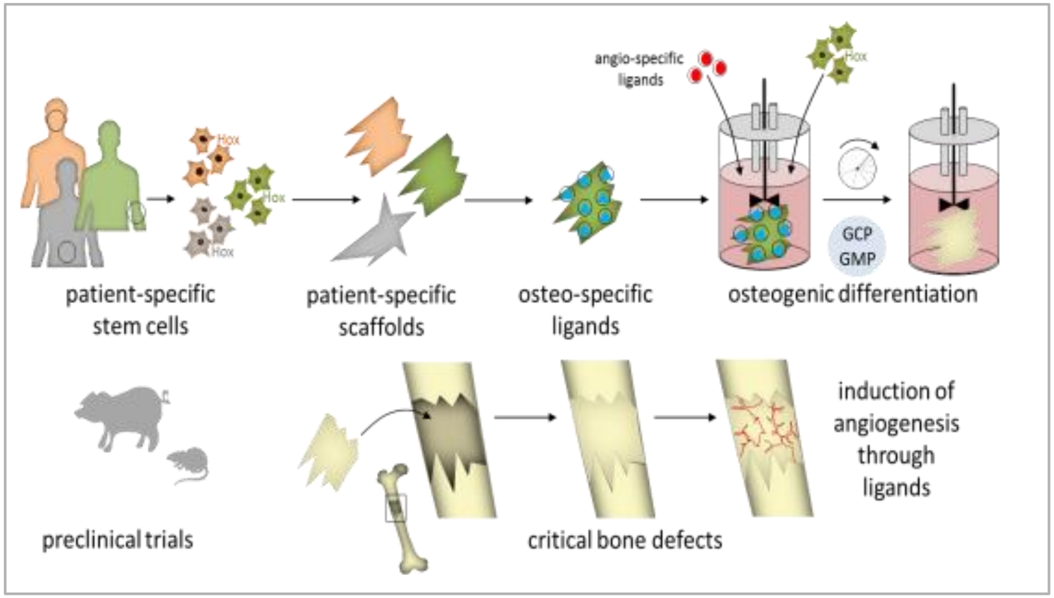
Outlook: access to lignin specifications

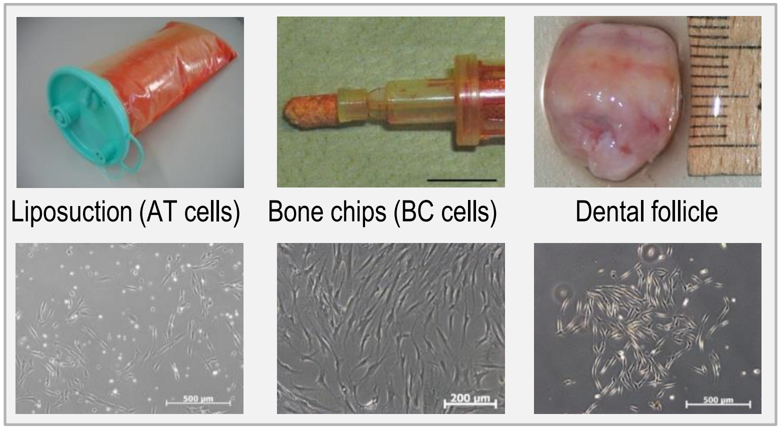
- Reproducibility of isolation (FTIR / PCA)
- GPC/DOSY NMR and PCA
- GPC standards *via* ozonolysis/photolysis
- Comparison to Fenton (Wessling *et al.* RWTH)



Monakhova *et al.* (**2018**) J Pharm Biomed Anal. 149, 128-132.
doi.org/10.1016/j.jpba.2017.11.016

Biomaterials for Bone Regeneration




Liposuction (AT cells)
Bone chips (BC cells)
Dental follicle

Schulze & Tobiasch (**2012**). In: Tissue Engineering III. Springer.
Leiendecker *et al.* (**2016**) Curr Stem Cells Res Therapy 12:103-123.

Commercial Inorganic Scaffolds

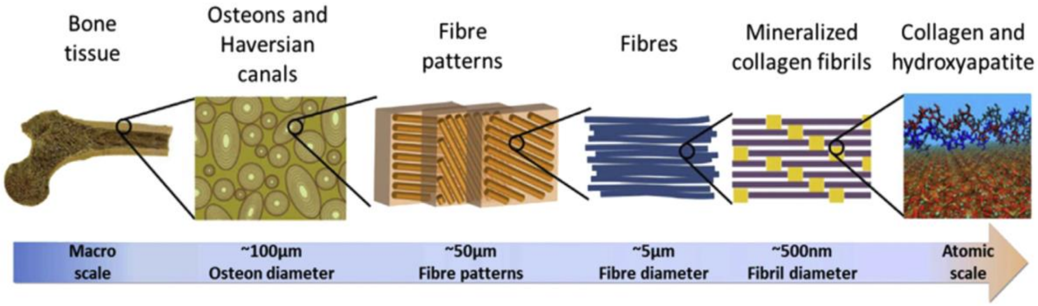
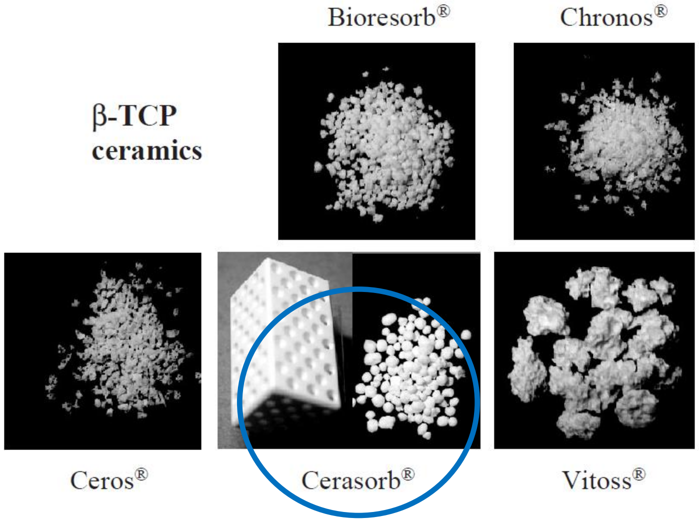
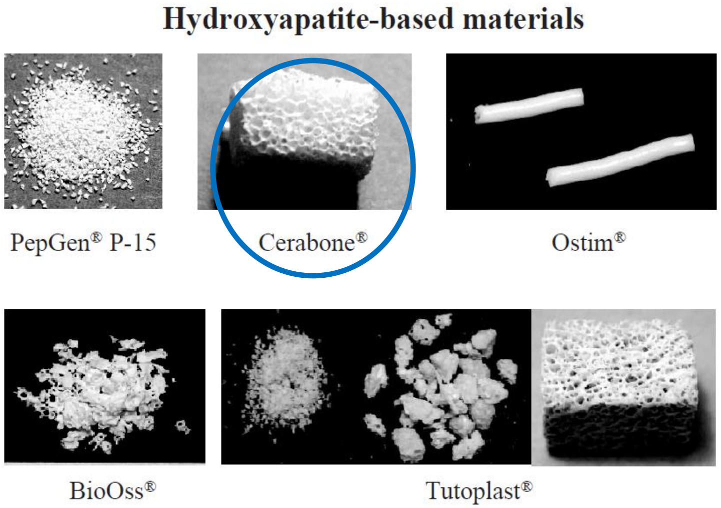


Fig. 1. The hierarchical structure of bone ranging from microscale skeleton to nanoscale collagen and hydroxyapatite. Reprinted by permission from Macmillan Publishers Ltd: Nature Communication [21], copyright (2013).

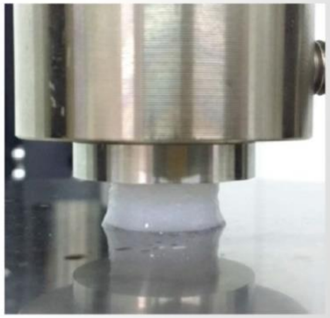


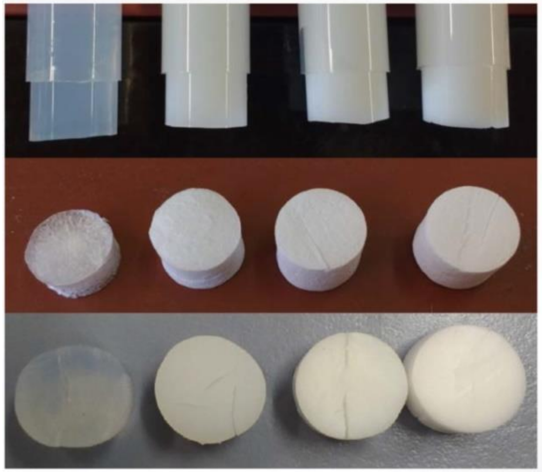


Hansen *et al.* (**2017**) In: eBook series "Frontiers in Stem Cell and Regenerative Medicine Research", Attaur-Rahman , Shazia Anjum (Eds.), p. 130-178, Bentham eBooks.

Agarose/Hydroxyapatite Hybrids

- comparison of
  - agarose 2%
  - agarose 2%, hydroxyapatite 1%
  - agarose 2%, hydroxyapatite 2%
  - agarose 2%, hydroxyapatite 4%
- as prepared gels, lyophylized, rehydrated

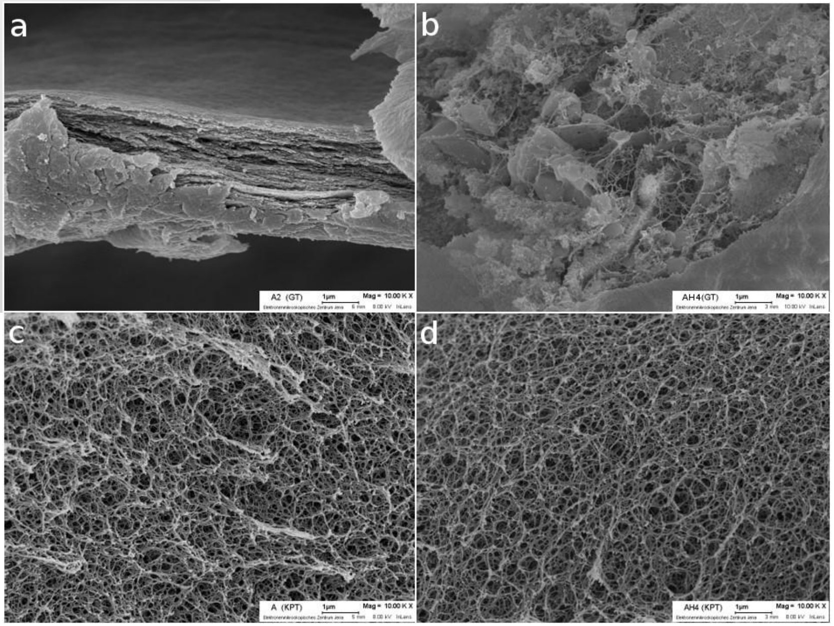




as prepared, before cutting
diameter: 16 mm
height: 10 - 11 mm

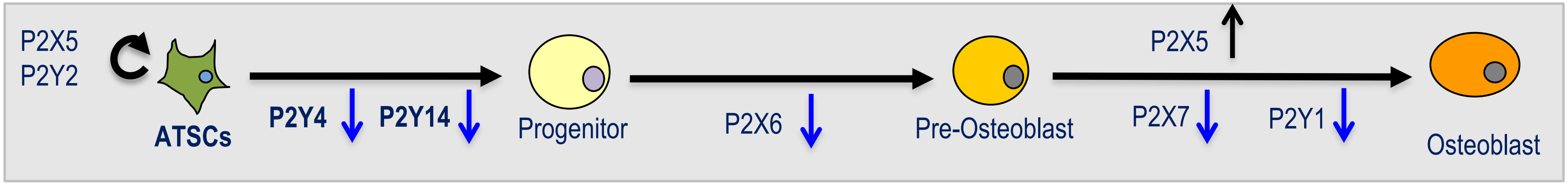
lyophylized,
approx. diameter: 14 - 16 mm
approx. height: 7 - 10 mm

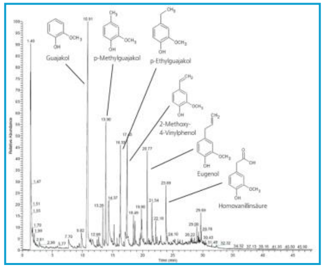
as prepared,
after testing



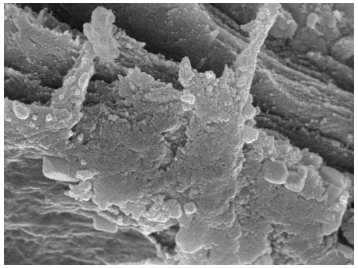
SEM of lyophilized agarose (**a**/**c**), AG33HA67 composite (**b**/**d**) supercritically dried samples. Scale bar is 1 µm.

Hybrid Scaffolds for Guided Osteogenesis

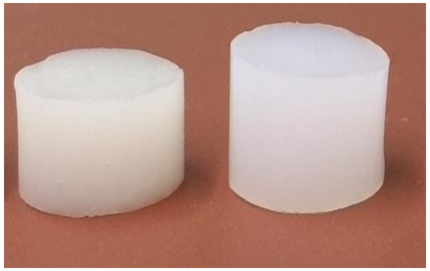




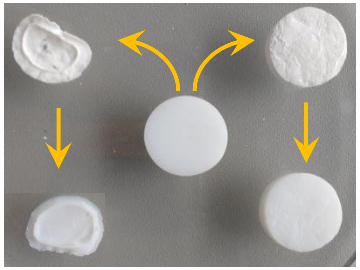
composition



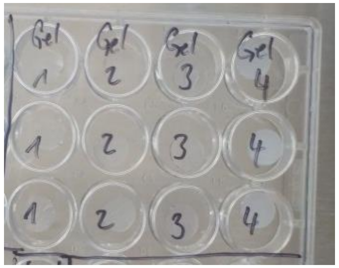
morphology



hydrogel formation



swelling & release

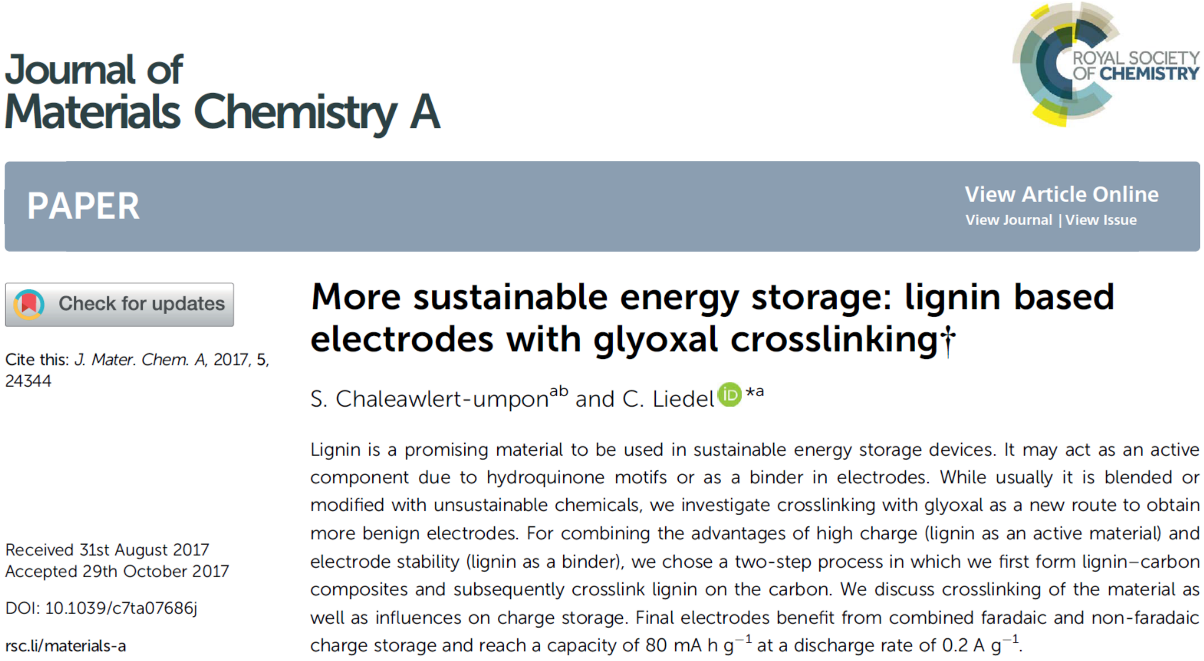


biocompatibility

Gericke M *et al. Functional Agarose Hydrogels and Composite Hydrogels*.
ACS Spring Meeting March 18-22, 2018 in New Orleans.

Ottensmeyer P *et al.* ***Small Molecules Enhance Scaffold-based Bone Grafts 2 via Purinergic Receptor Signaling in Stem Cells***.
Submitted to: Int J Mol Sci, Manuscript ID: ijms-367947

Lignin for Energy Storage



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More sustainable energy storage: lignin based electrodes with glyoxal crosslinking†

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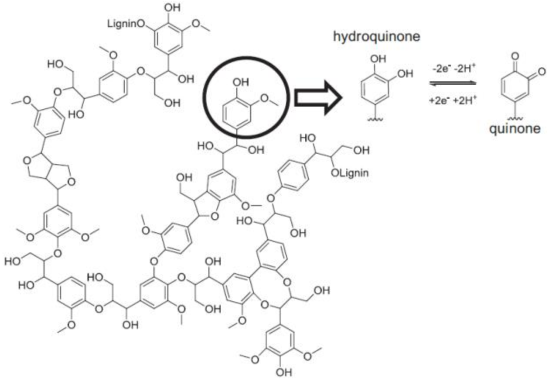
Lignin is a promising material to be used in sustainable energy storage devices. It may act as an active component due to hydroquinone motifs or as a binder in electrodes. While usually it is blended or modified with unsustainable chemicals, we investigate crosslinking with glyoxal as a new route to obtain more benign electrodes. For combining the advantages of high charge (lignin as an active material) and electrode stability (lignin as a binder), we chose a two-step process in which we first form lignin–carbon composites and subsequently crosslink lignin on the carbon. We discuss crosslinking of the material as well as influences on charge storage. Final electrodes benefit from combined faradaic and non-faradaic charge storage and reach a capacity of 80 mA h g^{-1} at a discharge rate of 0.2 A g^{-1}.



Scheme 1. Lignin structure and the reversible redox reaction between quinone and hydroquinone.

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