Characterization of Green Carbons Produced by the Hydrothermal Carbonization of a Biorefinery Lignin Waste-Stream

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Overview

- The forest biorefinery in a circular economy
- Why waste lignin?
- Hydrothermal carbonization
- Results and conclusions

Integrated Forest Biorefinery

Extraction | Saccharificaton | Gasification

Pulp, Oils and Fats | Sugars | Synthesis Gas

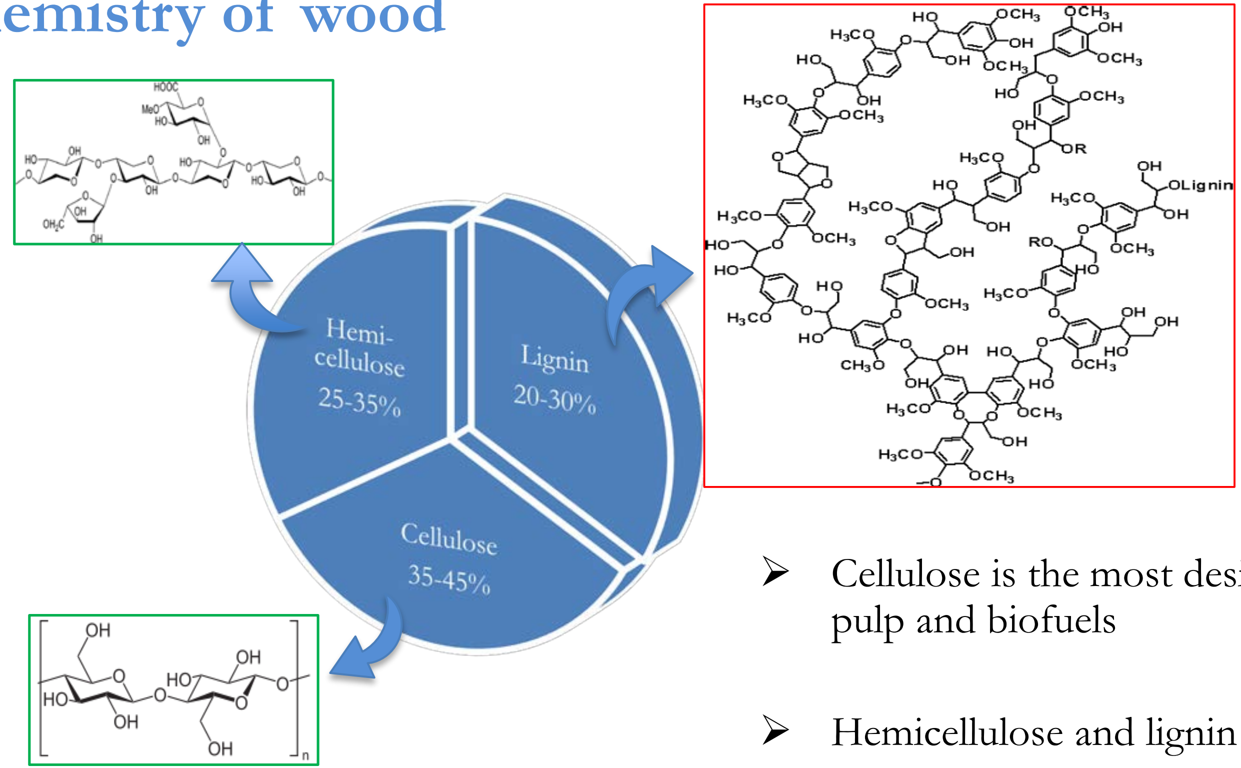
Bioprocesses

Fuels

Chemical products

Biomaterials

Chemistry of wood



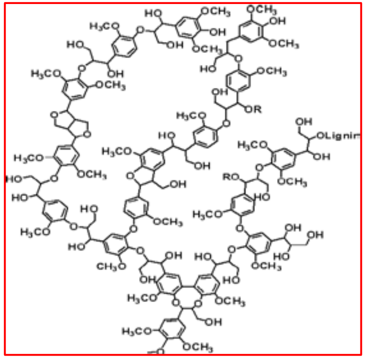
- Cellulose is the most desired fraction for making pulp and biofuels
- Hemicellulose and lignin have great potential
- Circular economy advocated through upgrading of lignocellulosic wastes

Background……Lignin

- Polyaromatic compound built on phenyl propane units
- Chemistry defined by method of isolation
- Approximately 130 MT/year worldwide
- Only 2% commercialized (dispersants, adhesives and surfactants)
- Current research includes carbon fibers, adsorbents, active carbons, electrochemistry etc
- Greatest challenge is depolymerization into lower fragment molecules

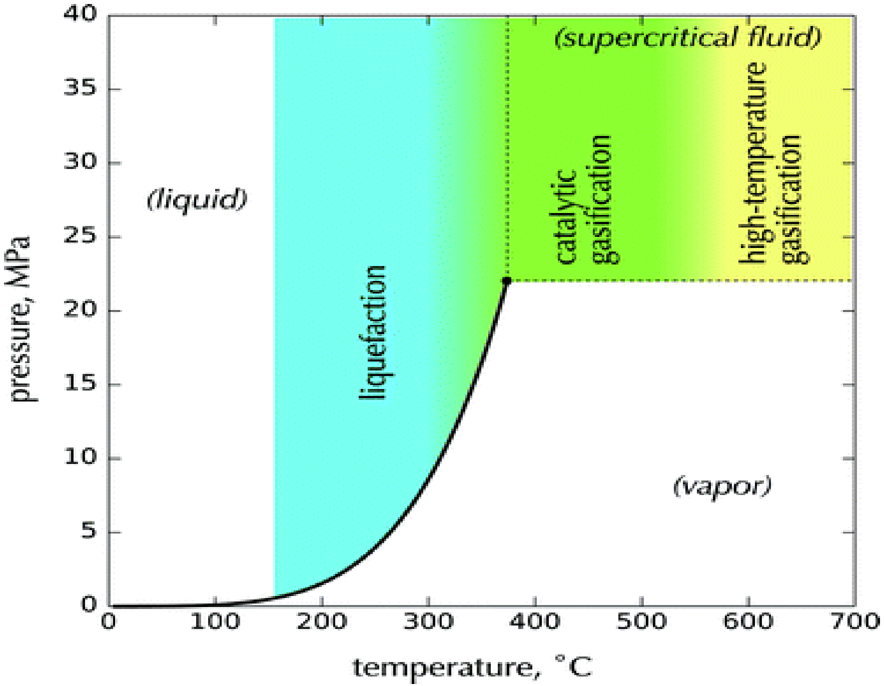
" You can make anything out of lignin….*except money*"

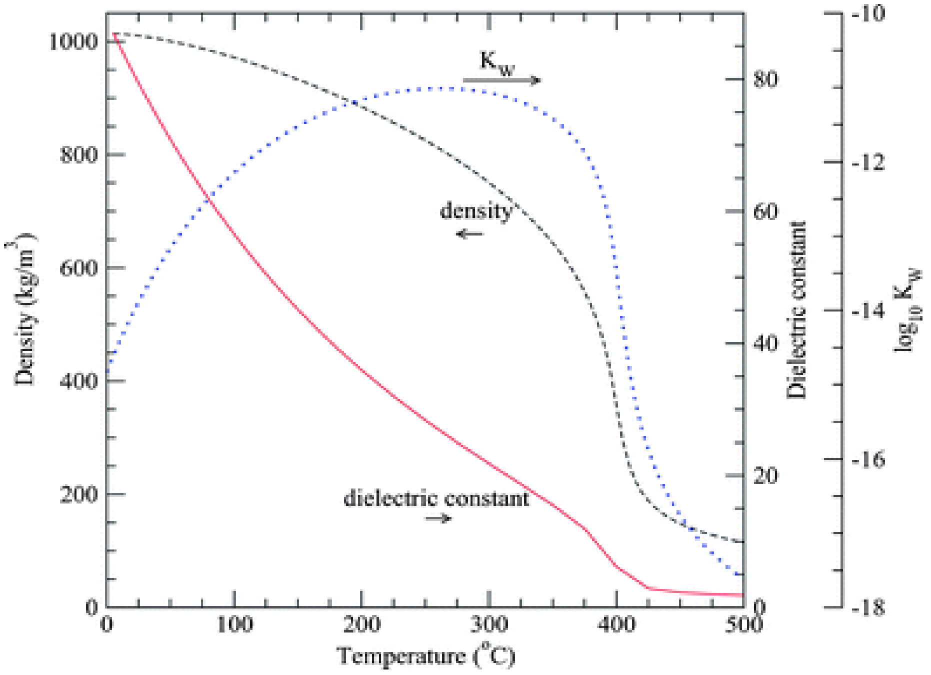
Our approach



- Solvent: Water (70 ml) ± (acid or base)
- Reaction conditions: ($T \leq 374\ ^{o}C$, $P \leq 2.2$ MPa)
- Time: 60 minutes
- Lignin: 5 g

Hydrothermal carbonization?





A. A. Peterson, F. Vogel, R. P. Lachance, M. Fröling, J. Michael J. Antal and J. W. Tester, *Energy & Environmental Science*, 2008, **1**, 32–65.

Subcritical water properties

Advantages of HTC

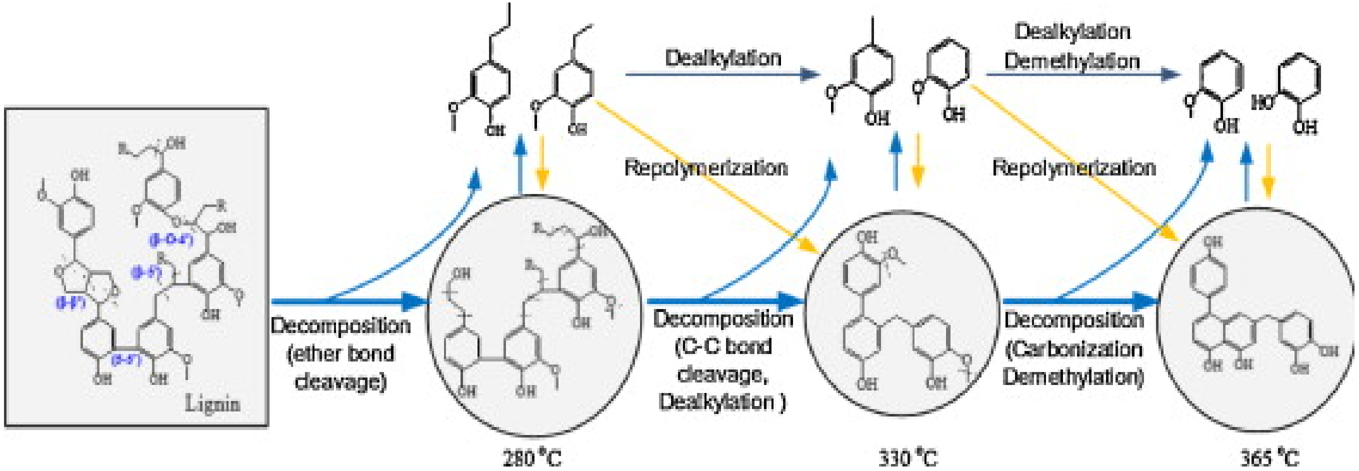
- Environmentally friendly
- Energy saving
- Well controlled morphology, composition and structure
- Specific surface functional groups (OH, COOH, CHO)

Yield of solid products (carbonaceous material)

Sample	Temperature (^{0} C)	Final mass (g)	Yield (%)
L200	200	4.4	88
L250	250	4.5	88.6
L300	300	3.9	78
L350	350	3.4	68

Table 1: Effect of temperature on char yield

Proposed lignin depolymerization pathway



Lignin undergoes:

- Hydrolysis
- Dealkylation
- Repolymerization

J. Hu, D. Shen, S. Wu, H. Zhang and R. Xiao, *Journal of Analytical and Applied Pyrolysis*, 2014, **106**, 118–124.

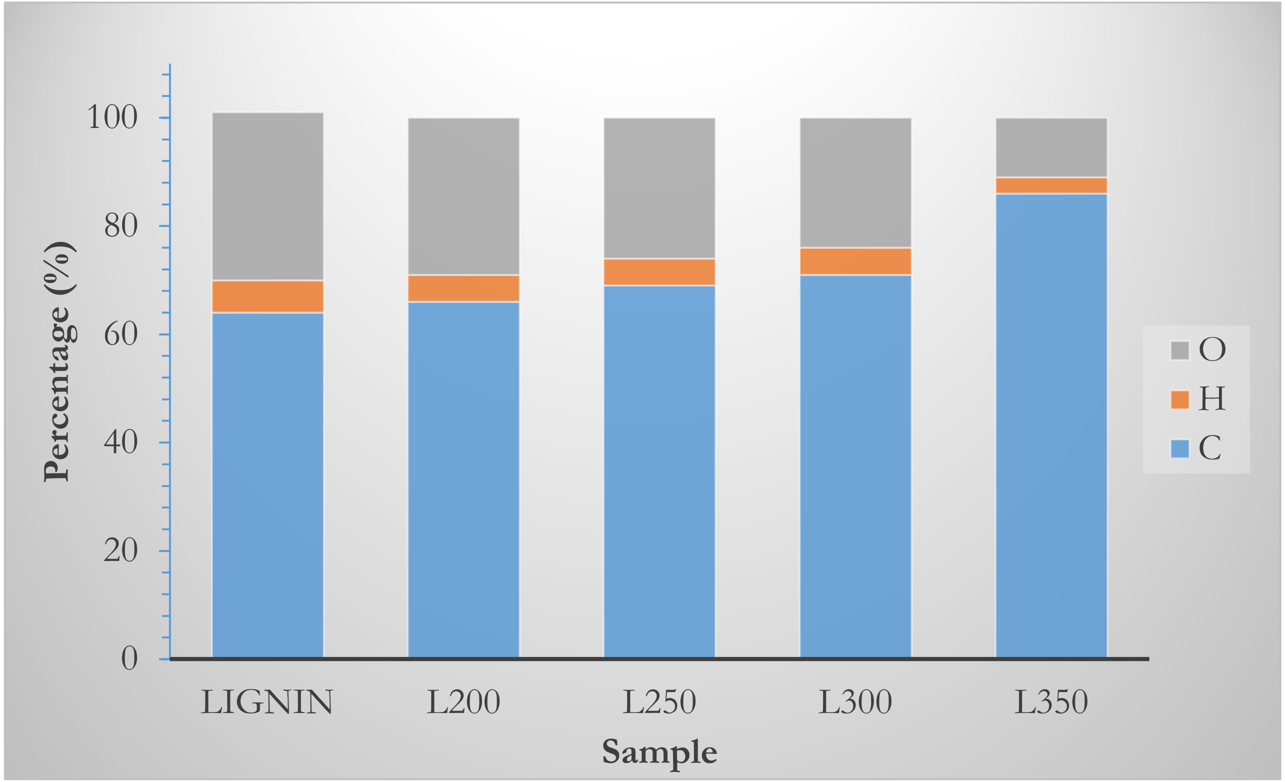


Figure 1. Elemental analysis of untreated lignin and CMs

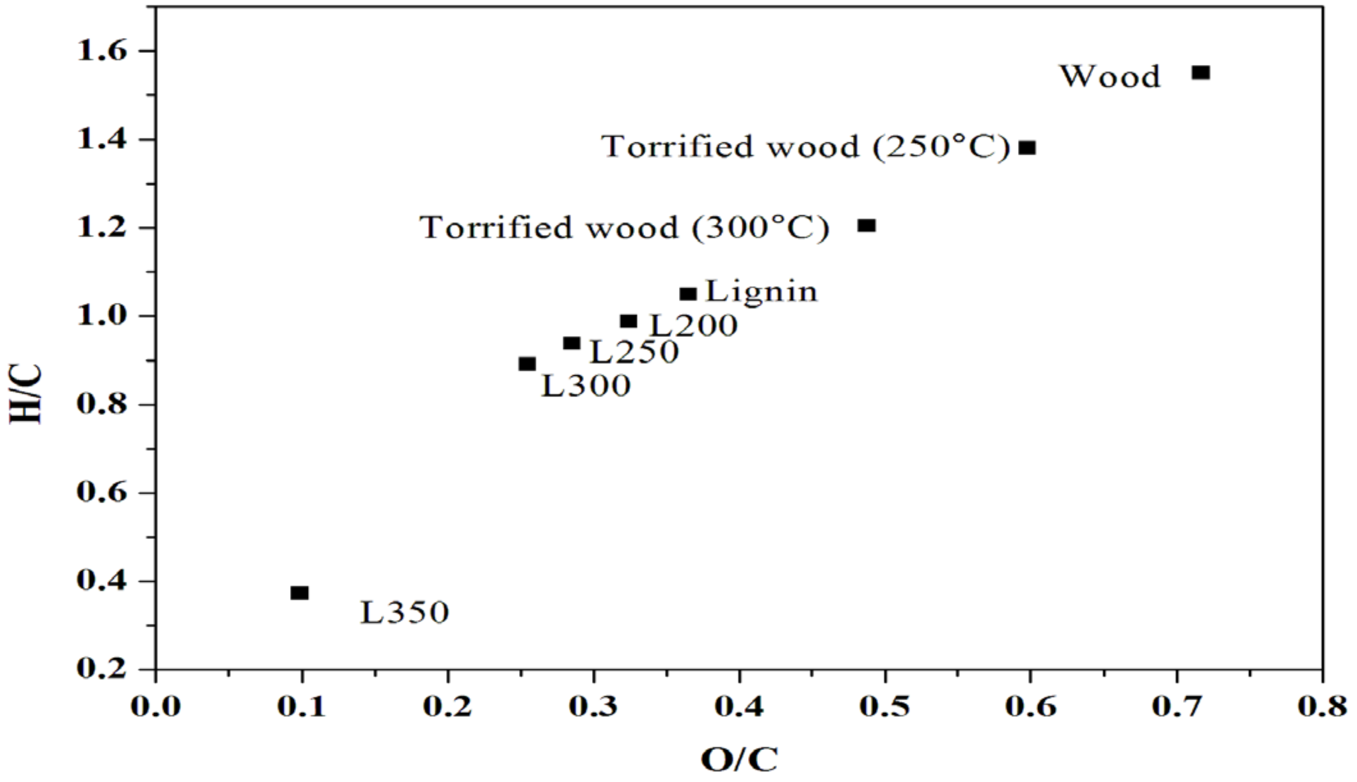


Figure 2. Van Krevelen diagram of carbonaceous materials compared with wood and torrefied wood

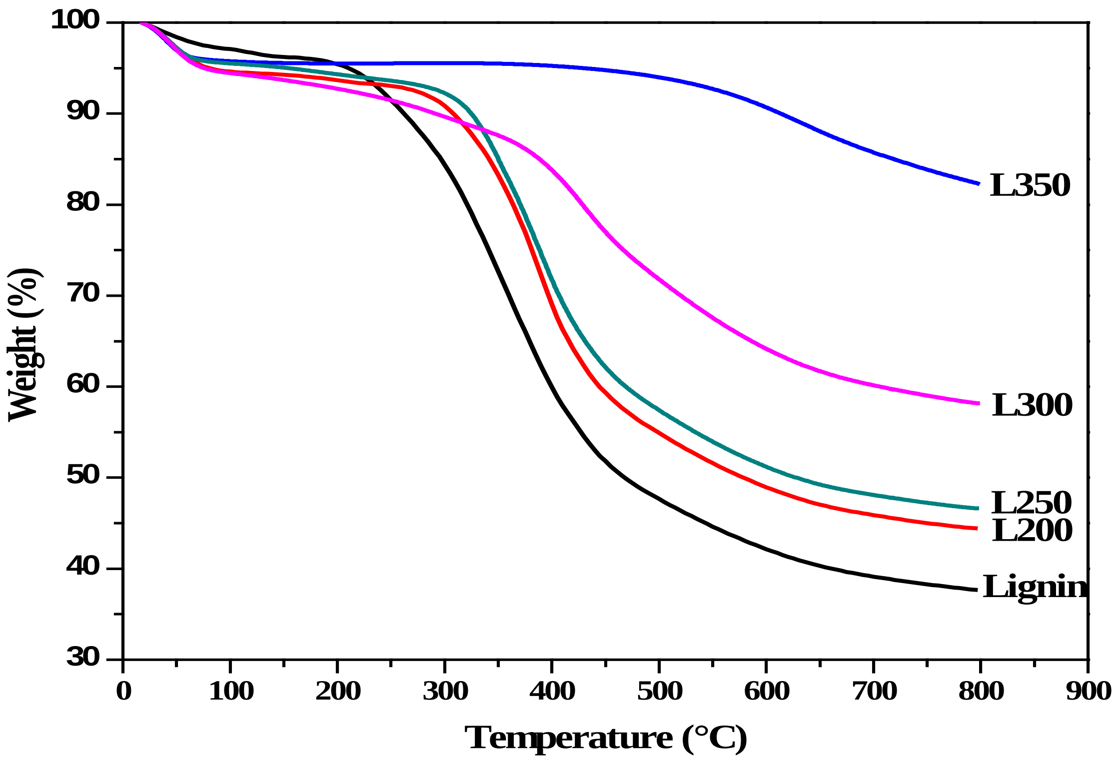


Figure 2: Comparison weight loss (%) with temperature (°C) for untreated lignin and CMs

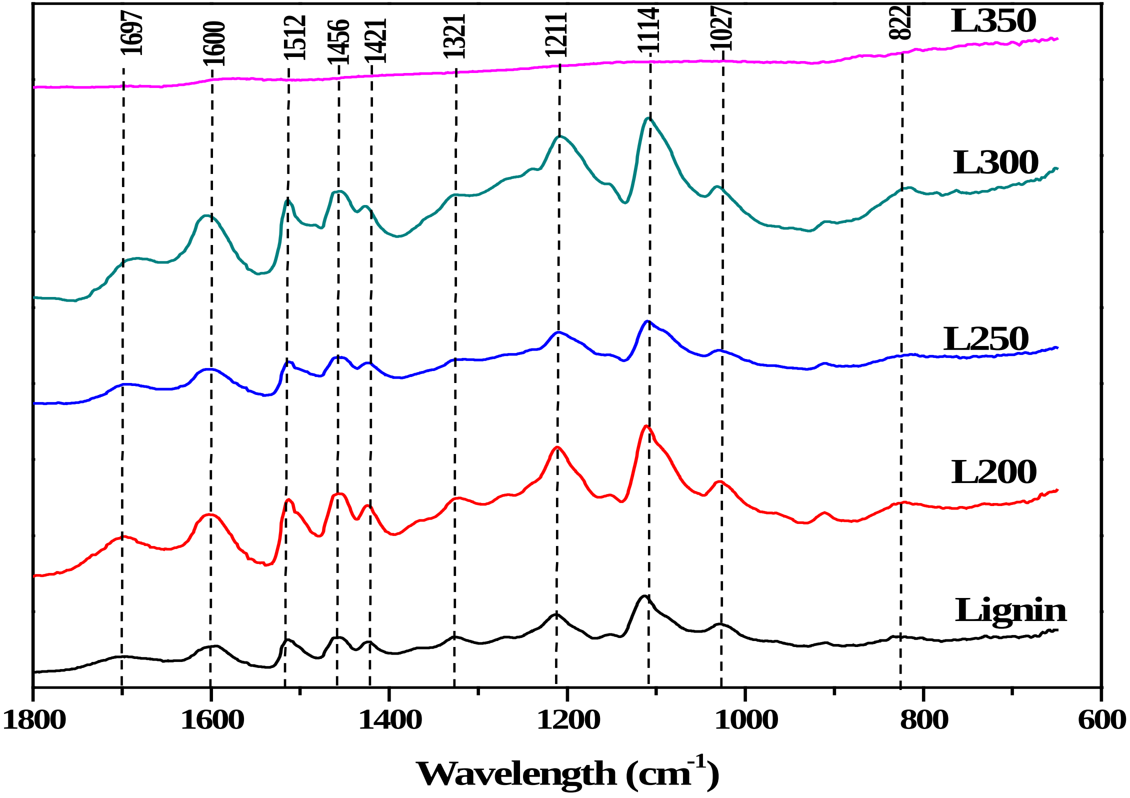


Figure 3. IR spectra of untreated lignin and their HTC-derived CMs

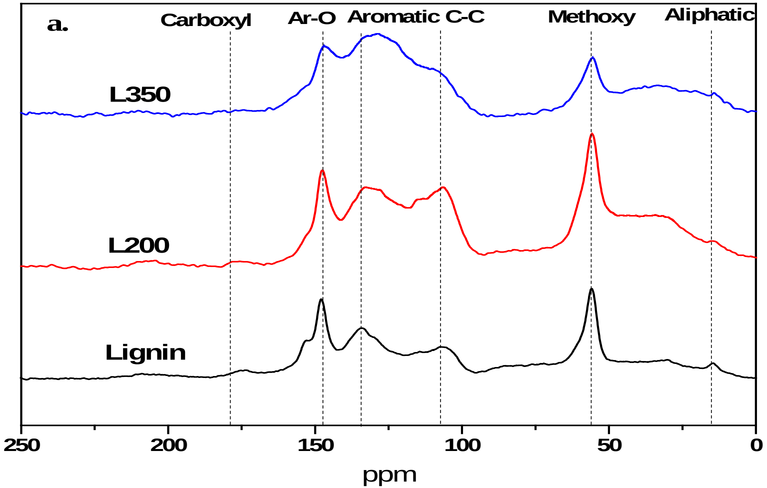


Figure 4: ^{13}C CP solid state NMR of untreated lignin and their HTC-derived CMs

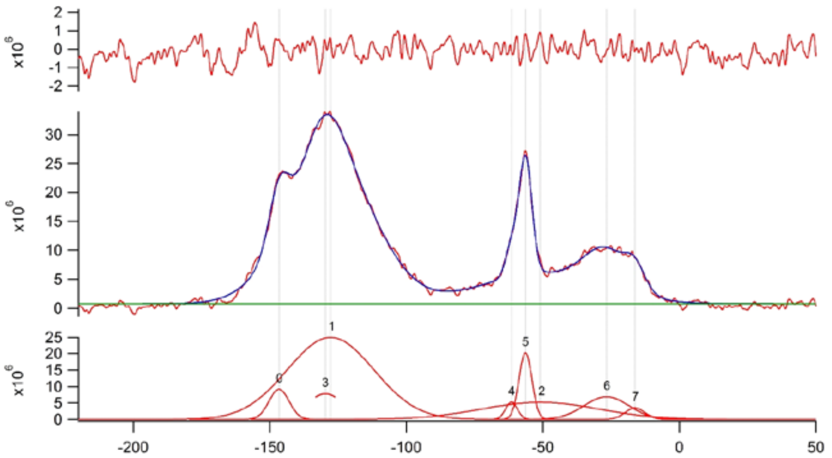


Figure 5: L350 DP spectrum and fitted peaks from deconvolution

	Aromatic (%)	Methoxy (%)	Aliphatic (%)	Aromatic : Methoxy
Lignin	25	41	34	0.61
L200	34	25	41	1.36
L350	77	9	14	11

Table 2: Composition of functional groups (%) in hydrothermally treated lignin obtained by quantitative DP/NMR analyses

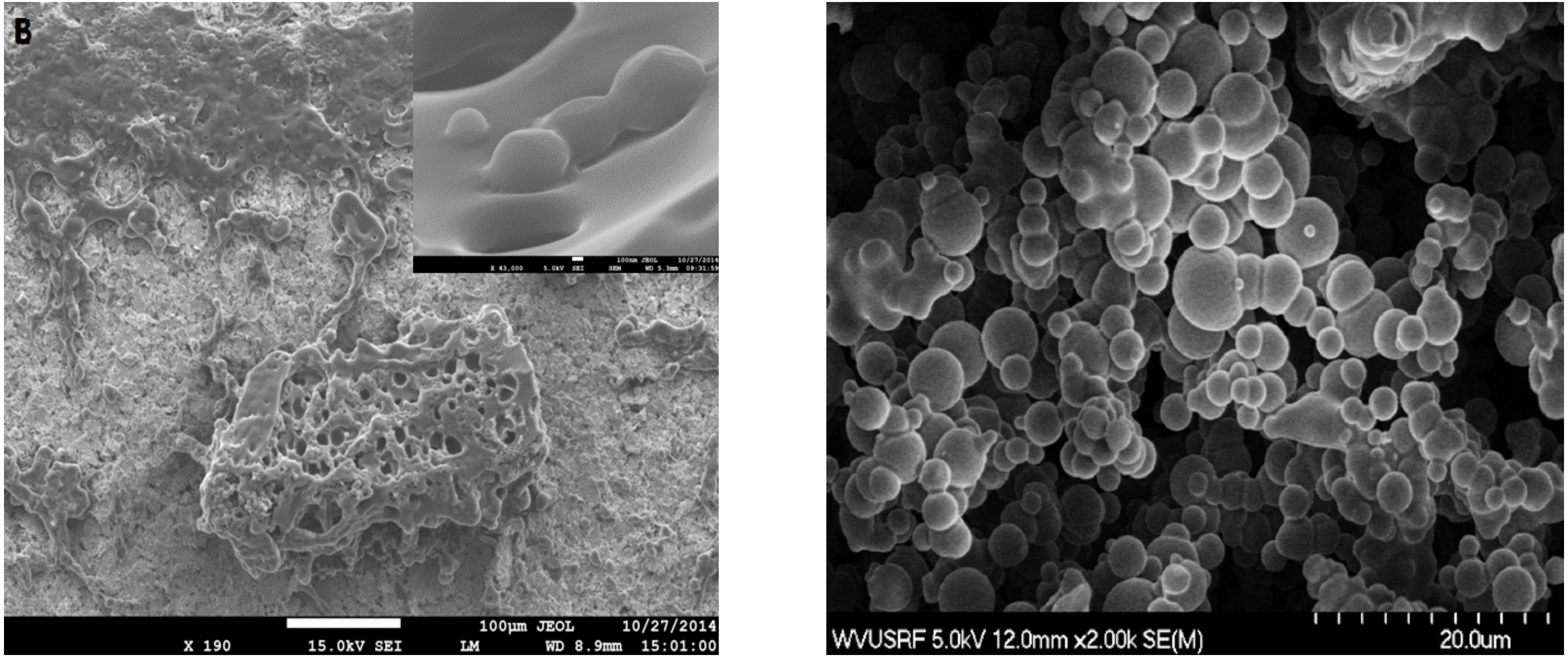


Figure 6: SEM images of (A) 350 °C with scale bar 100µm (100nm) and (B) lignin treated with 0.1M NaOH at 350 °C .

Conclusions

- Carbonaceous materials (CMs) were produced from organosolv lignin using hydrothermal carbonization process (HTC).
- Increasing temperature affected yield, chemical and morphological properties of HTC derived CMs.
- Structural modifications in lignin only occurred after 300 °C.
- 350 °C is optimum temperature for HTC lignin since significant aromatization occurred at this point.

Future work

- Surface functionalization of Lignin CMs with amine groups
- Test for CO_2 adsorption capacities of functionalized CMs