In situ synchrotron-based X-ray diffraction and micro-raman study of biomass at hydrothermal conditions

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In-situ synchrotron-based XRD and micro-Raman study of biomass at hydrothermal conditions

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SCW Applications

- Water recycling in space stations

Extraction in herbal industry (SC CO$_2$
31.1$^\circ$C~73atm, possibly SCW)

- Fuel production from biomass
  Production of nano-materials

- Destruction of chemical weapons

- Next generation of nuclear reactors (GEN IV)
Beetle - infested Pine Trees
Observed Percentage of Pine Killed* in 2008

* red- and grey-attack phase

Map/photos courtesy of British Columbia Ministry of Forestry and Range
• ~100 million m³ of biomass from the mountain pine beetle outbreak may be available in British Columbia alone for energy uses in the next 20 years

• Studies indicate possibility for fungus to spread from lodgepole pine to jack pine
Waste biomass

SCW processing

Fuel and value added chemicals
Hydrothermal DAC

- Bassett-type Hydrothermal Diamond-Anvil Cell (HDAC)

- The cell allows *in-situ* measurements of reactions at hydrothermal conditions

R. L. Smith and Z. Fang, *Journal of Supercritical Fluids*, 2009, 47, 431-446.
Flow reactor

- 3/8” OD stainless steel tubing, max. 350 bar at 425 °C, flow up to 1.5 L/hr

Experiments in semi-batch & continuous modes
Canadian Light Source
synchrotron
Synchrotron & HDAC

E-gun & Linear Accelerator
250 MeV

Transfer Line & Booster Ring
Commissioned Summer 2002

Storage Ring
2.9 GeV
200 mA
Commissioning 2003

Beamlines & End Stations
2004

~ 170m circumference
Fiber optic from Raman room for *in situ* measurement

High res camera for monitoring experiment during acquisition

HXMA beamline, Canadian Light Source

X-ray beam

Experimental hutch – no access during acquisition
Heater and thermocouple connections

HXMA beamline, Canadian Light Source

Experimental hutch – no access during acquisition
HDAC – synchrotron XRPD

- X-ray diffraction data collection – 2D image
• Change in crystallinity of cellulose?
• Disappearance of signal ~ 250 °C (seen also in Raman)
Flow reactor

• 250 bar, 400 °C, 1 g pine fibre*

*Aqueous sample headspace GC-MS

Bio-oil GC-MS#

*Jack pine sample taken January 2010 from Descharme Lake, SK, Canada by Saskatchewan Fire Protection

#after freeze-drying
Flow reactor

• 250 bar, 400 °C, 1 g pine fibre*

*Jack pine sample taken January 2010 from Descharme Lake, SK, Canada by Saskatchewan Fire Protection

#after freeze-drying, 500 MHz, d₆-acetone

Bio-oil ¹H NMR#
Flow reactor

- 250 bar, 400 °C, 1 g pine fibre

- Formation of solid residue (biochar)[8]

- Potential use as a pesticide adsorbent

Flow reactor

• 250 bar, 400 ºC, 1 g pine fibre*

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• Potential use as a pesticide adsorbent

\[ q_e = \frac{V(C_i - C_f)}{m} \]

\[ t = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \]

Summary

• Conversion of wet waste woody biomass to fuels using SCW technology

• Mountain pine beetle infestations produce large quantities of feedstock

• Development of continuous flow reactor ongoing

• Hydrothermal diamond-anvil cell (HDAC) for in-situ Raman and synchrotron XRPD measurements

• Synchrotron studies: cellulose pattern confirms Raman data – initial dissolution/reaction at ~250 °C

• Synchrotron studies: trying to develop simultaneous XRPD/Raman system
NASA – SCW Test Facility at York
designed to study reactions in supercritical water
The SCWO reactor (Hastelloy C–276; 480 cm³) ASME certified for a maximum allowable working pressure of 40.7 MPa at 550 °C.
York’s Engineering Expansion

$250 million
In all of these changes that we are making – partnering is the focus