

X-Ray Raman Spectroscopy of Hydrothermally Processed Biofuel at APS and ESRF

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Introduction

Hydrothermal carbonization (HTC; hydrochar) has, in recent years, become an increasingly exciting method for producing sustainable carbon from biomass and waste materials. Hydrochars are currently being investigated for a wide range of applications including combustion fuels, catalysis, sensing and environmental remediation. In terms of their chemistry, hydrochars are predominantly built of a complex, amorphous structure of aromatic carbon formed by the dehydration and aromatization of residual organic tissues and the polymerization of monosaccharides and furfural-like compounds. Changes in the carbon chemistry of these materials due to production processes are important for scaling up. This study has applied X-ray Raman Spectroscopy (XRS) at both the ESRF and the APS, to study changes in hydrochar carbon chemistry for the bulk material.

Methods

Hydrochar produced for this work had been used as part of a study looking into the influence and implications of recycling hydrothermal process waters on hydrochar chemistry. Recycling of these acids back into the HTC process has been shown to catalyze the reaction and can improve the yields at little or no cost, however analysis of the chars against non-recycled controls had indicated recycling the process waters had appeared to change the carbon chemistry. The recycled chars and controls were taken to both ESRF ID20 and APS 20ID beamlines for XRS analysis. During XRS the incident photon is scattered, resulting in a change of momentum and energy. The scattered photon, at low q , provides the same information as the electronic excitation of the carbon K edge. The spectra were produced at ESRF and APS with an initial photon energy of 6keV and 10keV respectively. Resulting spectra were analyzed by subtracting the inelastic scattering energy to give the energy loss spectrum, and subsequently fitted with a series of Gaussian functions at known electronic transition energies. Following this, analysis was carried out using the method of *Bergmann et.al* [2003] by analysis of the FWHM of the Gaussian functions beneath the $1s-\pi^*$ region of the spectrum.

Results and Discussion

The ESRF's ID20 can utilize up to four consecutive undulators to produce a highly brilliant beam. The beam line is equipped with a liquid-nitrogen cooled Si(111) pre-monochromator, the beam was then directed to a Si(311) monochromator and focused using a Kirkpatrick-Baez mirror. The internally-developed Maxipix spectrometer at the ESRF beamline is composed of 72crystal analyzers (six arrays) in both the horizontal and vertical scattering geometries; the energy resolution of the inelastic peak was found to be 0.5eV. Similarly, APS's 20ID is an undulator beamline, a Si(311) geometry was applied at the monochromator before focusing using a Kirkpatrick-Baez mirror; the scattered radiation is analyzed using the LERIX spectrometer using 19 Si(555) crystals operating in the vertical plane only; the resolution was found to be 0.56eV. Results clearly showed the presence of fused aromatic structures in hydrochar, the intensity of which increased with increasing reaction severity and process recycling.

Furthermore, a peak at 286.6eV suggests the presence of furan linked carbon species, potentially confirming that the polymerization stage in HTC is with HMF or furfural units. The beamline results were compared with more conventional characterization techniques, such as X-ray Photon Spectroscopy (XPS) solid state and liquid state Nuclear Magnetic Resonance (NMR) and pyrolysis-Gas Chromatograph-Mass Spectroscopy (py-GCMS). The results of the study were used to validate the beamline results and using a combination of all the methods a detailed understanding of the carbon chemistry of both the hydrochar and the influence of recycling the process waters developed.

Conclusions

Non-resonant Inelastic X-ray Scattering or X-ray Raman (XRS) spectroscopy is a promising tool for investigating the bulk carbon functionality of sustainable green carbon materials that are currently being investigated for a wide-range of applications. XRS investigation of these complex amorphous carbon materials has been shown to provide insight that is difficult to gain, even with other synchrotron techniques. XRS promises to be an important tool in future work on these materials, also offering insights at the high pressures and temperatures required to produce hydrothermal carbons.

References

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