Analysis of Soot Produced on Combustion of Biomass

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Objectives

- Determine composition of particles generated in the combustion of conventional fuels and biomass
- Determine composition of particles generated through oxidation of combustion products by ozone
Why investigate biomass soot?

- Biomass smoke and associated black carbon has huge implications for atmospheric chemistry
- Climate effects

IPCC report 2007
- Conventional soot mechanisms do not fully describe soot formation from biomass.

- The role of oxygenates appears to be important according to previous off-line analysis.

- A new mechanism involving intermediates such as eugenol has been proposed and is to be investigated using an on-line technique - the ATOFMS (Aerosol Time of Flight Mass Spectrometer) (TSI inc).
Collaboration

• Collaboration with a group from the Energy and Resources Research Institute (ERRI), University of Leeds.
  
  Emma Fitzpatrick
  Jenny Jones
  Alan Williams

Previous work carried out by them has looked at:

• Pyrolysis GC-MS of pine wood and eugenol
• Surface analysis via Scanning Electron Microscopy (SEM) and X-ray Photoelectron Microscopy (XPS)

OFF-LINE TECHNIQUES
Mechanism from ERRI

Wood (Pine) → Cellulose, Hemi-cellulose, Lignin → Tar species

I. CO, H₂, CH₄

II. C₂H₂, C₃H₃

II (a) H⁺ → OH, CH₃

II (b) HACA → PAH species

III. methylated compounds, phenols

I (c) oxidation → Soot

Oxygenated soot species

eg. Eugenol, levoglucosan and furfural

Temperature

Unburned CO, VOC & Smoke Species

Why analyse on-line?

On-line vs. Offline analysis:

- Advantages of off-line analysis
  - Preparation of samples can give reproducible quantitative analysis
  - Electron microscopy techniques give information on particle morphology

- Limitations of off-line analysis
  - Volatile compounds can be lost
  - Chemical transformations due to time lapse between collection and analysis

- Advantages of on-line analysis
  - Minimal chemical modification of particles
  - High temporal resolution
  - Analysis of single particles

- Disadvantages of on-line analysis
  - Are there any ??
The experimental set-up

Extractor

Chimney

Quartz tube

Clean air

Burner (wick) containing eugenol/n-decane

Conductive tube

Inlet: Aerodynamic Focusing Lens (d=100-3000 nm)

ATOFMS

How does the ATOFMS work?

3 regions

- **Sampling region**
  - Particles introduced at atmospheric pressure then accelerated to terminal velocity

- **Sizing region**
  - Particle velocity measured by 2 continuous wave laser beams (532 nm)
  - Velocities compared with a calibration curve

- **Mass spectrometry region**
  - UV laser (266 nm) fired to hit particle at centre of ion source
  - Particle compounds desorbed and ionised
  - Bipolar time-of-flight mass spectrometer analyses both positive and negative ions

Taken from Series 3800 Aerosol Time-of-Flight Mass Spectrometers (ATOFMS) with Aerodynamic Focusing Lens Operation and Service Manual P/N 1930036, Revision C May 2007
What can we do with this? (1)
What do we do with this? (2)

High power positive n-Decane - Eugenol
1.6 x 10^8 W cm^-2

High power negative n-Decane - Eugenol
1.6 x 10^8 W cm^-2

m/z = 95?
What do we do with this? (3)

Low power positive n-Decane - Eugenol
1.5 x 10^7 W cm^-2

Low power negative n-Decane - Eugenol
1.5 x 10^7 W cm^-2
Average spectra only tell us about bulk properties. What about individual particles?

- Current problem with size analysis – too many eugenol particles
- CLUSTERING
  - Cannot analyse hundreds or thousands of spectra individually
  - Cannot categorise hundreds or thousands of spectra by eye
  - Need a computer programme to do it for us
Clustering programmes

Two analytical tools available:

- **YAADA**
  - http://www.yaada.org/
  - Developed by Jonathan Allen, Arizona State University
  - Runs in MatLab
  - Clusters using ART-2a algorithm

- **Enchilada** (Environmental Chemistry through Intelligent Atmospheric Data Analysis)
  - http://www.cs.carleton.edu/enchilada/
  - Open source, written in Java
  - Three clustering algorithms available
    - ART-2a
    - K-means
    - K-medians
Clustering with Enchilada

Clustering data using K-means needs:

- A user defined number of clusters

Method of finding number of clusters:

- Try clustering with different numbers of clusters
- Plot ‘average distance of all points from their centers on final assignment’ against number of clusters
Need to decide where the ‘elbow region’ is – when increasing the number of clusters no longer significantly improves the analysis.

Decided on 10 clusters here.
Cluster analysis

Cluster 2 – low power
Cluster 7 – medium power
Cluster 8 – medium to high power
Cluster 10 – high power

Clusters 3 and 4 mainly n-decane
Clusters 5 and 10 mainly eugenol
Cluster 2 – low powers

Positive spectra more intense than negative

+39 $\text{C}_3\text{H}_3^+$
Building block of $\text{C}_6\text{H}_6$ and $\text{C}_5$ rings

-26 $\text{C}_2\text{H}_2^-$
Building block of aromatic rings

-47?
-94?
-132 $\text{C}_{11}^-$?
Cluster 3 – n-Decane

+39 $C_3H_3^+$
Building block of $C_6H_6$ and $C_5$ rings

(-93 $C_6H_5O^-$)
-94?
-95?
Cluster 7 – medium power (mainly eugenol)

**Cluster 7, Positive ions**

- $C_3H_2^+$
- $C_3H_3^+$
- $C_4^+$
- $C_5^+$

**Cluster 7, Negative ions**

- $C_n^-$
- $C_2^-$
- $C_3^-$
- $C_4^-$
- $C_5^-$
- $C_6^-$
- $C_7^-$
- $C_8^-$
- $C_8H^-$

Principally $C_n^+$
Cluster 10 – high power

Small intensity peaks at high values of m/z up to m/z = 249

-93 C₆H₅O⁻
Very low intensity
Summary

Experimental observations:
• More particles produced on combustion of eugenol

Data analysis:
• At high powers eugenol contains $C_n^+$ and $C_n^-$
• At high powers n-decane contains $C_3H_3^+$ and $C_2H_2^-$, the building blocks of aromatic rings
• At low powers eugenol appears to contain $C_3H_3^+$ while decane contains $C_n^+$
• At low powers n-decane still contains $C_2H_2^-$ but eugenol appears to contain $C_nH^-$ and $C_nH_2^-$ (not $C_2H_2^-$)
• Low intensity peaks seen at much higher m/z values at low power but difficult to find peaks that stand out for analysis
Future improvements to experiments

• Analysis of “clean” air – zero air generator vs. compressor and filters
• Better set-up of ATOFMS – alignment and calibration (User improvement!) to improve sensitivity
• Use of other fuels in burners – both biomass based and traditional fuels
  • Octane/hexane
  • Furfural
• New inlet (30-300 nm)
• Reduce the number of particles to get better information on the relationship between particle size and composition
• Repetition and further analysis – statistics!
Further future experiments

• Once experiments to analyse particles produced on combustion of biomass and traditional fuels are completed satisfactorily I intend to move on to analysing the result when combustion products are oxidised by ozone

• This will utilise the environmental chamber at the University of Leeds
  • Temperature controllable from -60 to +40°C
  • Intend to set up a smog chamber inside using a Teflon reactor within which combustion particles can be resuspended
  • UV lamps to initiate reaction by forming $O_3$
3 take home messages

1. Organic aerosols produced on combustion of fuels depend on many conditions e.g. temperature, fuel levels, air/fuel ratios

2. Differences in composition between fossil fuel and biomass combustion particles could mean important differences in their properties and effect on health

3. Analysis of ATOFMS data can release important information at the single particle level but is not necessarily easy to get out

THANK YOU

AND

ANY QUESTIONS?