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Biomass Enhanced Carbon Capture and Storage (BECCS) - experiments and modelling

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Bio4Fuels Days 2020, Norwegian University of Science and Technology

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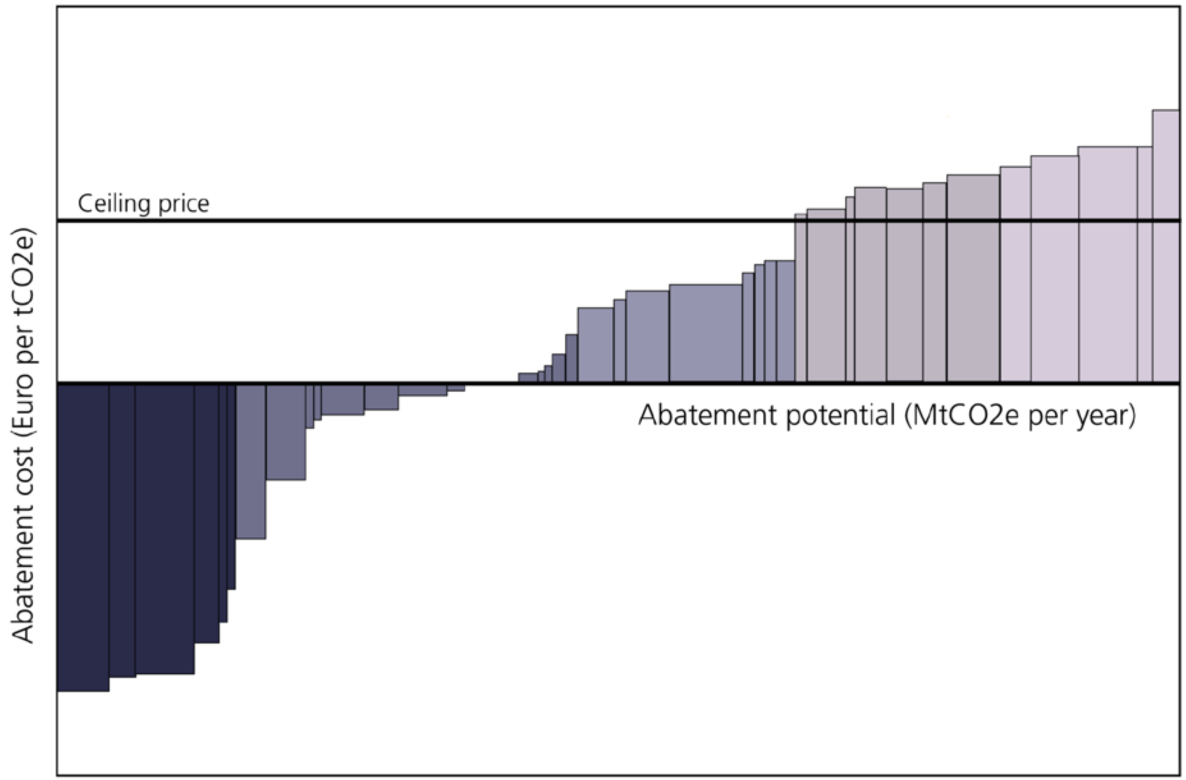
Outline

- Context
- Experimental Equipment
- Experimental Results
- Summary

Why Negative Emissions?



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Socio-Technological Context

- Part of armoury of options to achieve net zero emissions by 2050
- Key focus of UK 2050 targets is on mitigation (reduction) options
  - e.g. Demand reduction, supply decarbonisation
- However, negative emissions technologies are important:
  - where mitigation is not happening fast enough
  - where alternative abatement costs are too high
  - where non fossil fuel alternatives are not available
  - where lifestyle changes are too painful
- Some approaches to CO_2 removal from the atmosphere could increase options available due to potential **flexibility** in location for deployment

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BECCS and “GGR” technologies

System	State of Stored Carbon	Description	Published Cost Estimates
Afforestation & Reforestation	Biomass and soil organic carbon	Restoring cleared forests and planting new forests on suitable land	\$20-100/tCO_2
Wetland Restoration	Biomass and soil organic carbon	Restoring damaged, carbon-dense wetlands such as peatlands and mangrove forests.	On the order of \$10-100/tCO_2 in some cases
Agricultural Soil Sequestration	Soil organic carbon	Adopting a range of practices on arable and grazing lands that enhance soil carbon levels, including reduced tillage and new cropping patterns.	\$0-100/tCO_2, and can be cost negative
BECCS	Pressurised CO_2 in geological storage	Capturing CO_2 from biomass-fuelled power plants or industries and storing it in geological reservoirs.	\$60-120/tCO_2, but perhaps as little as \$25/tCO_2 in niches such as bioethanol production
Direct Air Capture (DAC)	Pressurised CO_2 in geological storage	Capturing CO2 directly from the air using chemical sorbents and storing it in geological reservoirs.	Widely varying, from \$30-1000/tCO2, depending on system and assumptions
Enhanced Silicate Weathering	Dissolved bicarbonate and carbonate in groundwater or oceans	Spreading finely ground silicate mineral powder on land or ocean to accelerate natural reaction with atmospheric CO2	\$20-130/tCO2 assuming complete reaction
Ocean Liming	Dissolved bicarbonate and carbonate in oceans	Adding lime or other metal oxides / hydroxides to the ocean to convert dissolved CO2 to bicarbonate and drive drawdown from the atmosphere.	\$70-160/tCO2

Source: Lomax, G. et al, Energy Policy, 2015

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BECCS

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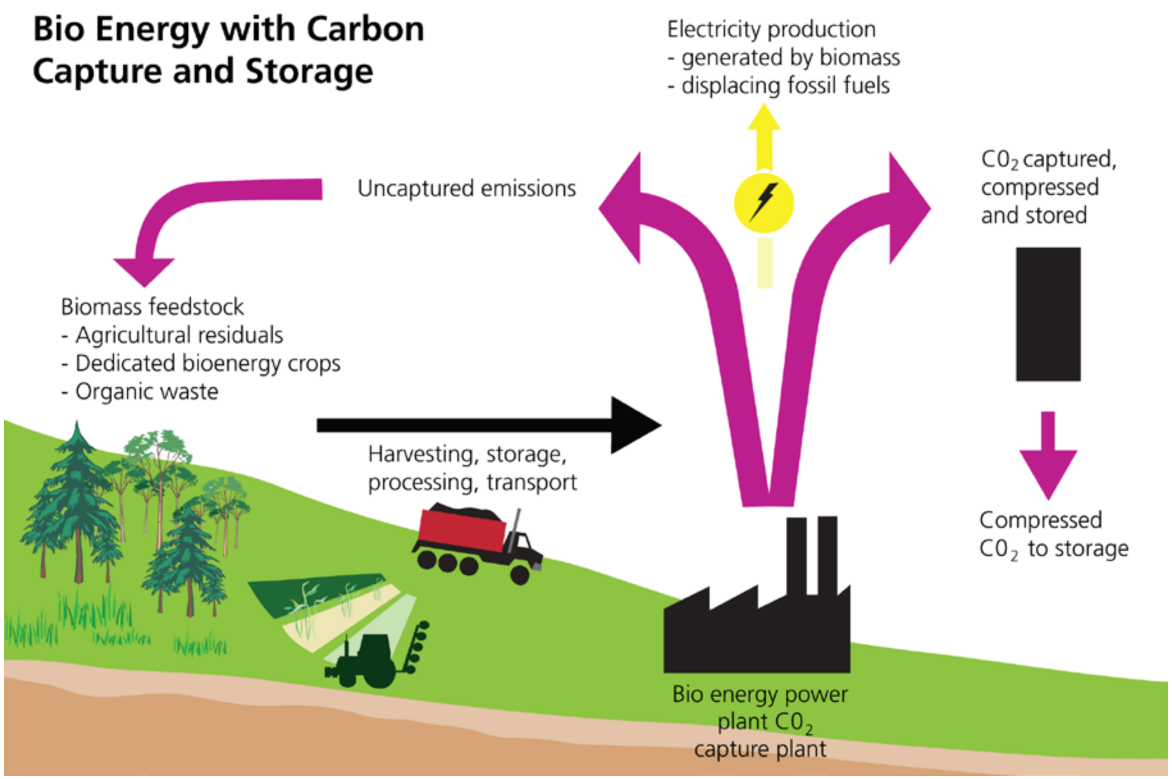

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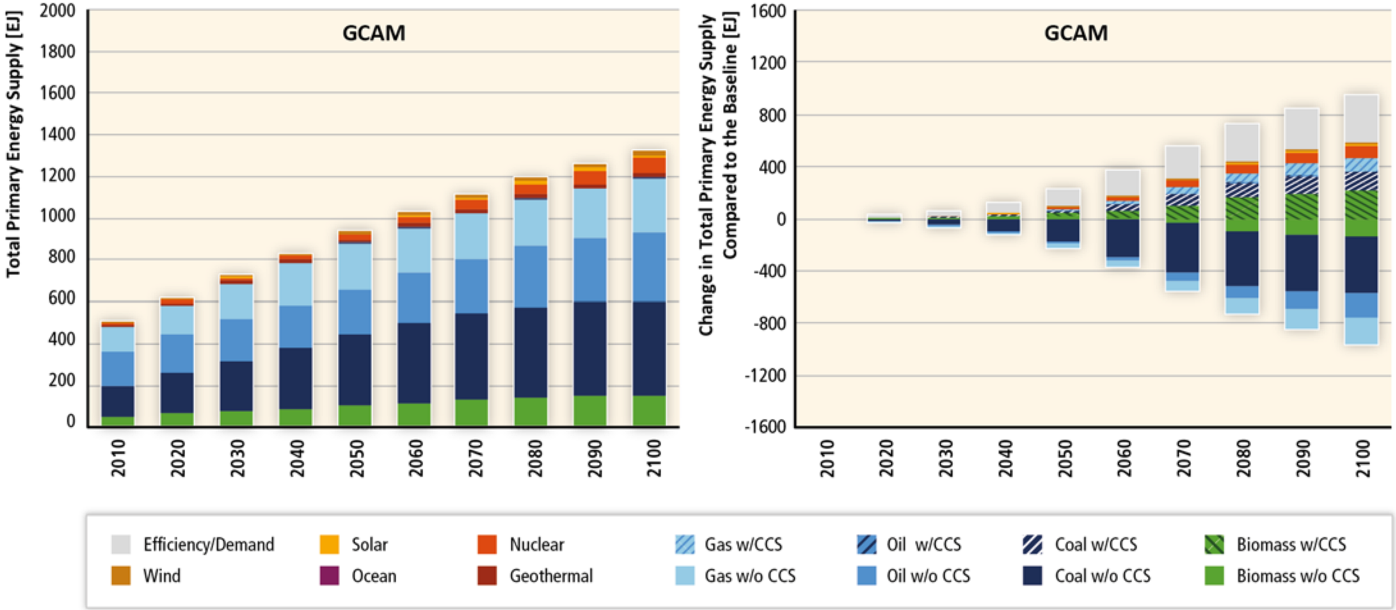
BECCS becomes increasingly important



- Several sources indicate that BECCS will become increasingly important as a share of total generation capacity as the century progresses

Source: IPCC, Climate Change 2014: Mitigation of Climate Change, Chapter 7: Energy Systems

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CO_2 Capture, utilisation and Storage (CCuS)

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CO_2 utilisation

USA ONLY

Source	Annual CO2 production (MtCO2)	Percentage of Total Emissions
Power	2530	84.0%
Refineries	154	5.1%
Iron & Steel	82	2.7%
Gas Processing	77	2.6%
Cement	62	2.1%
Ethylene	61	2.0%
Ethanol	31	1.0%
Ammonia	7.8	0.3%
Hydrogen	6.8	0.2%
Ethylene Oxide	1.2	0.0%
TOTAL	**3013**	**100%**

Global ~ 10 x USA emissions

GLOBAL

Process	Global Annual CO2 Usage	Typical source of CO2 used	Lifetime of storage
Urea	65-146Mt^	Industrial	6 Months
Methanol	6-8Mt	Industrial	6 Months
Inorganic Carbonates	3-45Mt#	?	Decades
Organic Carbonates	0.2Mt	?	Decades
Polyurethanes	10Mt	?	Decades
Technological	10Mt	?	Days to Years
Food and drink	8Mt	?	Days to Years
TOTAL	**102 – 227Mt**		

Notes:
^, # The demand for CO_2 in Urea and Inorganic Carbonate production is particularly uncertain. Various sources have quoted figures with orders of magnitude differences.

- Sources outweigh sinks by several orders of magnitude (more than a factor of 150).
- The storage of CO_2 is frequently short term – especially for largest sinks; methanol and urea.
- The use of CO_2 as a novel feedstock is a good idea if it is justified by the economics – but will not have significant climate benefit, particularly if the storage is short term.

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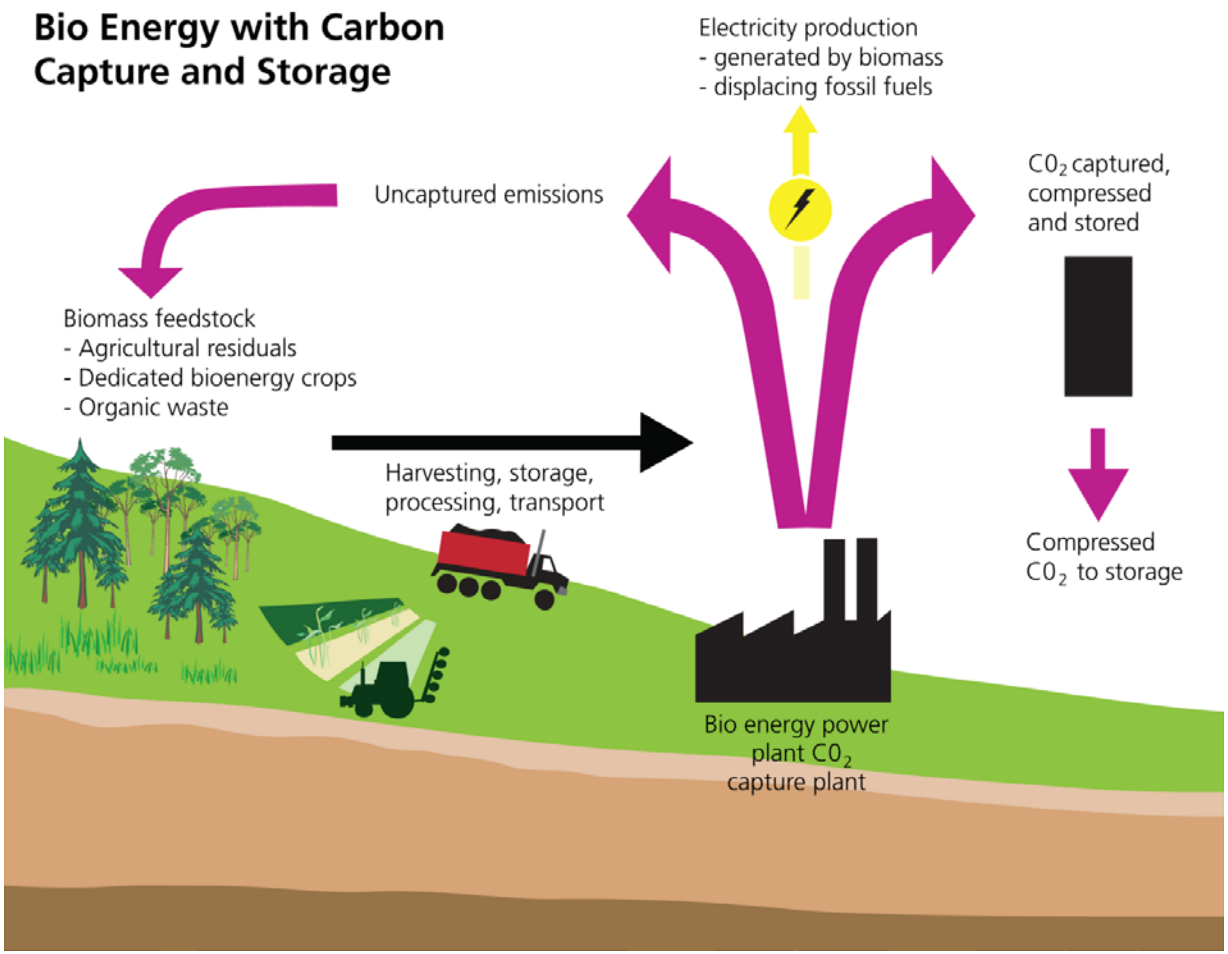
BECCS (Bio Energy with Carbon Capture and Storage)



http://gcep.stanford.edu/pdfs/06gG_uIuKMpe8tjCYMOJZQ/14_PaulFennell_NegEmissions2012.pdf

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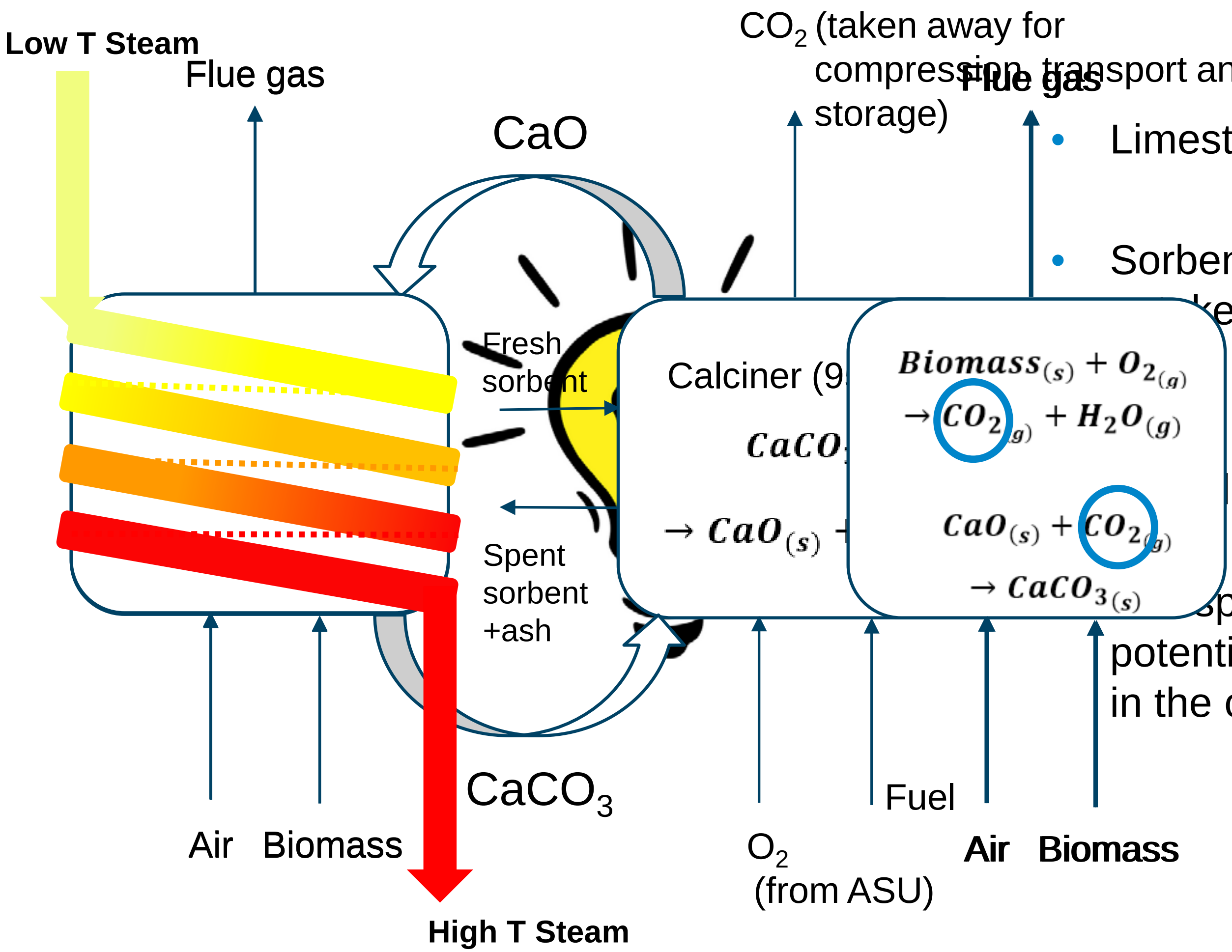
The Calcium Looping Cycle with *in situ* Biomass Combustion



- Limestone is abundant and cheap.
    - Biomass combustion and carbonation occur at the same temperature range
- Sorbent has a high theoretical ...ke of CO_2: 0.786 kgCO_2/1kg
- ...uality heat can be recovered
    - Can reduce number of unit operations
- ...pent CaO sorbent can potentially be used as feed material in the cement industry
    - Both use fluidised bed reactors

J. C. Abanades, M. Alonso and N. Rodriguez, Experimental validation of in situ CO2 capture with CaO during the low temperature combustion of biomass in a fluidized bed reactor, International Journal of Greenhouse Gas Control, 2011, **5**, 512-520.

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Tars

Thick dark-coloured organic liquids composed of HCs (typically) heavier than benzene

- **Primary**: *derivatives of cellulose, hemicellulose, lignin (oxygenated aromatics)*
- **Secondary**: *derivatives of 1^0 tars (phenolic & olefins)*
- **Tertiary**: *methyl derivatives of aromatics*
- **Condensed tertiary**: *polyaromatic hydrocarbons (PAHs) without substituent*

Problems:

- Causes **blockages downstream** (gas lines, filters etc)
- **Fouling** and **slagging** of heat exchangers
- **Reduce** overall **combustion** and **thermodynamic efficiency** of plant
- **Difficult to remove**!

Mild pressurisation of the carbonator

May allow **higher temperatures** for **combustion** and **alleviate thermodynamic limitations** on carbonation

J. L. Milne and C. B. Field, Assessment Report from the GCEP Workshop on Energy Supply with Negative Carbon Emissions, Global Climate & Energy Project, Stanford University, 2012.

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EXPERIMENTAL WORK

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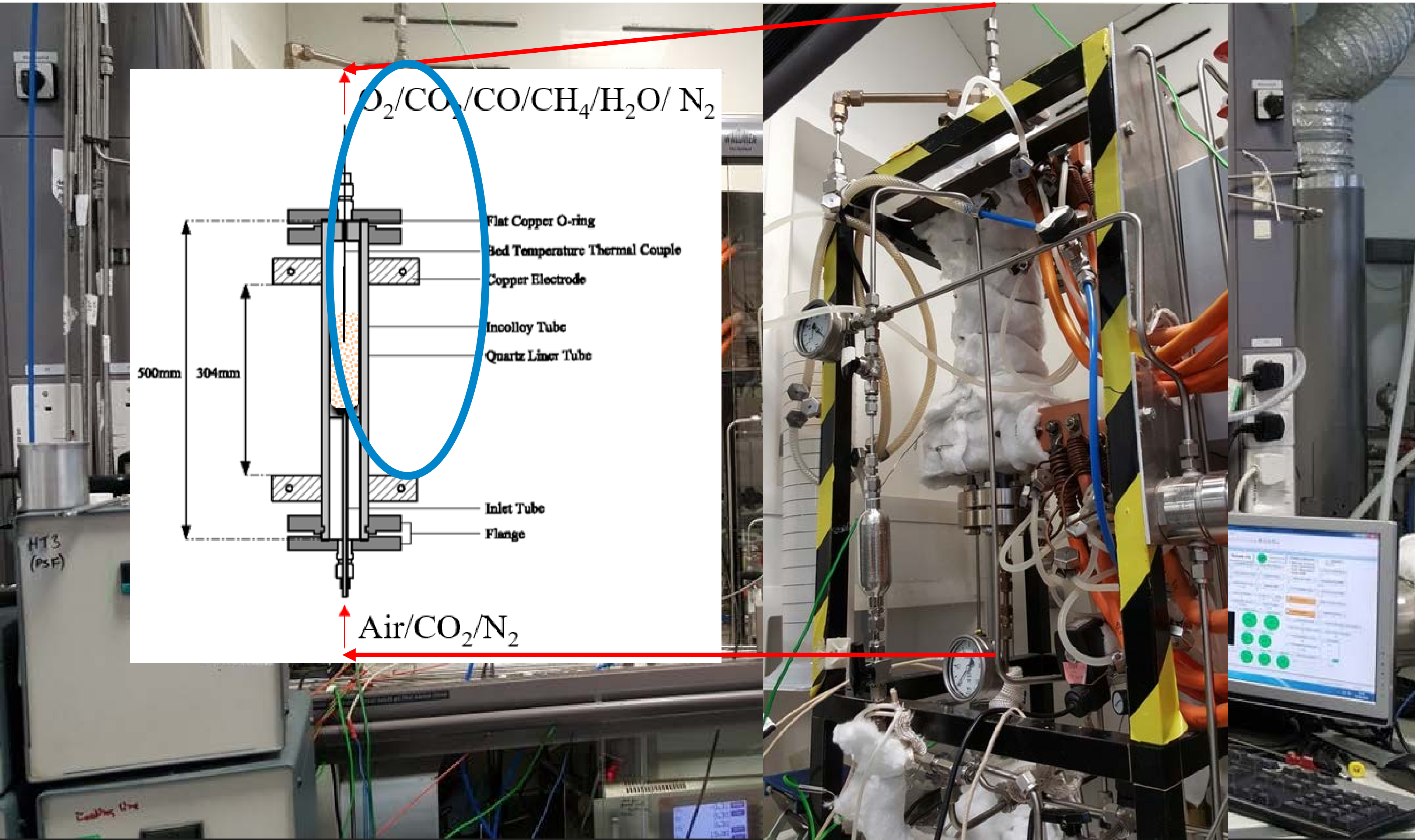
Pressurised Spout-Fluidised Bed Reactor (FBR)



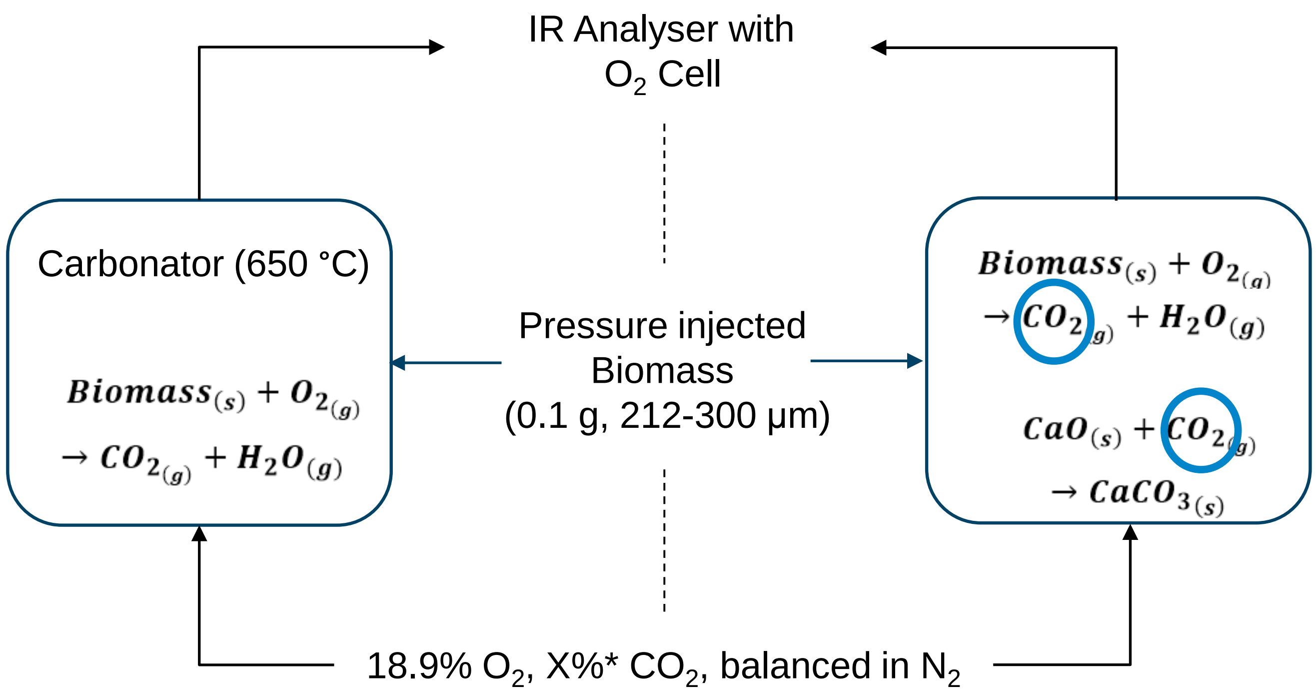
Standard Combustion vs in situ CO_2 Capture Setup

Standard Combustion Experiment

Fluidised Bed of 50 g Sand 425-500 μm

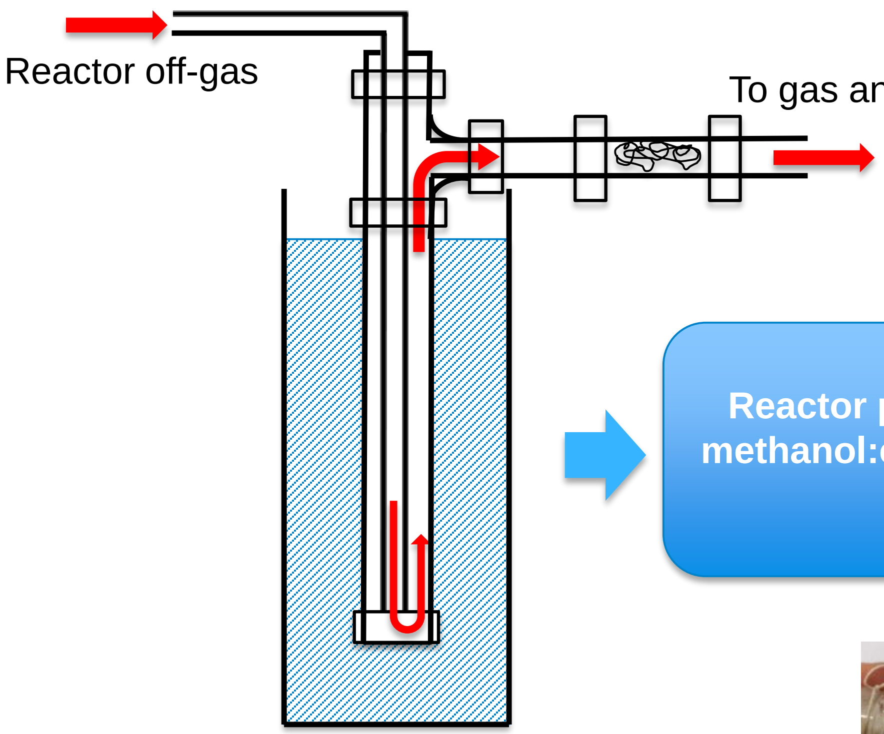
in situ CO_2 Capture Experiment

Fluidised Bed of 25 g Sand 425-500 μm
&
25 g CaO 212-355 μm



*CO_2 concentration chosen to match partial pressure of CO_2 inside reactor with the equilibrium partial pressure for carbonation/calcination at the operating temperature

Tar Recovery



Tars condensed out in trap with ice-water bath

Reactor parts washed with methanol:chloroform (4:1 v:v) solvent

Washings filtered, solvent evaporated and dried

Analysis:

- Gravimetric
- Size exclusion chromatography
- X-ray fluorescence

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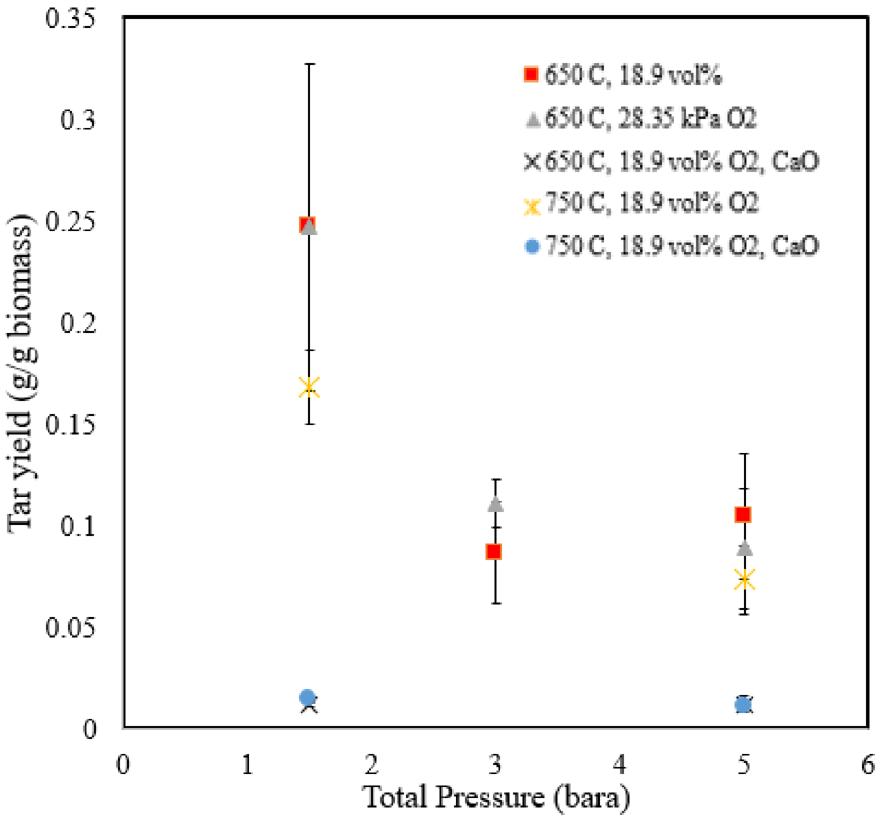
Tar Gravimetric Yields



- **Decreases** with **temperature**
- **Decreases** with presence of **CaO**
- **Decreases** with **total pressure** (grey triangles)
- **Not influenced** by **O_2 partial pressure** (see red squares vs grey triangles)

Conditions: 0.3 g beechwood (212-300 µm), 18.9 vol% O_2 in N_2, 25 g CaO/sand bed, Q=39-47 ml s^{-1} (SATP)

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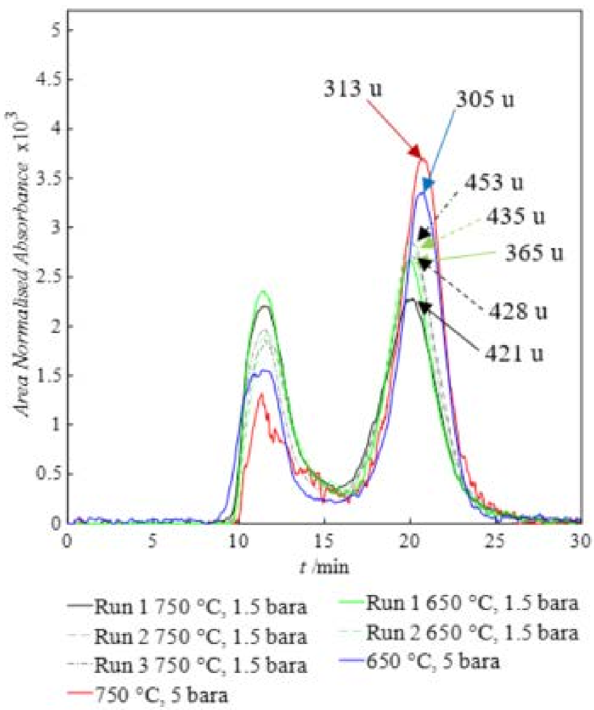
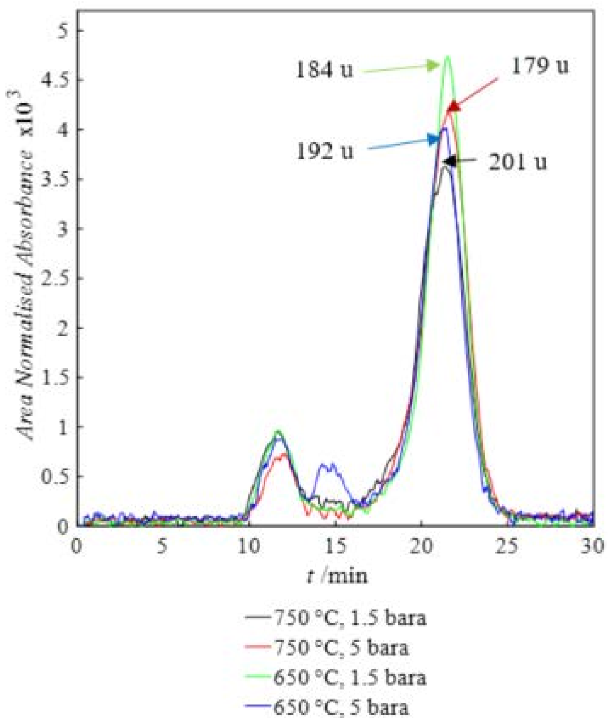
SEC (Size Exclusion Chromatography)

Standard Combustion



in situ CO_2 Capture



Sand bed:

Inc in **O_2 partial pressure** => oxidise heavier tar species to l <u>lighter</u> tar species

No clear effect of T

CaO bed:

<u>Smaller excluded peak</u> = smaller portion of <u>heavier</u> tar species

No obvious difference in effects of T&P

*Note total pressure increased with constant O_2 vol%

Conditions: 0.3 g beechwood (212-300 μm), 18.9 vol% O_2 in N_2, 25 g CaO/sand bed, Q=39-47 ml s^{-1} (SATP)

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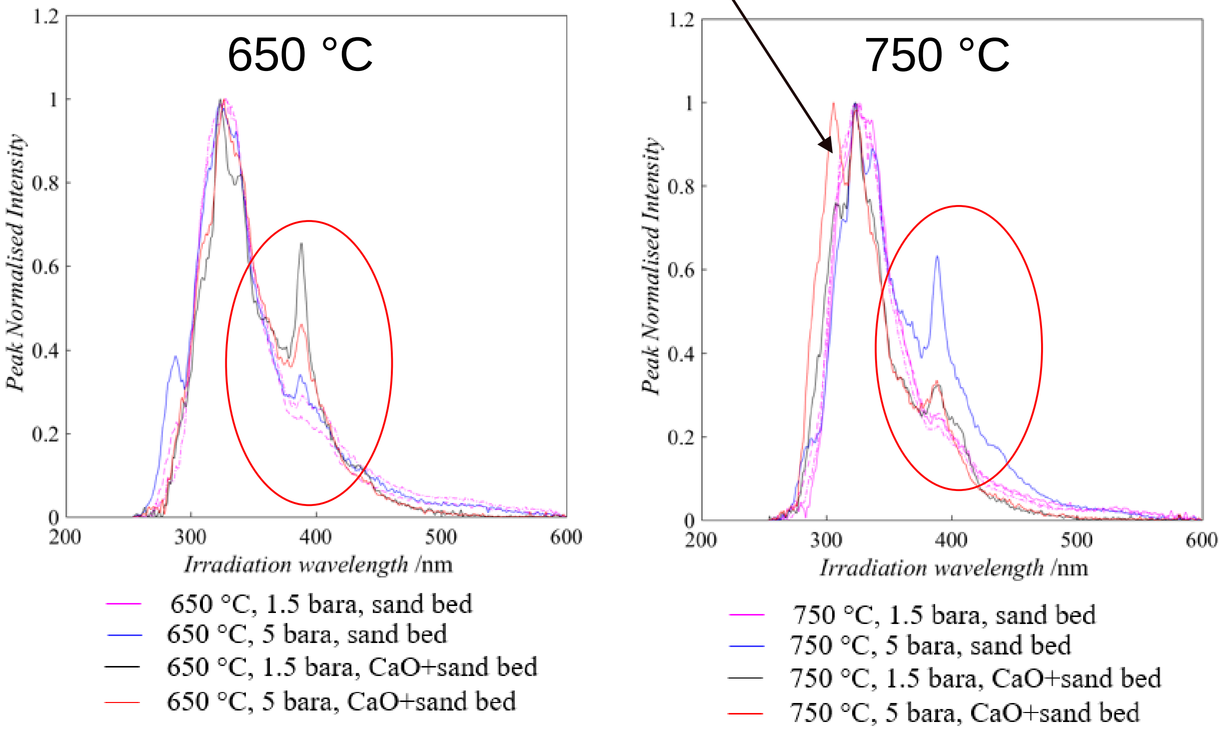
UVF (Ultra Violet Florescence)

High P, T and CaO combined reduce conjugated tar species



Inc. in degree of conjugation of species

CaO:
Greater portion of more-conjugated tar species at lower temperatures

High T+P:
Greater portion of more-conjugated tar species

High T+P+CaO:
Destruction of both 'less-conjugated' and 'more conjugated' tar species

*Note total pressure increased with constant O_2 vol%

Note: UVF gives proportion of less-conjugated to more-conjugated tar species

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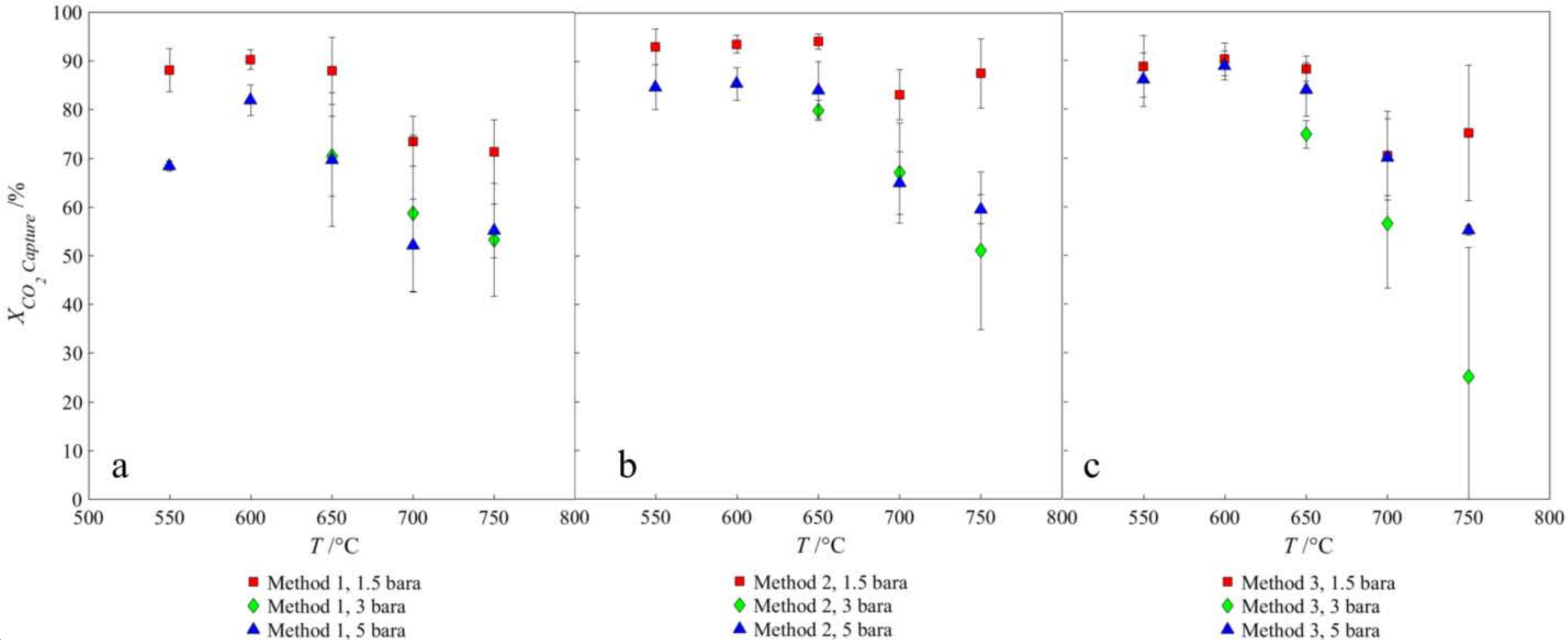
in situ CO_2 Capture at Different Pressures/Temperatures

$$CO_2 \text{ Captured Method 1 (\%)} = \left(1 - \frac{n_{CO_2,Gen} + n_{CO,Gen} + n_{CH_4,Gen}}{\frac{C\ Content\ in\ Biomass}{M_C} - \frac{C\ Content\ in\ Tars}{M_C}}\right) \times 100\%$$

$$CO_2 \text{ Captured Method 2 (\%)} = \left(1 - \frac{n_{CO_2,Gen}}{n_{O_2,Cons} + \frac{1}{2}\frac{O\ Content\ in\ Biomass}{M_O} - 1/2 n_{CO\,Gen} - \frac{1}{4}\left(\frac{H\ Content\ in\ Biomass}{M_H} - \frac{1}{4} n_{CH_4,Gen}\right)}\right) \times 100\%$$

$$CO_2 \text{ Captured Method 3(\%)} = \left(1 - \frac{n_{CO_2,Gen}(CaO\ Present)}{n_{CO_2,Gen}(No\ CaO)}\right) \times 100\%$$



Conditions: 0.1 g beechwood (212-300 µm), 18.9 vol% O_2 in N_2, 25 g CaO/sand bed, Q=39-56 ml s^{-1} (SATP)

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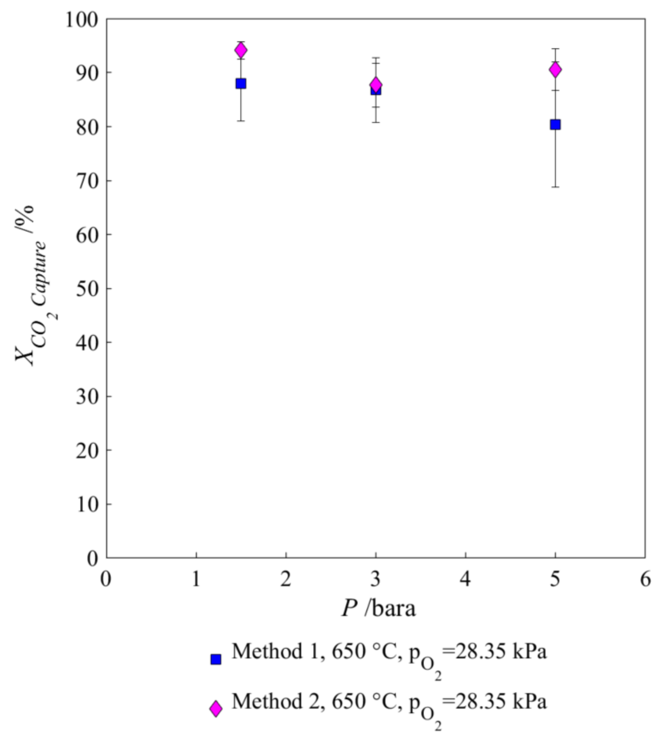
in situ CO_2 Capture at constant partial $P(O_2)$

$$\text{CO}_2\text{ Captured Method 1 (\%)} = \left(1 - \frac{n_{CO_{2,Gen}} + n_{CO,Gen} + n_{CH_4,Gen}}{\frac{C\ Content\ in\ Biomass}{M_C} - \frac{C\ Content\ in\ Tars}{M_C}}\right) \times 100\%$$

$$\text{CO}_2\text{ Captured Method 2 (\%)} = \left(1 - \frac{n_{CO_{2,Gen}}}{n_{O_{2,Cons}} + \frac{1}{2}\frac{O\ Content\ in\ Biomass}{M_O} - 1/2 n_{CO_{Gen}} - \frac{1}{4}\left(\frac{H\ Content\ in\ Biomass}{M_H} - \frac{1}{4} n_{CH_{4,Gen}}\right)}\right) \times 100\%$$

$$\text{CO}_2\text{ Captured Method 3 (\%)} = \left(1 - \frac{n_{CO_{2,Gen}}(CaO\ Present)}{n_{CO_{2,Gen}}(No\ CaO)}\right) \times 100\%$$



Effect of <u>Total Pressure</u> under <u>Constant O_2 Partial Pressure</u>

Conditions: 0.1 g beechwood (212-300 μm), 5.6-18.9 vol% O_2 in N_2, 25 g CaO/sand bed, Q=47 ml s^{-1} (SATP)

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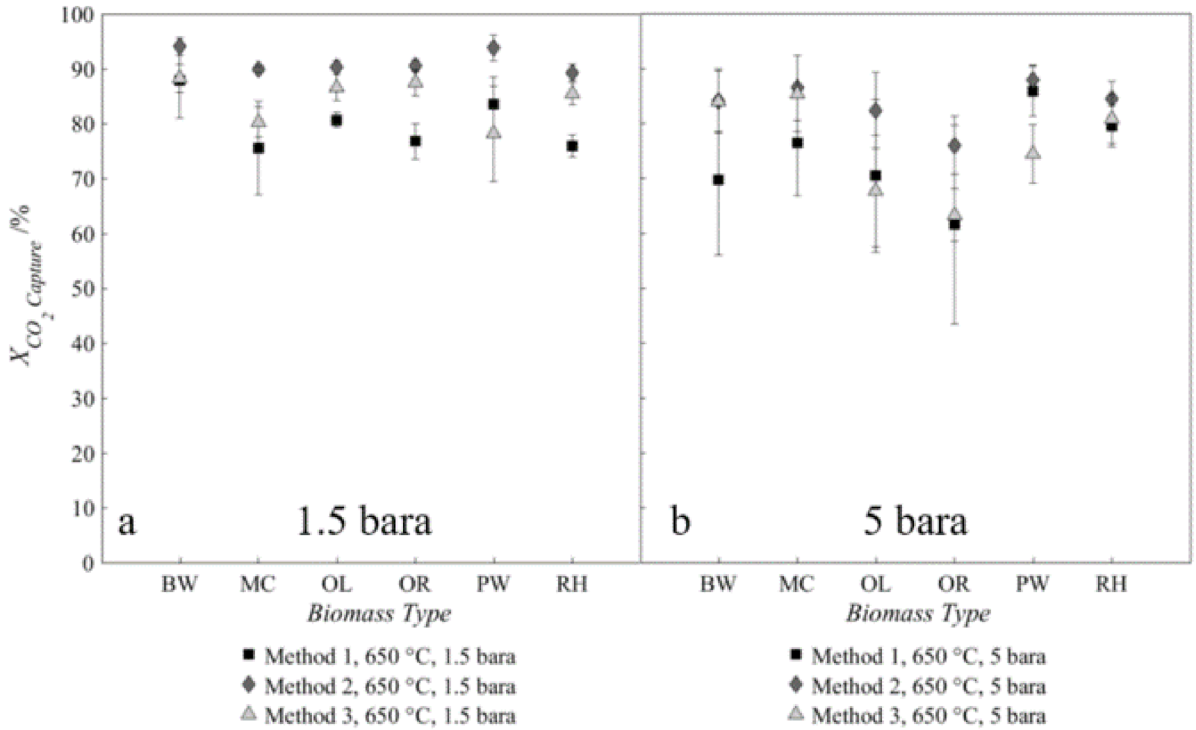
in situ CO_2 Capture for different biomass varieties

$$CO_2\ \text{Captured Method 1 (\%)} = \left(1 - \frac{n_{CO_2,Gen} + n_{CO,Gen} + n_{CH_4,Gen}}{\frac{C\ Content\ in\ Biomass}{M_C} - \frac{C\ Content\ in\ Tars}{M_C}}\right) \times 100\%$$

$$CO_2\ \text{Captured Method 2 (\%)} = \left(1 - \frac{n_{CO_2,Gen}}{n_{O_2,Cons} + \frac{1}{2}\frac{O\ Content\ in\ Biomass}{M_O} - 1/2 n_{CO_{Gen}} - \frac{1}{4}\left(\frac{H\ Content\ in\ Biomass}{M_H} - \frac{1}{4} n_{CH_4,Gen}\right)}\right) \times 100\%$$

$$CO_2\ \text{Captured Method 3 (\%)} = \left(1 - \frac{n_{CO_2,Gen}(CaO\ Present)}{n_{CO_2,Gen}(No\ CaO)}\right) \times 100\%$$



CO_2 Capture from Combustion of Different Biomasses:

BW: Beechwood
MC: Miscanthus
OL: Olive Pith
OR: Orange Peel
PW: Pinewood
RH: Rice Husk

Conditions: 0.1 g biomass (212-300 μm), 18.9 vol% O_2 in N_2, 25 g CaO/sand bed, Q=47 ml s^{-1} (SATP)

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Summary

- **Basic Idea Validated, with potential issues.**
- **Tar yield lowered** by presence of **CaO**, **high temperatures** and **total pressure**. O_2 partial pressure has no effect

- CaO helps crack heavier tars into lighter tars. Higher P_{O2}/inclusion of CaO found to **crack less-conjugated tar species more readily** than more-conjugated tar species. **Increase** in P_{O2}, T and CaO together **cracks more-conjugated tar species** as well.

- Although higher CO_2 partial pressures can be achieved at high P, rate of in situ CO_2 capture appears to be limited by **rapid combustion kinetics** at **high O_2 partial pressures**, especially **at higher operating pressures and temperatures**. May be better to use two reactors.

- Initial tests show **no constraint** with **biomass species**

- **Pressurised operation feasible** but not necessary optimal

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Acknowledgements

We gratefully acknowledge the EPSRC for the PhD Studentship

EPSRC Engineering and Physical Sciences Research Council

UKCCS RESEARCH CENTRE

Research Councils UK Energy For a Low Carbon Future

Thank you for listening!

Questions?

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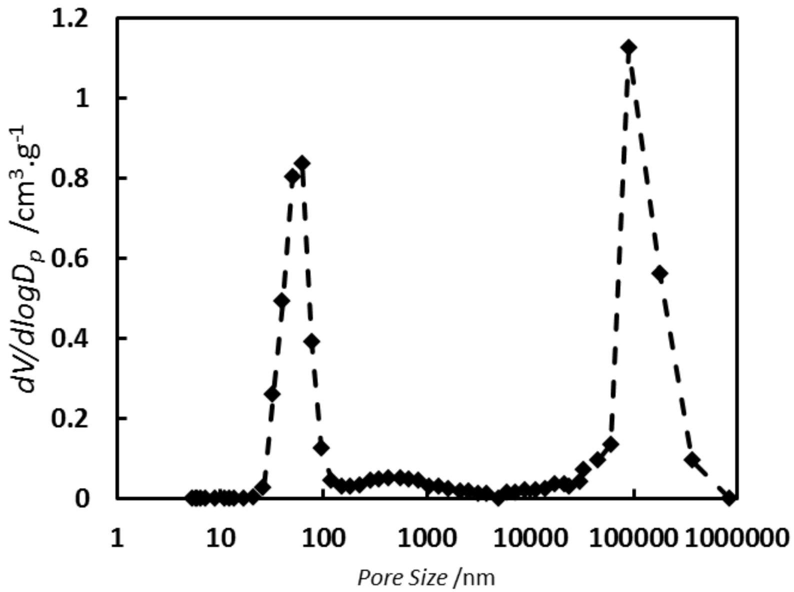
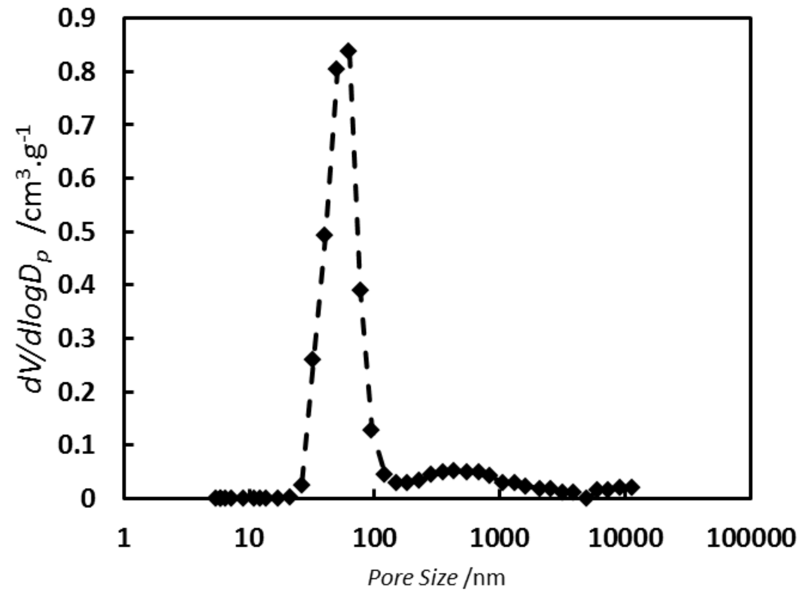
Back up slides

Supporting Slide 1: MIP Pore size distribrution

All pore sizes



Pore sizes <10 µm (discounting the interstitial voids)



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Sample (CaO) Properties

Measurement	Average	Standard Deviation
BET Surface Area (m^2/g)	19.40	3.28
Envelope Density (g/cm^3)	1.57	0.05
Skeletal Density (g/cm^3)	3.15	0.10
Porosity <10 µm	0.50	0.01

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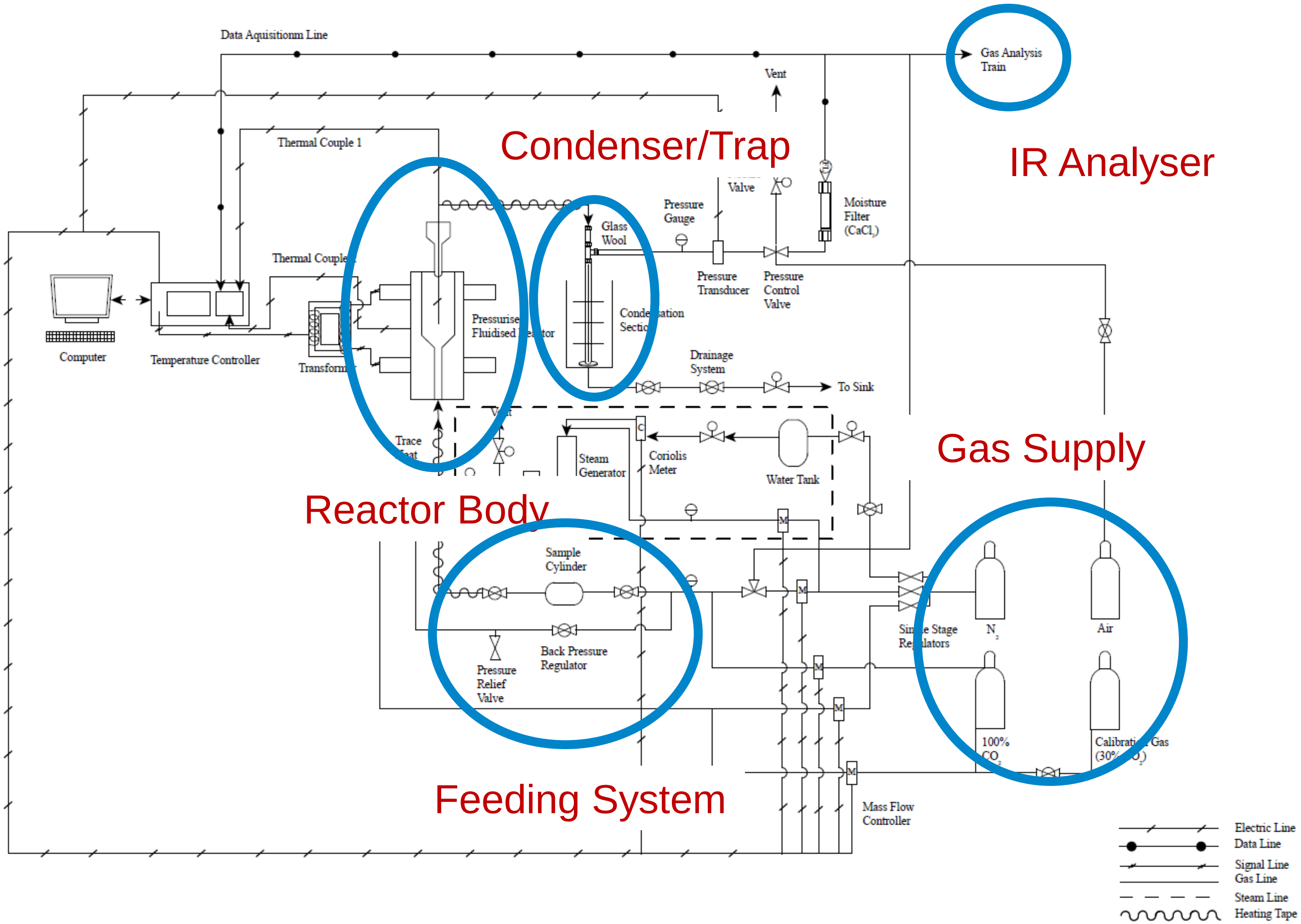
Equipment (PFD)



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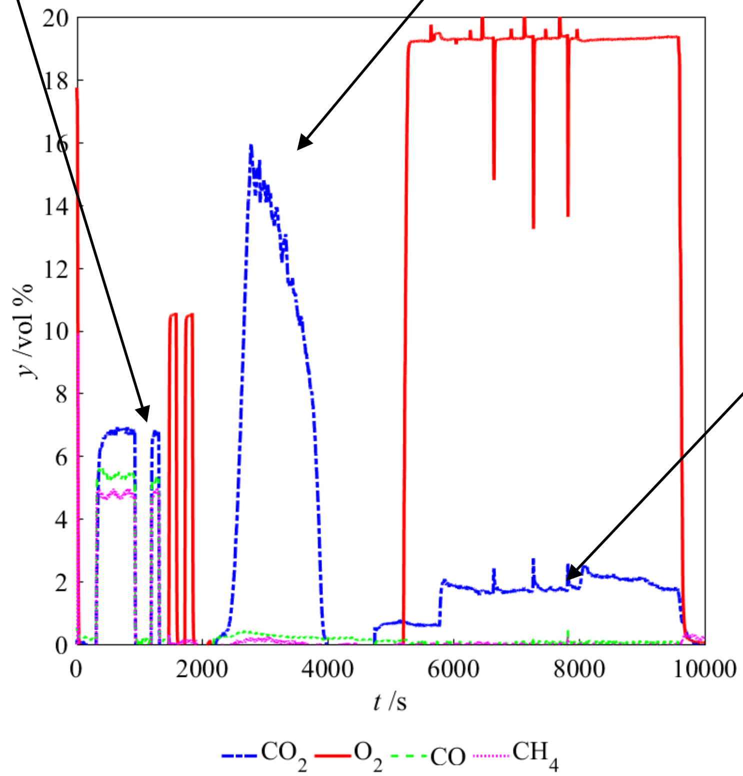
Concentration Profile

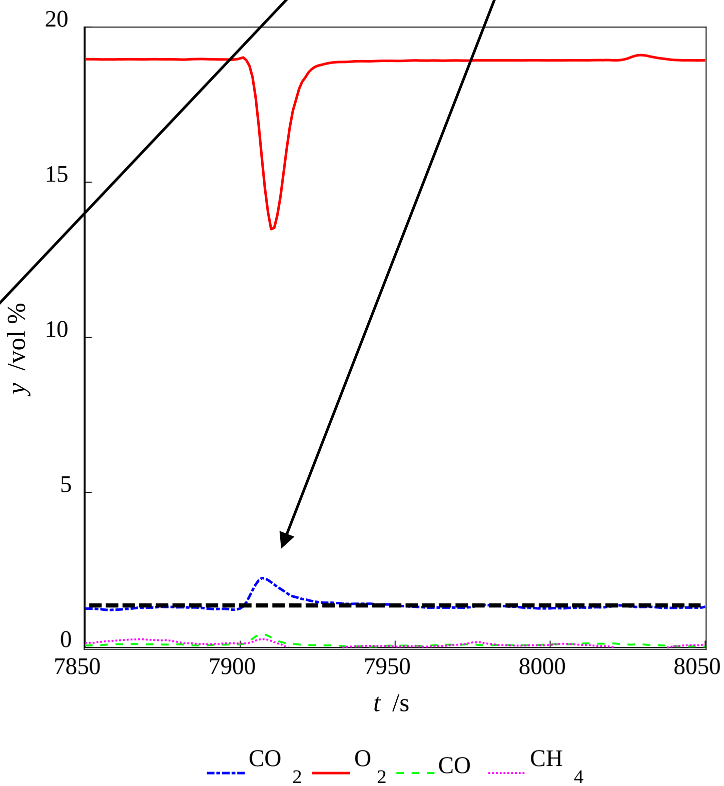
in situ Calcination @ 850 °C, 1.5 bara

Calibration

in situ CO_2 capture (@ 700 °C, 3 bara)



Full Concentration Profile



Reaction Profile

Biomass Type	Ultimate Analysis (wt%)^{daf}					Proximate Analysis (wt%)			
	C	H*	N	O†	S	Fixed Carbon^{daf}	Volatiles^{daf}	Moisture	Ash^{db}
Beech wood	49.3	5.5	0.3	44.9	<0.04	14.7	85.3	5.9	0.6
Miscanthus	48.6	6.1	0.1	45.1	0.1	14.3	85.7	5.5	1.1
Olive stone	51.9	7.2	0.5	40.4	0	21.2	78.8	5.6	0.5
Orange peel	44.0	7.1	0.9	48.0	0	21.6	78.4	5.1	3.6
Pine wood	51.7	7.0	0	40.9	0.4	13.4	86.6	5.9	1.5
Rice husk	50.0	6.8	1.0	41.6	0.6	19.3	80.7	5.9	17.7

^{daf} *dry, ash-free basis*

^{db} *dry basis*

**not including H in the moisture*

†*calculated by difference*

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Carbon Balance

Operation	Fluidising bed material		Temperature (°C)	Pressure (bara)	O_2 Partial Pressure (kPa)	Tar Yield (g tar/g biomass)	σ	Combined Carbon Recovery (%)	σ
	Sand (g)	CaO (g)							
Combustion	50	-	650	1.5	28.35	0.247	0.008	109	12
	50	-	650	3	28.35	0.110	0.012	87	7
	50	-	650	3	56.70	0.087	0.024	97	12
	50	-	650	5	28.35	0.089	0.029	67	9
	50	-	650	5	94.50	0.105	0.031	105	16
	50	-	750	1.5	28.35	0.168	0.018	120	19
	50	-	750	5	28.35	0.047	0.005	89	26
	50	-	750	5	94.50	0.073	0.017	100	4
Capture	25	25	650	1.5	28.35	0.012	0.001	78	3
	25	25	650	5	94.50	0.012	0.004	80	15
	25	25	750	1.5	28.35	0.014	0.001	64	22
	25	25	750	5	94.50	0.011	0.001	81	10

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Affect of pressure on tars

When the external pressure of inert gas is raised above atmospheric pressure, volatile and tar yields initially tend to diminish rapidly, up to about 5 bars. With increasing pressure, this trend slows down and appears to level off above 40 bars. Compared with atmospheric pressure results, the overall decline in total volatiles may be as much as ~10–12%. The effect was first reported and explained by Howard and co-workers [cf. Howard, 1981], in terms of the partial suppression of volatile release by the physical effect of increasing external pressure.

R. Kandiyoti, A. A. Herod and K. D. Bartle, in *Solid Fuels and Heavy Hydrocarbon Liquids*, Elsevier Science Ltd, Oxford, 2006, DOI: http://dx.doi.org/10.1016/B978-008044486-4/50003-9, pp. 36-90

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