Summary

This char sample was found to be well-carbonised with the carbon being nanostructurally developed. Based on comparisons to chars previously analysed using this method it was estimated that the Cone kiln (TFOD) sample had been exposed to effective HTTs (heat treatment temperature) in the range between ≈ 700°C and 1000°C and all the parts of the sample analysed appeared to have a similar level of nanostructural development. Currently, the Raman method is able to compare char samples to each other in terms of the development of polyaromatic/graphene-like domains from the amorphous carbon formed at lower temperatures. The effective HTT values estimated are based these comparisons and it is expected that the more direct measurements obtained from the Raman analysis will become more useful for comparing chars as more samples are analysed and correlations are made to other properties of chars.

Sample Details

Name	Precursor	Process	Date produced
Cone kiln (TFOD)	Douglas fur mill ends	Cone kiln Top-fed Open draft device (TFOD), water quenched	April 2014

Contributed by Kelpie Wilson (Wilson Biochar Associates).

Methodology

Raman spectra using a Ramanstation400 instrument (PerkinElmer) equipped with a 785 nm laser. Samples were mixed and five randomly selected surfaces (sub-samples) of the as-received samples were analysed. Each sub-sample Raman spectrum was collected from a spot (100-200 µm in diameter) using five consecutive exposures to the laser. 20 second exposure times were used routinely with an alternative five second exposure times needing to be used on a small number of chars produced at lower temperatures. Instrument settings, data processing procedure and interpretation of spectral features are detailed in the paper *Carbonisation of biomass-derived chars and the thermal reduction of a graphene oxide sample studied using Raman spectroscopy* [1].

Raman Spectra

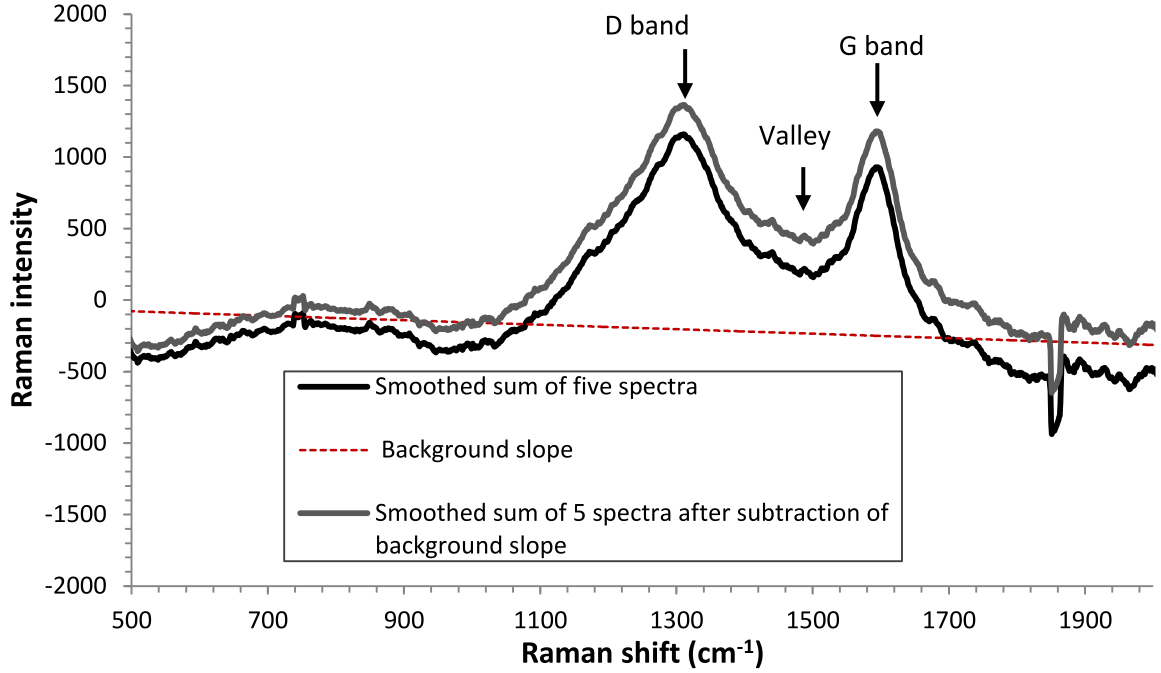

Figure 1: Spectra based on sum of five sub-samples showing subtraction of photoluminescence slope for the Cone kiln sample.

Results

Apparent Signal positions				
	D band position (cm^{-1})		G band position (cm^{-1})	
Sample		**99% CI**		**99% CI**
Cone kiln (TFOD)	1307.6	±6.9	1595.2	±3.3

Signal height ratios								
	D band / G band		Valley / G band		A band / G band		Slope/ G band (µm)	
Sample		**99% CI**		**99% CI**		**99% CI**		**99% CI**
Cone kiln (TFOD)	1.14	±0.04	0.41	±0.01	0.58	±0.02	-1.3	±0.6

Estimated effective HTT (°C)*				
	Based on apparent G band position		Based on Valley / G band ratio	
Sample		**99% CI**		**99% CI**
Cone kiln (TFOD)	724	±45	842	±29

*Based on comparisons to laboratory produced chars prepared at HTTs between 400°C and 700°C and typically held at this HTT (heat treatment temperature) for 20 minutes.

Interpretation of Raman Results

General:

Raman spectroscopy is sensitive to carbon nanostructure. The nanostructural development which occurs in chars as they are carbonised with exposure to higher temperatures is interpreted in terms of nanometre-sized polyaromatic/graphene-like domains growing by consuming and organising the amorphous carbon formed at lower temperatures. Chars prepared at higher heat treatment temperatures (HTTs) usually have a more developed nanostructure and contain less amorphous carbon.

- "A band / G band", "Valley / G band" and "Slope / G band" signal height ratios are associated with hydrogen- and oxygen-rich amorphous carbon in the samples and these values decrease as the char is carbonised (usually with increasing HTT).
- "Apparent G band position" and the "D band / G band" height ratio are both associated with carbon contained in condensed polyaromatic structures and the growth graphene-like domains at a nanometre-scale. Values of these measurements increase as the char is carbonised and the nanostructure develops.
- "Apparent D band position" tends to decrease as HTT increases and can be used to estimate effective HTTs in well-carbonised chars.

Specific to these samples:

- The Cone kiln sample was estimated to have been produced at high effective HTT above 700°C. Being a well-carbonised char the D band position value is more relevant, and this sample had a value similar to laboratory-produced chars produced at an HTT of 1000°C.
- 1000°C was highest HTT laboratory-produced char analysed so far using this particular method. It is possible that the Cone kiln sample has an effective HTT higher than 1000°C.
- The Cone kiln sample had Raman spectra typical of well-carbonised chars (or turbostratic chars [2]) which have developed nanometre-scale domains of polyaromatic/graphene-like carbon with little sign of truly amorphous carbon remaining.
- The variations within the Cone kiln sample were small as indicated by small 99% confidence intervals in the results. This suggests that all sub-samples of this sample that were analysed were cooked (or nanostructurally developed) to a similar degree.

References

1. McDonald-Wharry, J., M. Manley-Harris, and K. Pickering, *Carbonisation of biomass-derived chars and the thermal reduction of a graphene oxide sample studied using Raman spectroscopy.* Carbon, 2013. **59**(0): p. 383-405.
2. Keiluweit, M., P.S. Nico, M.G. Johnson, and M. Kleber, *Dynamic molecular structure of plant biomass-derived black carbon (biochar).* Environmental Science & Technology, 2010. **44**(4): p. 1247-1253.