A New Classification System for Biomass and Waste Materials for Use in Combustion

Research Engineer: Philip Jenkinson  
Academic Supervisors: Prof. Colin Snape & Prof. John Patrick; Industrial Supervisor: Karl Bindemann (EPRI)
Agenda

- Background and Rationale
- Project Objectives
- Methodologies
- Results: Char Formation, Reactivity and Inorganic Interactions Under Slow Heating and Simulated PF Combustion Conditions
- Implications
- Summary and Future Work
Background

- Drives to reduce CO₂ emissions and prolong the operation of the ageing UK coal fleet has led to a large increase in co-firing

- 100% biomass conversion appears advantageous under current legislation

- Advantages include:
  - Rapid, Balanced Biogenic Carbon Cycle
  - Universal Availability
  - Continuously Replenishing Fuel Stocks
Current Status

- Wide variety of biomass and waste feedstocks exist
- Each differs greatly in their chemical and physical characteristics
- This has a dramatic impact on combustion performance, further analysis is required to ensure efficient utilisation
Project Objectives

• To develop a new classification system for biomass and waste materials for use as a predictive tool of the efficacy of their combustion behaviour for use in power generation.

• This scheme has the potential to provide an effective guide to combustion characteristics of a range of biomass and waste materials, both for co-firing with coal and dedicated biomass combustion.

• Allow for enhanced ease of biomass/waste utilisation
• Increasing the variety of biomass and fossil fuels available for power generation
• Encourage more widespread biomass application
The Coal industry is comfortable with utilising maceral analysis to predict combustion performance.
- No such system exist for biomass
Biomass Composition

Source: [1]

- Lignin: 25-35%
- Cellulose: 40-60%
- Hemicellulose: 20-35%
$^{13}\text{C}$ NMR provides a quantitative indication of biomass structural composition allowing for more in depth investigation of component thermal decomposition.

- This approach has been utilised successfully to quantify aromatic carbon content of coals and is now being used for lignocellulosic biomasses.
Sample Fractionation

EtOH Extraction

Filtration and Precipitation

Lignin and Holocellulose

Centrifugation
Characterisation

- Utilising $^{13}$C NMR alongside Elemental Analysis and ICP-OES techniques allows for a comprehensive understanding of the structural and chemical composition of chosen fuels.

- Thermogravimetric analysis (TGA) can then be utilised to determine the physical behaviour of these fuels during devolatilisation and combustion processes.
Influence of Inorganic Minerals (K+Ca)

% Fixed Carbon / % Aromatic Carbon (Daf)

Mass % K + Ca (Daf)

- Pine Fractions
- Olive Fractions
- Corn Stover Fractions
- Softwood Fractions
- Torrefied Pine
Non-Isothermal Combustion

Derivative Weight (%min⁻¹)

Temperature (°C)

- Olive Pellet Residue
- Olive Pellet Raw
- Olive Pellet Lignin
In order to further study the char combustion properties of the chosen fuels and their isolated pseudo-components chars were prepared under slow heating (30 °C/min) using a horizontal tube furnace as shown below.

These chars were then studied as to their morphology (Optical oil-immersion microscopy and BET surface area) and char reactivity (isothermal char combustion kinetics at 350, 375, 400, 425, and 450°C).
Oil immersion optical microscopy reveals that slow pyrolysis chars from raw pine largely retains its original natural structure giving rise to a highly porous char material which is open to oxygen diffusion during combustion and thus undergoes high rates of carbon burnout.

BET surface area analysis reveal that the available char surface area is in the order of 342.09 m²/g (< 63 μm) and 376.40 m²/g (125 – 250 μm)
The holocellulosic fraction likewise retains its original fibrous structure during slow charring processes.

Char combustion rates are expected to be somewhat faster than those of raw pine chars due to the removal of unreactive lignin components and the greater observed surface area of 431.03 $m^2/g$ (< 63 µm).
Pine Char Morphology: Lignin

- Unlike the other pseudo-components lignin is fully softened during pyrolysis, undergoing a glass-phase transition at relatively low temperatures. This softening followed by significant char formation results in a highly fused char material.

- Such fused monolithic structures are relatively closed to oxygen diffusion processes and contain few active carbon sites for combustion, exhibiting an extremely low BET surface area of 0.1525 m²/g (< 63 μm) and 0.0121 m²/g (125 – 250 μm) are thus likely to undergo slow char burnout.
## Slow Heating Char Burnout Reactivity

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$A$ (min$^{-1}$)</th>
<th>1st Order Rate Constant at 400°C (min$^{-1}$)</th>
<th>90% Char Burnout Time at 400°C (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine Raw Char</td>
<td>134.504</td>
<td>4.09x10$^9$</td>
<td>0.149</td>
<td>80.26</td>
</tr>
<tr>
<td>Pine Residue Char</td>
<td>143.079</td>
<td>5.27x10$^9$</td>
<td>0.044</td>
<td>271.2</td>
</tr>
<tr>
<td>Pine Lignin Char</td>
<td>163.105</td>
<td>2.66x10$^{10}$</td>
<td>0.017</td>
<td>557.72</td>
</tr>
<tr>
<td>Raw Olive Char</td>
<td>145.076</td>
<td>3.05x10$^{10}$</td>
<td>0.131</td>
<td>84.06</td>
</tr>
<tr>
<td>Olive Residue Char</td>
<td>85.352</td>
<td>1.08x10$^6$</td>
<td>0.263</td>
<td>42.05</td>
</tr>
<tr>
<td>Olive Lignin Char</td>
<td>103.978</td>
<td>8.13x10$^7$</td>
<td>0.051</td>
<td>246.89</td>
</tr>
<tr>
<td>Olive – Extractives Char</td>
<td>72.31</td>
<td>1.02x10$^5$</td>
<td>0.26</td>
<td>35.43</td>
</tr>
<tr>
<td>Raw Corn Stover Char</td>
<td>77.148</td>
<td>3.12x10$^5$</td>
<td>0.213</td>
<td>29.95</td>
</tr>
<tr>
<td>Corn Stover Residue Char</td>
<td>44.644</td>
<td>1.37x10$^4$</td>
<td>0.624</td>
<td>19.11</td>
</tr>
<tr>
<td>Corn Stover Lignin Char</td>
<td>109.268</td>
<td>7.36x10$^7$</td>
<td>0.238</td>
<td>51.72</td>
</tr>
</tbody>
</table>
Drop Tube Furnace (DTF) testing employed to generate char samples under simulated pulverised fuel combustion conditions with rapid heating rates ($\sim 10^6$) and low residence times (15-600 ms) – this allows for assessment of ignition, char production and carbon burnout processes occurring during actual power plant combustion.
Simulated PF Volatile Yields

Volatile Matter Content (%) vs Mass % Aromatic Carbon

- Pine Fractions
- Corn Stover Fractions
- Torrefied Pine
- Straw Fractions

The graph shows the relationship between volatile matter content and mass % aromatic carbon for different biomass fractions.

The data points indicate a negative correlation between the two variables, suggesting that as the mass % aromatic carbon increases, the volatile matter content decreases.
Burnout Profiles

Char Remaining (%) vs. Time (mins)

- Corn Stover Residue
- Corn Stover Raw
## Simulated PF Char Combustion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ea (kJmol⁻¹)</th>
<th>A (min⁻¹)</th>
<th>1st Order Rate Constant at 450°C (min⁻¹)</th>
<th>90% Burnout Time at 450°C (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Pine</td>
<td>82</td>
<td>3.7x10⁵</td>
<td>0.056</td>
<td>28.4</td>
</tr>
<tr>
<td>Pine Residue</td>
<td>90.12</td>
<td>4.7x10⁵</td>
<td>0.034</td>
<td>54.8</td>
</tr>
<tr>
<td>Torrefied Pine 240°C</td>
<td>93</td>
<td>1.8x10⁶</td>
<td>0.044</td>
<td>34.7</td>
</tr>
<tr>
<td>Torrefied Pine 260°C</td>
<td>99</td>
<td>3.7x10⁶</td>
<td>0.027</td>
<td>56.3</td>
</tr>
<tr>
<td>Torrefied Pine 280°C</td>
<td>107</td>
<td>1.3x10⁷</td>
<td>0.015</td>
<td>61.1</td>
</tr>
<tr>
<td>Raw Corn Stover</td>
<td>87.43</td>
<td>3.85x10⁶</td>
<td>0.364</td>
<td>4.9</td>
</tr>
<tr>
<td>Corn Stover Residue</td>
<td>82.26</td>
<td>2.9x10⁵</td>
<td>0.068</td>
<td>26.1</td>
</tr>
<tr>
<td>Raw Straw</td>
<td>143.46</td>
<td>8.85x10⁹</td>
<td>0.080</td>
<td>22.5</td>
</tr>
<tr>
<td>Straw Residue</td>
<td>157.34</td>
<td>2.00x10¹⁰</td>
<td>0.021</td>
<td>179.75</td>
</tr>
</tbody>
</table>
Implications

• It is clear from the results presented that lignocellulosic composition will have a dramatic impact on the combustion performance of biomass fuels.

• This has profound implications on fuel choice, burner design and other combustion infrastructure.

• There are also some clear indications of synergistic interaction of biomass constituents during combustion – this may be utilisable in encouraging combustion performance of poor quality coals.
Summary and Future Work

- Initial studies have revealed the differing devolatilisation and char burnout reactivities of the three major biomass constituents and the role played by both aromatic carbon and inorganic mineral matter during devolatilisation and char combustion.

- Experimental data collected on sample composition and thermal conversion processes will be used to indicate how variations in biomass constituents correlate with devolatilisation and char burn-out behaviour during combustion.

- From this information a new biomass/waste characterisation system can be proposed, verified at bench and pilot scales and utilised as a predictive tool for combustion behaviour.

- It is envisaged that this classification scheme will facilitate easier utilisation of a wider range of biomass fuels whilst ensuring efficient, environmentally acceptable use of valuable fuel resources.
THANK YOU!

ANY QUESTIONS ARE MORE THAN WELCOME