

# FTIR/chemometric analysis of pyrolytic gas from conifer and broadleaf timber, root and branch samples from trees grown on 11 sites in the UK

Gordon G. Allison<sup>1\*</sup>, Sian Jones<sup>1</sup>, Ewan Mackie<sup>2</sup>, Douglas Phillips<sup>3</sup> and Iain S. Donnison<sup>1</sup>

\* Corresponding author (goa@aber.ac.uk)

1. Institute of Biological Sciences, Aberystwyth University Gogerddan, Aberystwyth, Ceredigion, U.K. SY23 3EE
2. Forest Research, Alice Holt Lodge, Farnham, Surrey, UK. GU10 4LH
3. Energy Research Institute, School of Chemical and Process Engineering, University of Leeds, UK. LS2 9JT

## Introduction

378.12 kt-1 yr-1 of wood, equating to an estimated 3.76 PJ yr-1 could be sourced sustainably from UK forests for use as bioenergy. Biological variation and growth location are known to influence biomass composition and thermal conversion efficiency but few if any studies have investigated these effects in commercially grown trees.

This study reports on the relationship between species, tissue, and growth location on gases emitted by samples under pyrolytic thermal decomposition.

**This investigation is the first to determine whether mid-IR spectra of pyrolysis gases can give information on plant cell wall composition.**

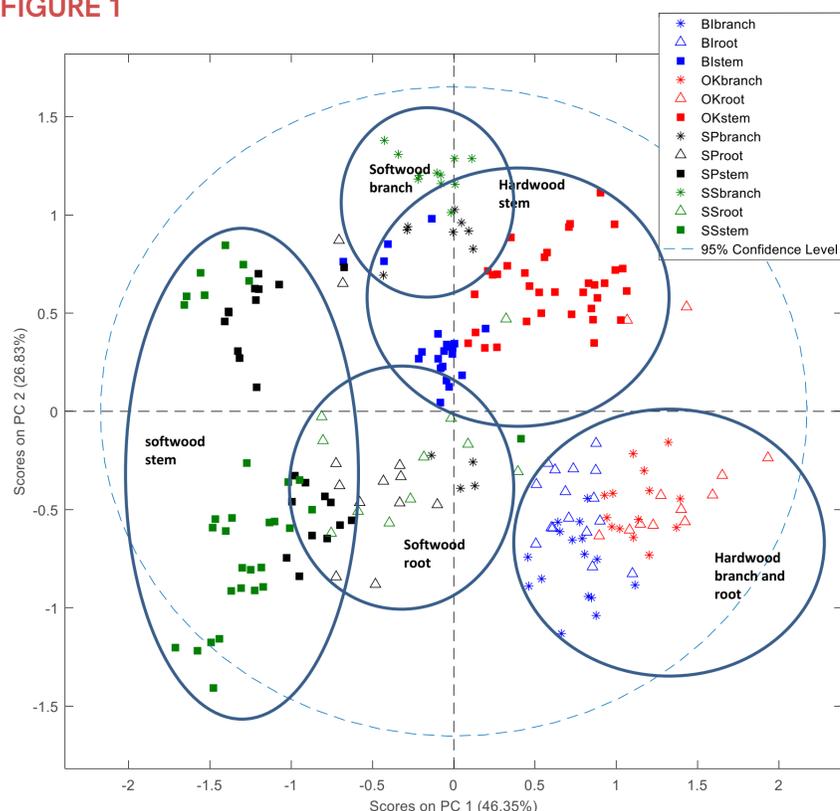
This knowledge gives better understanding of how best to use these feedstocks for gasification, pyrolysis and combustion.

## Method

We report on the PCA of time course mid-infrared spectra of pyrolytic gases emitted from samples of coniferous and deciduous stem, branch and root samples subjected to thermal degradation. Samples of trunk, branch and root were collected from Sitka spruce (*Picea sitchensis*), Scot's pine (*Pinus sylvestris*), birch - diffuse porous (*Betula pendula*) and oak - ring porous (*Quercus robur*) growing on 14 sites in Scotland and England in 2010. 20mg of milled samples were subjected to thermogravimetric analysis in a Mettler TGA/ DSC1 (30°C - 905°C at 25°C/min) in a continuous flow of Ar.

Gases from the TGA passed along a heated transfer line into a gas cell at 295°C (Pike Technologies). Spectra were collected continuously (41 spectra for each sample) during TGA using a Shimadzu IR-Tracer-100 FTIR spectrophotometer (resolution of 1 cm-1 from 4000 cm-1 to 600 cm-1)

FIGURE 1



- Samples of hardwood were separated from softwood samples along PC1. Porosity structure of the hardwood was not apparent in the scores plot of PC1 vs 2.
- Hardwood branch (tension wood -high cellulose) and root samples grouped together and were separated from hardwood stem samples along PC2.
- Softwood branch samples (compression wood- high lignin, low cellulose) grouped separately from softwood root samples.
- Softwood stem samples seemed to form 2 clusters.

FIGURE 2

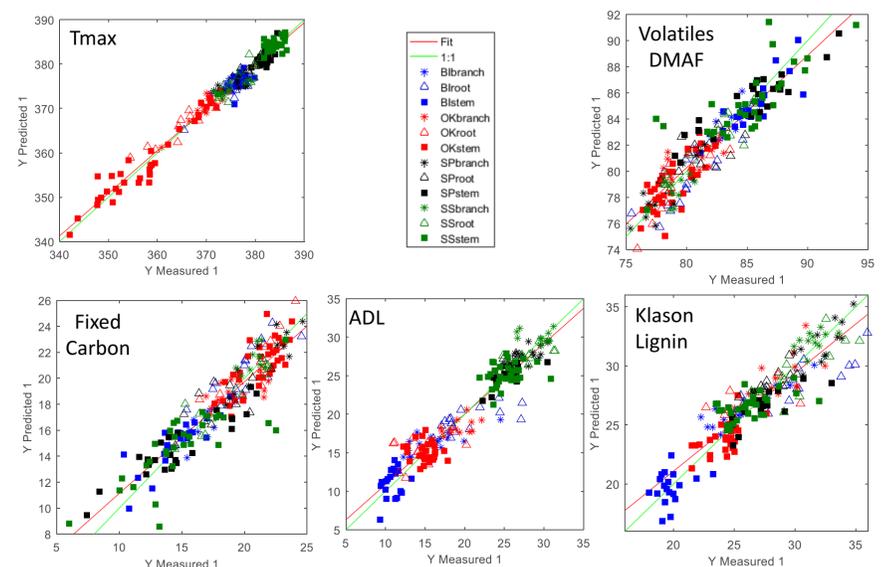


TABLE 1

Model	LV	%X var	%Y var	RMSEC	RMSECV	RMSEP
Tmax	5	78.98	95.62	1.991	2.500	2.072
% Volatiles	7	89.99	84.34	1.453	1.879	1.608
Fixed C (DMAF)	6	88.72	81.42	1.487	1.886	1.403
Klason Lignin	6	79.68	83.56	1.541	2.224	1.982
ADL	6	88.69	89.73	1.998	2.281	1.763

- Plots of measured vs predicted Y (Fig 2) shows good correlation, particularly with Tmax. The chemical composition of the pyrolytic gases is therefore dependent on the composition of the samples prior to pyrolysis. This confirms the need for control of feedstock composition for thermal conversion.
- % volatile content and % fixed carbon (dry matter ash free) in the samples inversely correlates.
- Both Klason and acid detergent lignin (ADL) are predicted from the spectral data. Surprisingly, although Klason is the gold standard measure of lignin for timber results indicates that in these samples ADL is predicted with greater accuracy.
- Furthermore, the samples do not rank in the same order for Klason lignin and ADL. Birch root samples are high in Klason lignin but have intermediate levels of ADL. It has long been suspected the 2 methods measure slightly different chemical parameters that possibly differ between tissues.

Spectra were extracted into MatLab files and imported into 3D array using MatLab R2016b (Mathworks) and EssentialFTIR v.3.5. This study reports on analysis of concatenated spectra by PCA and PLS using PLSToolbox 8.2.1 (Eigenvektor Research Inc). Data were smoothed (15 point window 1° polynomial, corrected for multiplicative scatter and mean centred prior to deconvolution by SVD.

Fig 1 shows the scores on PC1 and 2 of a 4 component PCA model explaining 85.9% variance (RMSEC=0.0013, RMSECV=0.0015). Data were smoothed (15 point, 1° polynomial), normalised by MSC and mean-centred prior to decomposition. The number of components was selected by cross validation using Venetian Blinds (10 data splits, 1 sample / blind).

The model used spectra corresponding to main mass loss and high Q or T2 outliers were removed. PLS regression was used to explore correlations between spectral data of pyrolytic gases with physical and compositional parameters (Fig. 2). 10% of data were used as a test set for model validation.



## Acknowledgements

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