Chars and Carbonised Chars

- Mostly (sp²) carbon in aromatic (and/or graphene-like) structures. Most of the major chemical changes and mass loss occur early (HTT < 400°C).
- Product properties change drastically when the heat treatment temperature (HTT) used in the production process is increased.

Nanostructural development of carbonaceous material (from hydrogen-rich amorphous carbon towards tangled network of graphene-like sheets).

Chars prepared at 300-400°C

- ≈ 6 orders of magnitude increase in electrical conductivity
- ≈ 1-2 orders of magnitude increase in specific surface area (N₂, BET)
- ≈ 1 order of magnitude increase in hardness and modulus

Well-carbonised Chars prepared at 700-1000°C

Aims of Raman Analysis

- Develop a method for reliably measuring the extent of chemical/nanostructural changes which have occurred during the carbonisation of biomass. Be able to use this method to rapidly estimate the heat treatment temperatures (HTTs) employed in the production of a given char sample. (Quality control, product consistency after scale-up).

- Continue testing a hypothesis about carbonised charcoals being more chemically and nanostructurally similar to thermally-reduced graphene oxide(s) than to other proposed structural analogues such as fullerenes and graphite.

- Start correlating Raman measurements to other values and properties considered important (such H/C atom ratios from IBI Guidelines).

Precursors poor in oxygen
- Pitch, coking coals, PAHs, heavy petroleum fractions.

Precursors rich in oxygen
- Carbohydrates, lignocellulosic biomass, low-rank coals, lignite, phenolic and furan-based resins.

Heating under an inert or oxygen-poor atmosphere

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Precursor Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C to 1000°C</td>
<td>Cokes</td>
</tr>
<tr>
<td>1500°C to 3000°C</td>
<td>Graphites</td>
</tr>
</tbody>
</table>

Heating under an oxygen-poor atmosphere

<table>
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<tbody>
<tr>
<td>500°C to 1000°C</td>
<td>Graphites</td>
</tr>
<tr>
<td>1500°C to 3000°C</td>
<td>Glassy carbons</td>
</tr>
</tbody>
</table>

(International Biochar Initiative 2012) (McDonald-Wharry et al. 2013)
**Raman Spectroscopy of graphite and graphene-like materials**

- Raman spectrometer excites an area of the sample with a laser (785 nm), then collects and records Raman scattering as a spectrum.

- Bands and signals on the Raman spectrum usually relate to the stretching of various bonds and lattice vibrations.

**G band**

Stretching of carbon-carbon $sp^2$ bonds

(Robertson 2002)(Ado et. al. 2010)(Gupta et. al. 2008)

**D band**

Breathing mode of hexagonal rings

Only seen in Raman spectrum if ring is close (< 10 nm) to sheet edge or other defect

(Robertson 2002)(Ado et. al. 2010)(Gupta et. al. 2008)
Order, Disorder and the D band

Maximum intensity of the D band relative to the G band occurs when nanostructure has ordered graphene-like domains where each hexagonal ring is within about 4 nanometres of an edge or other defect.


Sample Production and Precursors

Some precursors (harakeke leaf fibres, sucrose sugar crystals) were carbonised in electric furnaces under low oxygen conditions (N₂ purged or vacuum evacuated quartz vessels).

Radiata pine wood derived chars produced in Massey’s gas-fired drum pyrolyser. Other Radiata pine wood and pyrolysis tars were also carbonised in an electric furnace.

Samples were heated to a range of HTTs between 300°C and 1000°C (usually 20 min dwell time at max temperature and HTTs were calculated from average thermocouple reading over 12 min where they were highest).

Samples were analysed using the Raman spectrometer after they had cooled to room temperature.
Raman Methodology: Overview

- Developed method which will obtain adequate spectra from a wide range of different carbonaceous samples.

- Analysed a wide range of carbonaceous materials using the same excitation laser wavelength, the same data processing method, and similar instrument settings. (Goal of fair comparisons).

- Chars, carbonised chars, graphene oxides, and thermally-reduced graphene oxides all were analysed.

- Purchased, borrowed, and scavenged samples of various graphites, fullerenes, single-walled carbon nanotubes, glassy carbons, and PAN-derived carbon fibres for analysis and comparison.

(McDonald-Wharry et. al. 2013)
Radiata Pine Chars and Carbonised Chars

- HTT ≈ 340° C
- HTT ≈ 470° C
- HTT ≈ 700° C
- HTT ≈ 1000° C

Regular Fullerenes and Single-walled Carbon Nanotubes

- C_{60} fullerenes
- C_{70} fullerenes
- Single-walled carbon nanotubes
- Single-walled carbon nanotubes (Air oxidised at 550°C)

(McDonald-Wharry et al. 2013)
Graphites, Glassy Carbon, & PAN-derived Carbon Fibre

Colloidal graphite

Synthetic graphite

Glassy carbon

PAN-derived carbon fibre

Data Processing and Spectral Parameters

D band position

G band position

$I_D$ (D band height)

$I_G$ (G band height)

$I_V$ (Valley height)

Baseline value
Map of D band and G band positions

y = -1.2999x + 3386.7
R² = 0.9504
G band positions and heat treatment temperatures

\[ y = 0.0694x + 1544.1 \]
\[ R^2 = 0.986 \]

(Valley height) / (G band height) ratio and heat treatment temperatures

\[ y = 170.98x^{-0.896} \]
\[ R^2 = 0.9117 \]
(Photoluminescence slope) / (G band height) ratio and H/C ratios

Similar trend and scatter to synthetic hydrogenated amorphous carbon films

(Casiraghi et al. 2005)

Photoluminescence slopes and/or fluorescence slopes

Amorphous chars generate positive slopes, but tars and unpyrolysed biomass generate negative slopes in Raman spectra (when using 785 nm excitation)
Raman $I_d/I_G$ ratios correlate to the H/C ratios obtained from elemental analysis of these Radiatapine derived chars. 

**Interpretation:** Removal of hydrogen-rich amorphous carbon with increasing HTT.

$$y = 1.0447x - 0.2235$$
$$R^2 = 0.9096$$

Raman $I_d/I_G$ ratios also correlates to the H/C ratios obtained from elemental analysis of these Radiatapine derived chars. 

**Interpretation:** Growth of hydrogen-poor graphene-like structures with increasing HTT.

$$y = -0.9674x + 1.2781$$
$$R^2 = 0.9278$$
Conclusions

• A number of Raman parameters can be used to monitor the extent of carbonisation in chars. G band position correlates well and is measurable over the widest range of precursors and temperatures.

• I_v/I_G and I_D/I_G height ratios also useful for evaluating lower HTT chars and the conversion of amorphous carbon into polyaromatic/graphene-like carbon. So far I_v/I_G (and I_D/I_G ) values correlate well with H/C atom ratios for Radiata pine derived chars, indicating that Raman analysis could be used to estimate H/C_{org} values.

• Carbon nanostructure appears to become independent of precursor as HTT increases towards 700-1000°C

• Positive slopes which occur in Raman spectra of low HTT chars are different to the negative slopes which occur in Raman spectra obtained from pyrolysis tars and biomass precursors.

Acknowledgements

• Steven Newcombe for crafting the many pieces of quartzware needed for this work.

• Fatima Bashir for producing the radiata pine chars and production data.

• The University of Waikato Doctoral Scholarship.
References


Questions?