Biomass Co-firing Related Research at the University of Nottingham



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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









Efficient Power from Fossil Energy and Carbon Capture Technologies

- 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



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

Other projects

 Coal and biomass liquefaction Hui Deng, funded by BP
 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



End of October



Moisture 8.4% Volatile matter 71.6% Fixed Carbon 15.1% Ash 4.9% Moisture 9.6% Volatile Matter 69.5% Fixed Carbon 15% Ash 5.9%

Increase in ash content



TGA Proximate Analysis – Forestry Residue





• 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

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C.H. Vane, T.C. Drage and C.E. Snape, Biodegradation of Oak (*Quercus alba*) wood during growth of the Shiitake Mushroom (*Lentinula edodes*): A Molecular Approach, <u>J Agric. Food Chem.</u>, 2003, **51**, 947-956.

White oak decayed by Lentinula edodes



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

Diminishing side chain length in G & S units
Demethylation and demethothxylation

White oak decayed by Lentinula edodes





Wheat straw decay by oyster mushroom (Pleurotus ostreatus)



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C.H. Vane, S.C. Martin, C.E. Snape and G.D. Abbott, Degradation of lignin in wheat straw during growth of the oyster mushroom (*Pleurotus ostreatus*) using off-line thermochemolysis with tetramethylammonium hydroxide and solid-state ¹³C NMR, <u>J Agric. Food Chem.</u>, 2001, **49**, 2709-2716.

Wheat straw decay by oyster mushroom (Pleurotus ostreatus) – solid state ¹³C NMR



				% Carbon			
Sample	Acetyl	Lipid,	Methoxyl	Carbohydrate	Carbohydrate	Aromatic	Carboxyl
Time		Protein				lignin	/carbonyl
(days)							
0	1.9	1.4	4.6	65.0	9.8	12.4	4.9
7	1.7	2.2	2.8	64.0	10.0	14.4	4.9
14	2.8	2.4	3.1	63.8	10.8	11.8	5.3
21	2.1	1.9	2.6	64.9	10.5	11.9	5.1
28	2.6	2.4	2.6	63.6	10.7	11.4	6.7
35	2.6	2.8	2.0	63.7	10.6	11.5	6.8
42	3.2	3.1	2.9	61.9	9.4	11.8	7.7
49	4.2	2.9	2.6	61.5	9.9	11.5	7.4
56	3.4	4.0	3.2	59.7	9.9	11.3	8.5
63	2.4	3.1	2.8	59.4	9.4	14.1	8.8

C.H. Vane, S.C. Martin, C.E. Snape and G.D. Abbott, Degradation of lignin in wheat straw during growth of the oyster mushroom (*Pleurotus ostreatus*) using off-line thermochemolysis with tetramethylammonium hydroxide and solid-state ¹³C NMR, <u>J Agric. Food Chem.</u>, 2001, **49**, 2709-2716.

Combustion-enhancing additives Katie Le Manquais PhD study supported by Innospec



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TT.

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

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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



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

K. Le Manquais, C.E. Snape, I. McRobbie, J. Barker and V. Pellegrini, Comparison of the combustion reactivity of TGA and drop tube furnace chars from a bituminous coal, <u>Energy & Fuels</u>, 2009, **23(9)**, 4269-4277.



Particle size effects much less for biomass than for coal



TGA in situ char burnout in 21% O2/79% CO2 TGA in-situ char burnout in air 100 100 ←45µm **4**5-63µm →45µm 80 80 ★ 63-75µm Carbon burnout (%) **--**45-63um Carbon burnout (%) ×75-90µm ★ 63-75um * 90-106um <u>→</u>75-90µm 60 60 125-250µm * 90-106um 125-250µm 40 40 20 20 0 0 40 0 10 20 30 50 60 70 80 40 50 70 0 10 20 30 60 80 Time (min) Time (min)

Particle sizes Burnout in Air Burnout in oxy-fuel (µm) E (KJ/mol) A (min⁻¹) R^2 E (KJ/mol) R² A (min⁻¹) <45µm 116 7.09×10^8 1.00 101 3.46×10^{-7} 0.99 2.42×10^8 45-63µm 111 0.99 98 1.89×10^7 0.99 2.23 x 10⁸ 63-75µm 111 0.99 96 1.18×10^{7} 1.00 1.76×10^{8} 96 1.13×10^{7} 75-90µm 110 0.99 1.00 1.19×10^{8} 95 90-106µm 108 0.99 1.11×10^{7} 1.00 1.04×10^8 95 1.09×10^7 109 1.00 125-250µm 1.00

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 CO_2 /char reaction for a number of coals.



TGA co-combustion of sawdust and coal chars showing synergistic effect





Samples	Nitrogen chars and Air combustion		CO_2 chars and 21% $O_2/79\%$ CO_2 combustion		
	1st order rate constants	90% burnout time	1st order rate constants	90% burnout time	
	(min [_] _) (min) (min [_] _)	(min [−] □)	(min)		
sawdust char 700C	0.4901	6.60	0.3114	7.85	
Kleinkopje (KK) HTF char 1000C	0.0734	38.70	0.0526	48.00	
saw/KK char blend 50:50wt%)	0.1002	22.15	0.1089	20.65	
Predicted sawKK char blend	0.0829	25.60	0.0720	31.60	



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Effect of HCI Extraction of sawdust on burn-out with coal char UNITED KINGDOM · CHINA · MALAYSIA



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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 H_2 .

- 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





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Schematic of product work-up





- 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 asphatlene and maltene

Sludge conversion – dry ash free basis IT (100 - %DCM insolubes) UNITED KINGDOM · CHINA · MALAYSIA



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- Anhydrous (baseline) tests give conversion of $\sim 65\%$.
- 1:2 ratio of tetralin increases this to \sim 80-90%.
- Similar results obtained for other solvents and petroleum bitumen.

Overall Conversion rate by using miscanthus and different solvents



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Total conversion, bitumen & hydrocarbon gas yields at different temperatures





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Elemental compositions of biomass bitumens



Bitumen	Ν	С	Н	S	0*
Miscanthus 380°C	0.96	76.5	6.92	<0.1	15.7
Miscanthus 400°C	1.23	78.8	7.18	<0.1	12.8
Miscanthus 420°C	1.44	80.4	7.01	<0.1	11.1
Miscanthus 440°C	1.87	83.0	6.80	<0.1	8.3
Miscanthus 460°C	2.17	85.4	6.56	<0.1	5.8

High energy densities and compatible with petroleum fractions



Black carbon characterization by hydropyrolysis

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S K R C





Hydropyrolysis is a commercially available pyrolysis technique

Example of residual TOC variation from hypy for a typical soil sample. BC content is the carbon remaining when the plateau in carbon loss is reached at *ca*. 550°C.

Results for ¹⁴C measurement compare favourably with results from more time consuming clean up methods

Hydropyrolysis shows great potential as a new tool for rapid BC isolation and quantification, with benefits in for¹⁴C age determination

100% conversion for biomass means that contents in coal blends can easily be quantified from the remaining inertinite content.



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On-going and Future Research



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





