Biomass Co-firing Related Research at the University of Nottingham

EngD Centre in Efficient Fossil Energy Technologies

Colin Snape

- EngD Centre and overview
- Biomass storage
- Biomass reactivity, catalytic effects and oxy-fuel
- Biomass/waste conversion to liquids
The goal is to produce research leaders to tackle the major challenges over the next 15 years in implementing new fossil energy power plant with near zero emissions.

£9M total funding - £6.75M EPSRC with £2.4M industry including BF2RA.

60 Ph.Ds based in industry over the next 8 years (first intake of 11).

Wide industrial base – E.ON, RWE, SSE, Alstom, Doosan Babcock, Corus, CPL, Air products & Johnson Matthey

As well as carbon capture, projects cover materials, transport and biomass.
# Biomass projects - EngDs

<table>
<thead>
<tr>
<th>Industrial Partner</th>
<th>Project Title</th>
<th>Supervisor</th>
<th>Student</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.ON</td>
<td>Biomass Fuel Storage and Handling in Coal Co-firing Plants</td>
<td>Carol Eastwick</td>
<td>Shalini Graham</td>
</tr>
<tr>
<td>SSE</td>
<td>Biomass Combustion</td>
<td>Hao Liu</td>
<td>Tom Bennet</td>
</tr>
<tr>
<td>CPL</td>
<td>Biomass incorporation into smokeless fuel</td>
<td>Colin Snape</td>
<td>Jo Lenthall</td>
</tr>
<tr>
<td>BF2RA</td>
<td>Impact of Biomass Torrefaction on Combustion Behaviour in Co-firing</td>
<td>Colin Snape</td>
<td>Umair Hussain</td>
</tr>
<tr>
<td>Doosan Power</td>
<td>Prediction of Biomass Combustion</td>
<td>Carol Eastwick</td>
<td>Archi Sarroza</td>
</tr>
</tbody>
</table>

## Other projects

1. Coal and biomass liquefaction Hui Deng, funded by BP
2. Biomass reactivity with respect to oxyfuel combustion Salome Tipiere
Shalini Graham: EngD E.ON

Biomass Storage: Project goals

- Store a variety of biomass fuels in different storage environments
- Compare the levels of degradation
- Measure the impact of degradation on:
  - Fuel handling and milling characteristics
  - Combustion characteristics

Initial Research

- 7 different fuels artificially degraded in containers for four months
- A range of tests are being carried out on at different times to measure degradation
Storage environments

Piles stored outdoors

Indoor storage
Forestry residue

July 2010 – 2 weeks storage
Presence of fungal growth

Oct 2010 – 15 weeks in storage
Fungal growth but also structural damage and stickiness
TGA Proximate Analysis - Willow

End of July

- Moisture 8.4%
- Volatile matter 71.6%
- Fixed Carbon 15.1%
- Ash 4.9%

End of October

- Moisture 9.6%
- Volatile Matter 69.5%
- Fixed Carbon 15%
- Ash 5.9%

- Increase in ash content
TGA Proximate Analysis – Forestry Residue

- July
  - Moisture: 9.5%
  - Volatiles: 73.5%
  - Fixed Carbon: 13.5%
  - Ash: 3.5%

- October
  - Moisture: 10.9%
  - Volatiles: 68.5%
  - Fixed Carbon: 16.8%
  - Ash: 3.8%

- Decrease in volatile matter content, small increase in ash.
Future work

- Set up biomass piles indoor and outdoor
- In-situ measurement of temperature and moisture
- Sampling and tests at regular intervals to determine extent and impact of degradation
- Compare how different fuels store under different storage conditions
- Understanding of degradation mechanisms
White oak decayed by *Lentinula edodes*

**13C NMR**

<table>
<thead>
<tr>
<th>Month</th>
<th>Methoxyl</th>
<th>Carbohydrate</th>
<th>Carbohydrate</th>
<th>Aromatic Lignin</th>
<th>Carboxyl/Carbonyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-60</td>
<td>(C-2, C-3, C-4, C-5 and C-6 of cellulose and xylans)</td>
<td>(C-1 of cellulose and xylans and aliphatic lignin)</td>
<td>110-160 ppm</td>
<td>160-210 ppm</td>
</tr>
<tr>
<td>0</td>
<td>11.5</td>
<td>56.0</td>
<td>12.5</td>
<td>10.5</td>
<td>5.5</td>
</tr>
<tr>
<td>30</td>
<td>14.0</td>
<td>49.5</td>
<td>11.0</td>
<td>16.0</td>
<td>4.5</td>
</tr>
<tr>
<td>40</td>
<td>12.5</td>
<td>52.5</td>
<td>11.0</td>
<td>13.5</td>
<td>5.5</td>
</tr>
<tr>
<td>66</td>
<td>10.5</td>
<td>56.0</td>
<td>12.0</td>
<td>11.0</td>
<td>6.5</td>
</tr>
<tr>
<td>76</td>
<td>11.0</td>
<td>55.5</td>
<td>12.5</td>
<td>12.5</td>
<td>5.5</td>
</tr>
<tr>
<td>77</td>
<td>10.5</td>
<td>55.0</td>
<td>12.0</td>
<td>12.5</td>
<td>6.0</td>
</tr>
<tr>
<td>101</td>
<td>16.0</td>
<td>38.5</td>
<td>8.5</td>
<td>20.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

- Increasing aromaticity with time
- Decreasing carbohydrate (cellulose and xylans)
- Demethoxylation
- Increasing carboxylic acid (oxidation of lignin side chains)

White oak decayed by *Lentinula edodes*

**Pyrolysis–GC/MS**

<table>
<thead>
<tr>
<th>Decay Time</th>
<th>((S/G)_{\text{Pyrolysis}})</th>
<th>G:3-to-G lignin</th>
<th>S:3-to-S lignin</th>
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<tbody>
<tr>
<td>0</td>
<td>2.60</td>
<td>0.46</td>
<td>0.49</td>
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<tr>
<td>30</td>
<td>0.80</td>
<td>0.20</td>
<td>0.26</td>
</tr>
<tr>
<td>40</td>
<td>0.75</td>
<td>0.19</td>
<td>0.30</td>
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<tr>
<td>66</td>
<td>0.75</td>
<td>0.19</td>
<td>0.30</td>
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<tr>
<td>76</td>
<td>0.73</td>
<td>0.23</td>
<td>0.23</td>
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<tr>
<td>77</td>
<td>0.95</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>101</td>
<td>0.96</td>
<td>0.31</td>
<td>0.22</td>
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</tbody>
</table>

- Diminishing side chain length in G & S units
- Demethylation and demethoxylation
White oak decayed by *Lentinula edodes*

Thermochemolysis–GC/MS (Lignin specific)

(A) 0 months

(B) 30 months

(C) 77 months

(D) 101 months

- Increasing oxidation with time
- Diminishing side chain length
- Demethoxylation
Wheat straw decay by oyster mushroom (Pleurotus ostreatus)

## Wheat straw decay by oyster mushroom (Pleurotus ostreatus) – solid state $^{13}$C NMR

<table>
<thead>
<tr>
<th>Sample Time (days)</th>
<th>Acetyl</th>
<th>Lipid, Protein</th>
<th>Methoxyl</th>
<th>Carbohydrate</th>
<th>Carbohydrate</th>
<th>Aromatic lignin</th>
<th>Carboxyl /carbonyl</th>
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<tbody>
<tr>
<td>0</td>
<td>1.9</td>
<td>1.4</td>
<td>4.6</td>
<td>65.0</td>
<td>9.8</td>
<td>12.4</td>
<td>4.9</td>
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<tr>
<td>7</td>
<td>1.7</td>
<td>2.2</td>
<td>2.8</td>
<td>64.0</td>
<td>10.0</td>
<td>14.4</td>
<td>4.9</td>
</tr>
<tr>
<td>14</td>
<td>2.8</td>
<td>2.4</td>
<td>3.1</td>
<td>63.8</td>
<td>10.8</td>
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<td>5.3</td>
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<tr>
<td>21</td>
<td>2.1</td>
<td>1.9</td>
<td>2.6</td>
<td>64.9</td>
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<td>11.9</td>
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<tr>
<td>28</td>
<td>2.6</td>
<td>2.4</td>
<td>2.6</td>
<td>63.6</td>
<td>10.7</td>
<td>11.4</td>
<td>6.7</td>
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<tr>
<td>35</td>
<td>2.6</td>
<td>2.8</td>
<td>2.0</td>
<td>63.7</td>
<td>10.6</td>
<td>11.5</td>
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<tr>
<td>42</td>
<td>3.2</td>
<td>3.1</td>
<td>2.9</td>
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Combustion-enhancing additives
Katie Le Manquais PhD study
supported by Innospec

- Alkali and alkaline metals are amongst a number of effective catalysts.

DTF Carbon burn-outs
(106-150 µm)

<table>
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<tr>
<th>Additive</th>
<th>(%)</th>
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<tbody>
<tr>
<td>RbCl-1%</td>
<td>74</td>
</tr>
<tr>
<td>No Catalyst</td>
<td>66</td>
</tr>
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<td>CuBr-1%</td>
<td>62</td>
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Catalytic effects – TGA burn-out

- Alkali and alkaline metals are amongst a number of effective catalysts.
Particle size effects significant for coal chars

- Compensation effect evident for intra-particle diffusion regime (II)
- Intrinsic kinetic regime (I) not reached until extremely small particle sizes

Particle size effects much less for biomass than for coal.

<table>
<thead>
<tr>
<th>Particle sizes (µm)</th>
<th>Burnout in Air</th>
<th>Burnout in oxy-fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (KJ/mol)</td>
<td>A (min⁻¹)</td>
</tr>
<tr>
<td>&lt;45µm</td>
<td>116</td>
<td>7.09 x 10⁸</td>
</tr>
<tr>
<td>45-63µm</td>
<td>111</td>
<td>2.42 x 10⁸</td>
</tr>
<tr>
<td>63-75µm</td>
<td>111</td>
<td>2.23 x 10⁸</td>
</tr>
<tr>
<td>75-90µm</td>
<td>110</td>
<td>1.76 x 10⁸</td>
</tr>
<tr>
<td>90-106µm</td>
<td>108</td>
<td>1.19 x 10⁸</td>
</tr>
<tr>
<td>125-250µm</td>
<td>109</td>
<td>1.04 x 10⁸</td>
</tr>
</tbody>
</table>

TGA in situ char burnout in 21% O2/79% CO2

TGA in-situ char burnout in air
Oxyfuel and normal combustion using a drop tube furnace

Chenggong Sun, Donglin Zhao and Colin Snape
(EPSRC and BERR/DEC, Oxycoal UK project)

Oxy-fuel conditions give higher yields of total volatiles (5 ~ 20 wt%), attributable to the contribution of the \( \text{CO}_2/\text{char} \) reaction for a number of coals.

Increases in BET surface area arise at 1300\(^\circ\)C due to char activation in \( \text{CO}_2 \).
TGA co-combustion of sawdust and coal chars showing synergistic effect

Sawdust 700°C/coal 1000°C HTF CO₂ chars,

<table>
<thead>
<tr>
<th>Samples</th>
<th>1st order rate constants (min⁻¹)</th>
<th>90% burnout time (min)</th>
<th>1st order rate constants (min⁻¹)</th>
<th>90% burnout time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sawdust char 700°C</td>
<td>0.4901</td>
<td>6.60</td>
<td>0.3114</td>
<td>7.85</td>
</tr>
<tr>
<td>Kleinkopje (KK) HTF char 1000°C</td>
<td>0.0734</td>
<td>38.70</td>
<td>0.0526</td>
<td>48.00</td>
</tr>
<tr>
<td>saw/KK char blend 50:50wt%</td>
<td>0.1002</td>
<td>22.15</td>
<td>0.1089</td>
<td>20.65</td>
</tr>
<tr>
<td>Predicted sawKK char blend</td>
<td>0.0829</td>
<td>25.60</td>
<td>0.0720</td>
<td>31.60</td>
</tr>
</tbody>
</table>
Effect of HCl Extraction of sawdust on burn-out with coal char

- Synergistic effect of biomass char on coal char burn-out is lost
Limitations of traditional carbonisation & fast pyrolysis

▪ Traditional carbonisation for charcoal production gives relatively low oil/tar yields. Drying is still required for biomass.

▪ Bio-oil is produced by fluidised-bed pyrolysis in high yield (ca. 80% w/w) but has a low CV – high O content and water present.

▪ It is extremely acidic and hydrophilic in nature, not mixing with traditional petroleum fractions.

▪ Considerable additional hydroprocessing to produce suitable fuels.

▪ An alternative approach is to liquefy biomass using suitable organic solvents.
  - with the aim of maximize liquid yield and remove as much O as possible without using high pressure of H₂.
  - high energy density for transportation and storage

▪ Liquid Solvent Extraction (LSE) can operate successfully at a small scale of ca. 50 T/D.
Tubing/Parr reactor reactor immersed in fluidised sand bath
Toluene extraction is carried out for 24 hours.

After extraction, flask contents is filtered through a 0.5μm glass fibre paper to determine overall conversion to DCM/Toluene soluble products, water and gas.

Pyridine extraction for 24 hours.

Further concentrate by vacuum distillation to remove DCM/Toluene, tetralin and naphthalene.

Asphaltene determination separate bitumen to asphaltene and maltene.
- Anhydrous (baseline) tests give conversion of ~65%.
- 1:2 ratio of tetralin increases this to ~80-90%.
- Similar results obtained for other solvents and petroleum bitumen.
Overall Conversion rate by using miscanthus and different solvents

Conversion Rate (wt. %)

Solvents:
- No added solvent
- Tetralin
- Decalin
- Bitumen
- 1-methylnaphthalene
- Water
- Decalin/1-methylnaphthalene
- Polystyrene
- Polyethylene
- Polystyrene/Tetralin

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Total conversion, bitumen & hydrocarbon gas yields at different temperatures

- Total liquid product yields are ca. 60%
### Elemental compositions of biomass bitumens

<table>
<thead>
<tr>
<th>Bitumen</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>O*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscanthus 380°C</td>
<td>0.96</td>
<td>76.5</td>
<td>6.92</td>
<td>&lt;0.1</td>
<td>15.7</td>
</tr>
<tr>
<td>Miscanthus 400°C</td>
<td>1.23</td>
<td>78.8</td>
<td>7.18</td>
<td>&lt;0.1</td>
<td>12.8</td>
</tr>
<tr>
<td>Miscanthus 420°C</td>
<td>1.44</td>
<td>80.4</td>
<td>7.01</td>
<td>&lt;0.1</td>
<td>11.1</td>
</tr>
<tr>
<td>Miscanthus 440°C</td>
<td>1.87</td>
<td>83.0</td>
<td>6.80</td>
<td>&lt;0.1</td>
<td>8.3</td>
</tr>
<tr>
<td>Miscanthus 460°C</td>
<td>2.17</td>
<td>85.4</td>
<td>6.56</td>
<td>&lt;0.1</td>
<td>5.8</td>
</tr>
</tbody>
</table>

- High energy densities and compatible with petroleum fractions
Hydropyrolysis shows great potential as a new tool for rapid BC isolation and quantification, with benefits in for \(^{14}\)C age determination

100% conversion for biomass means that contents in coal blends can easily be quantified from the remaining inertinite content.
On-going and Future Research

- Torrefied biomass - structural variations for different feedstocks
- Assessing instances where biomass can improve coal burn-out
- $^{14}$C measurements – time-averaged flue gas to verify proportion of biomass combusted in co-firing
- Liquefaction for processing wastes
- Controlling biomass reactivity in smokeless fuels