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

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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 CO_2 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

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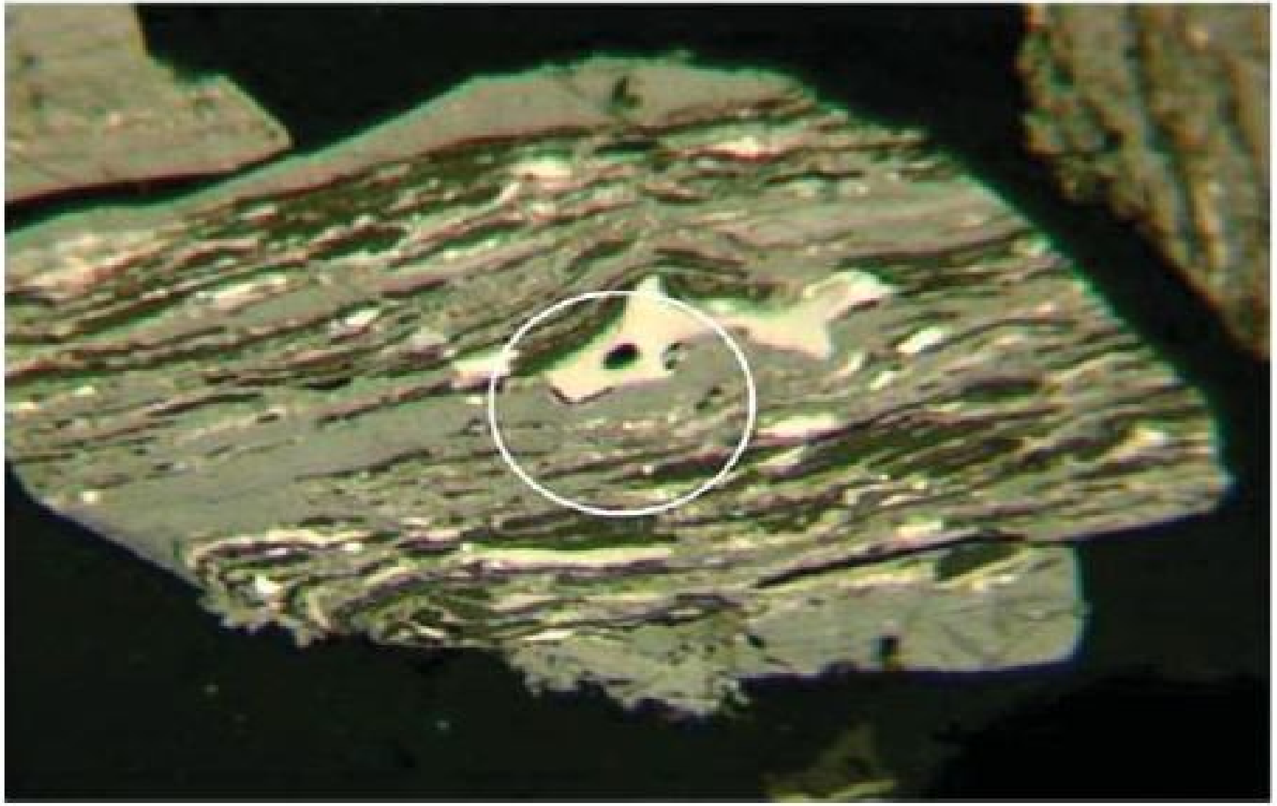
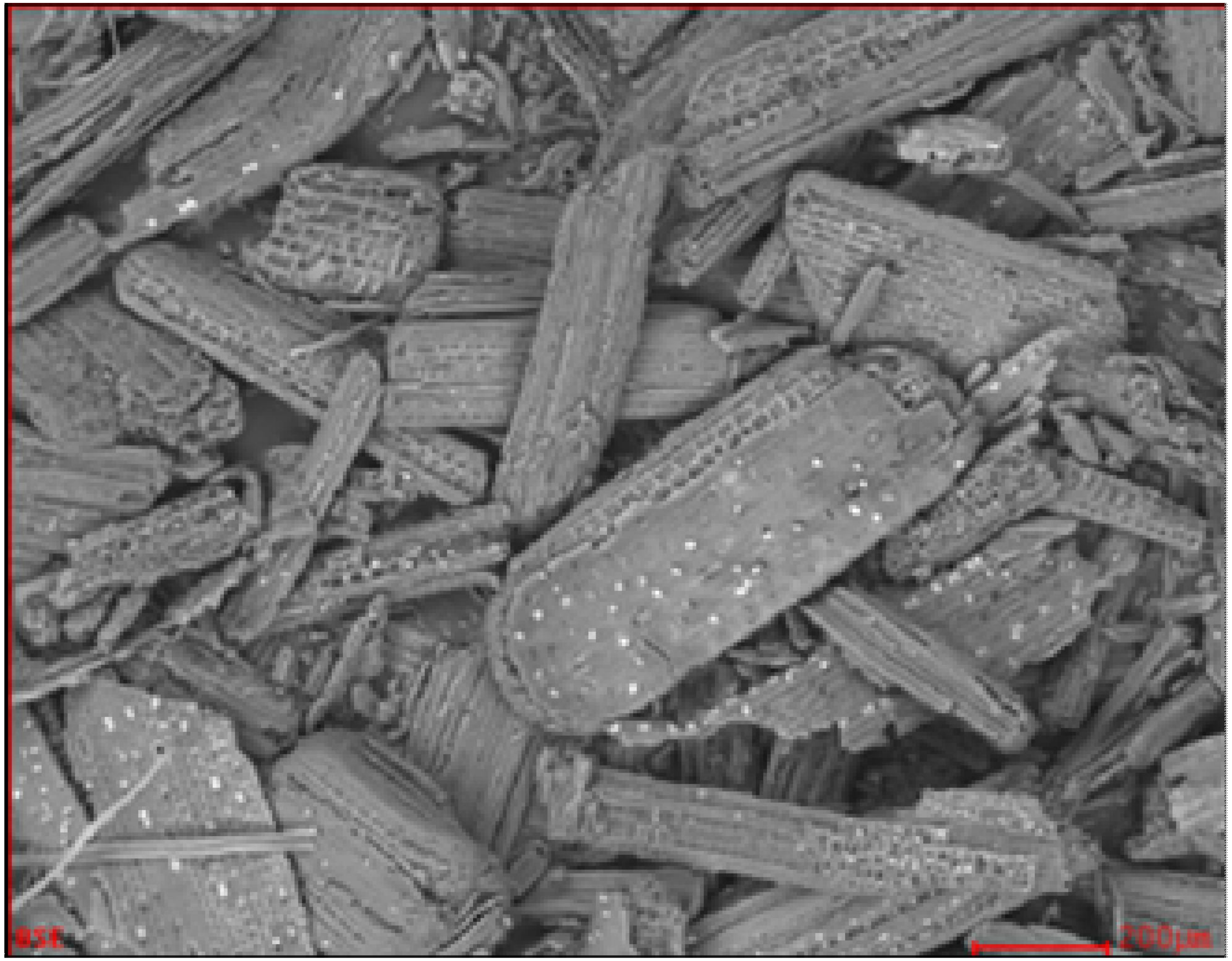
Classification

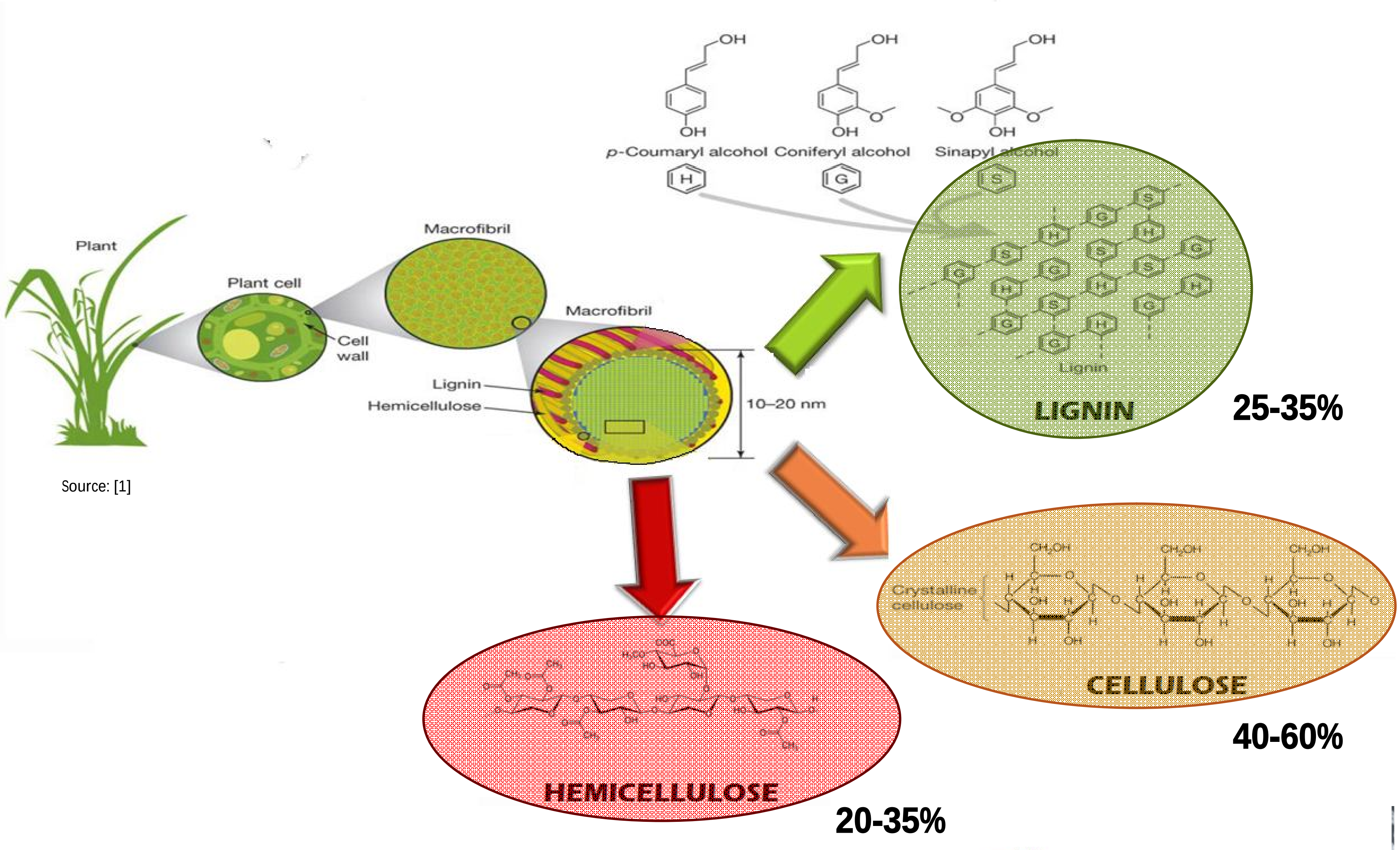


- The Coal industry is comfortable with utilising maceral analysis to predict combustion performance



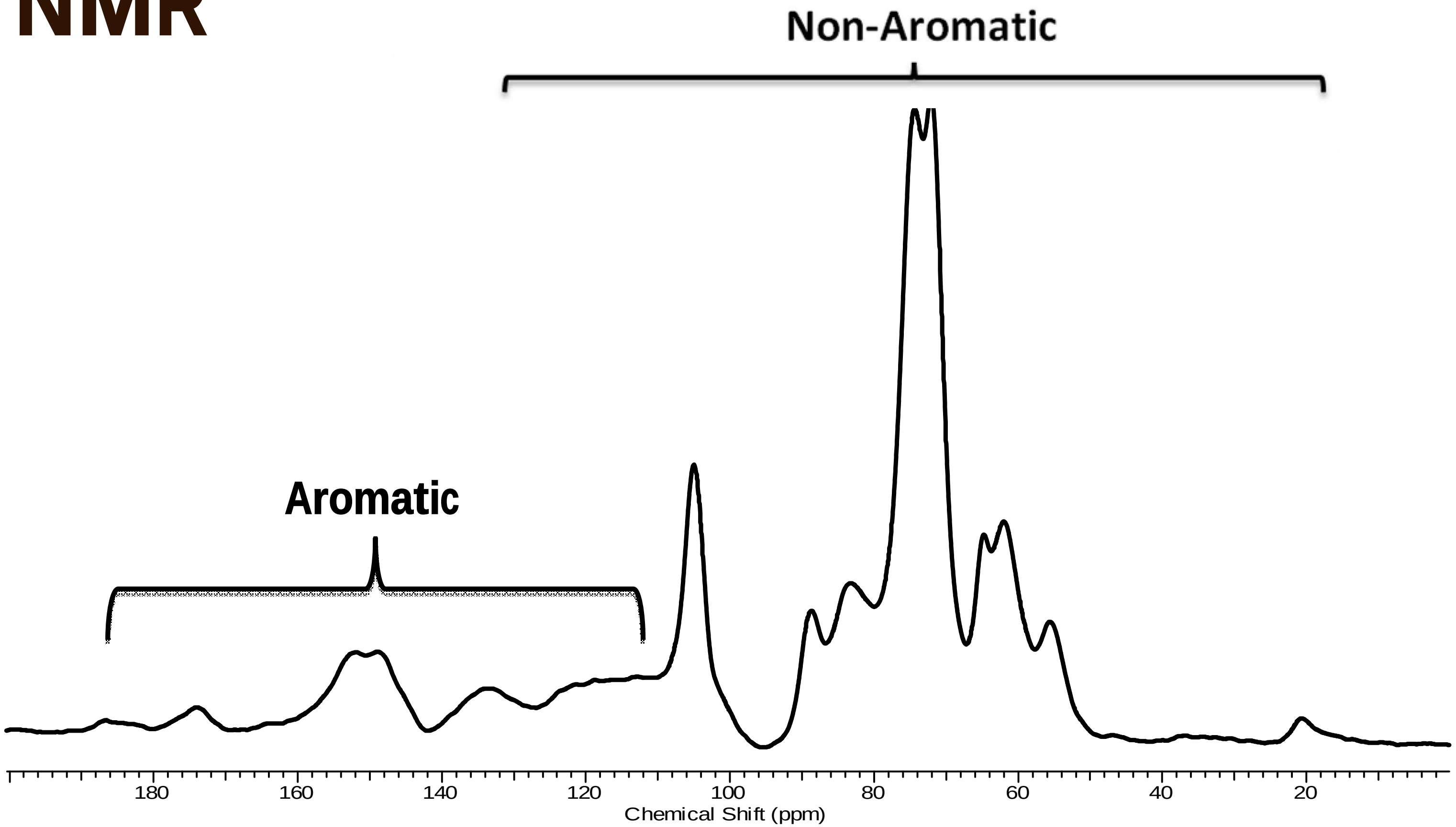
- No such system exist for biomass

Biomass Composition



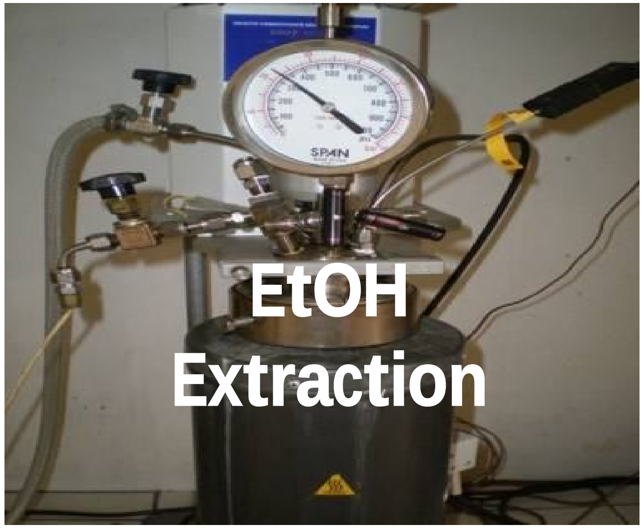
Source: [1]

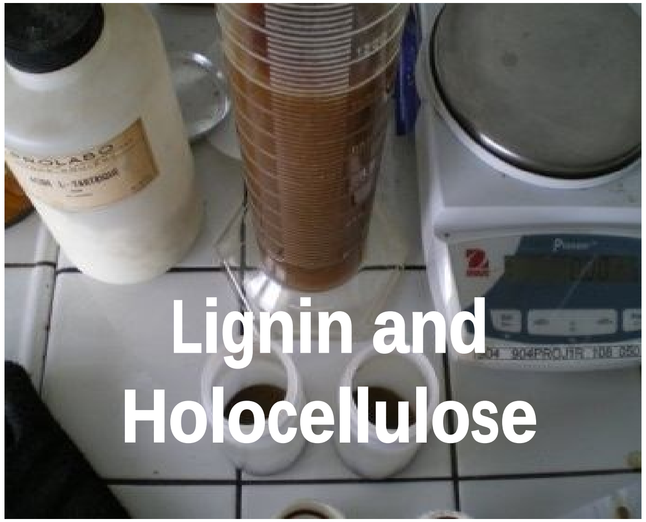
^{13}C NMR



- ^{13}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





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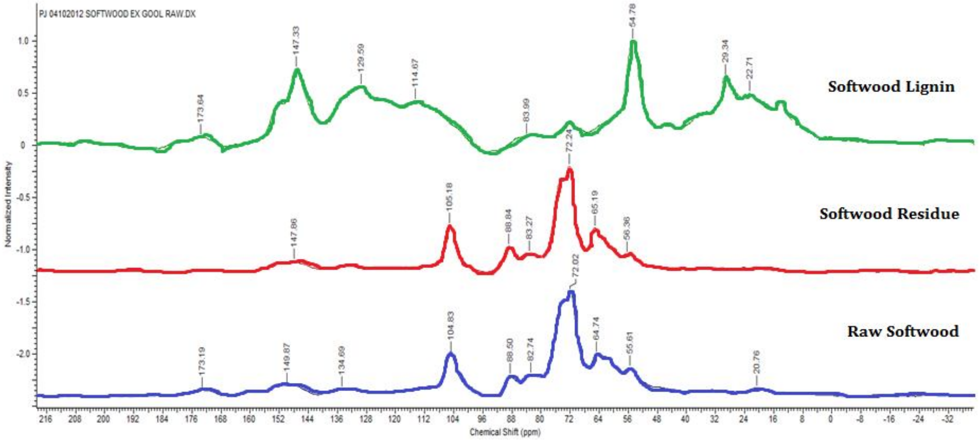
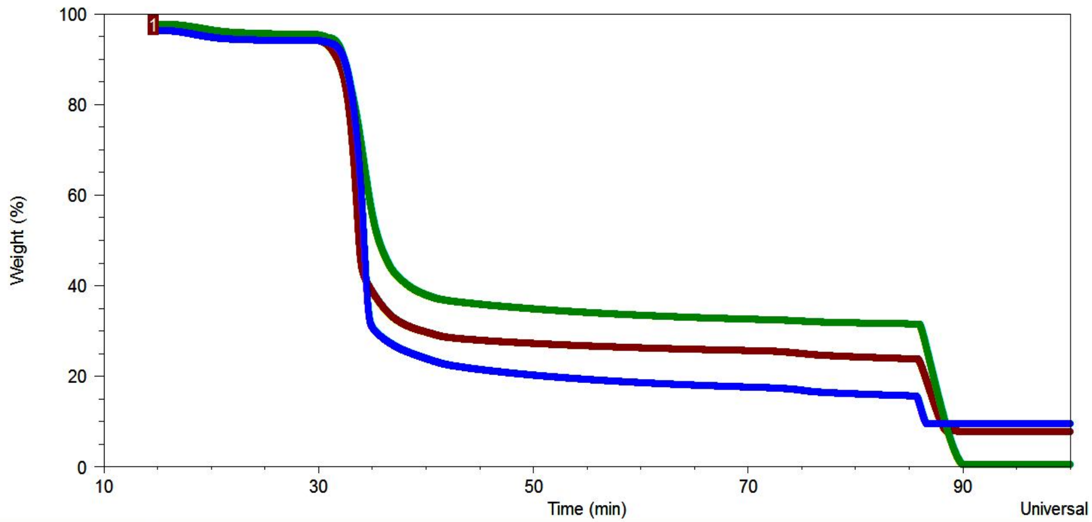
Characterisation



- 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



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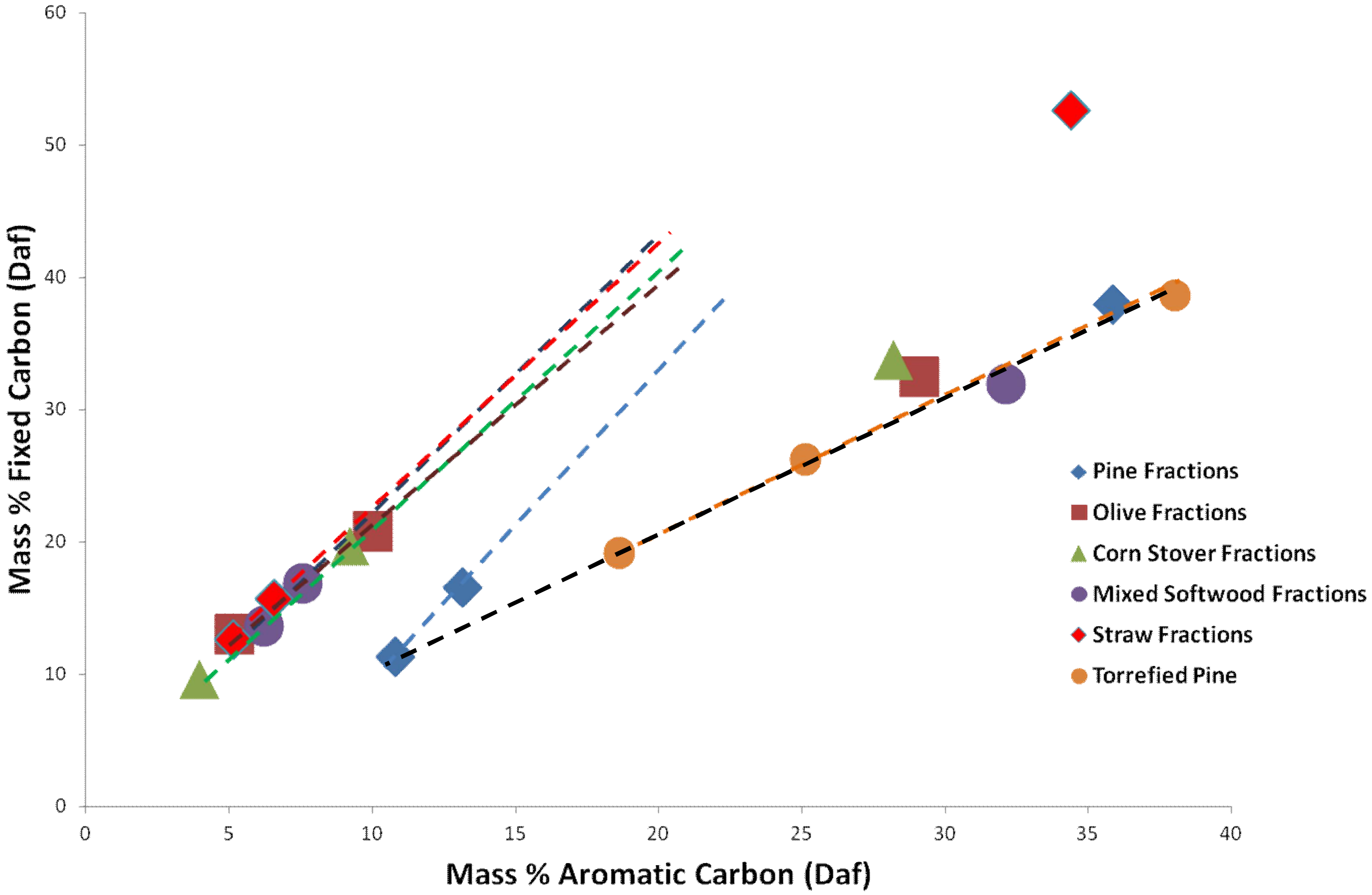
Aromatic Carbon and Char Yield



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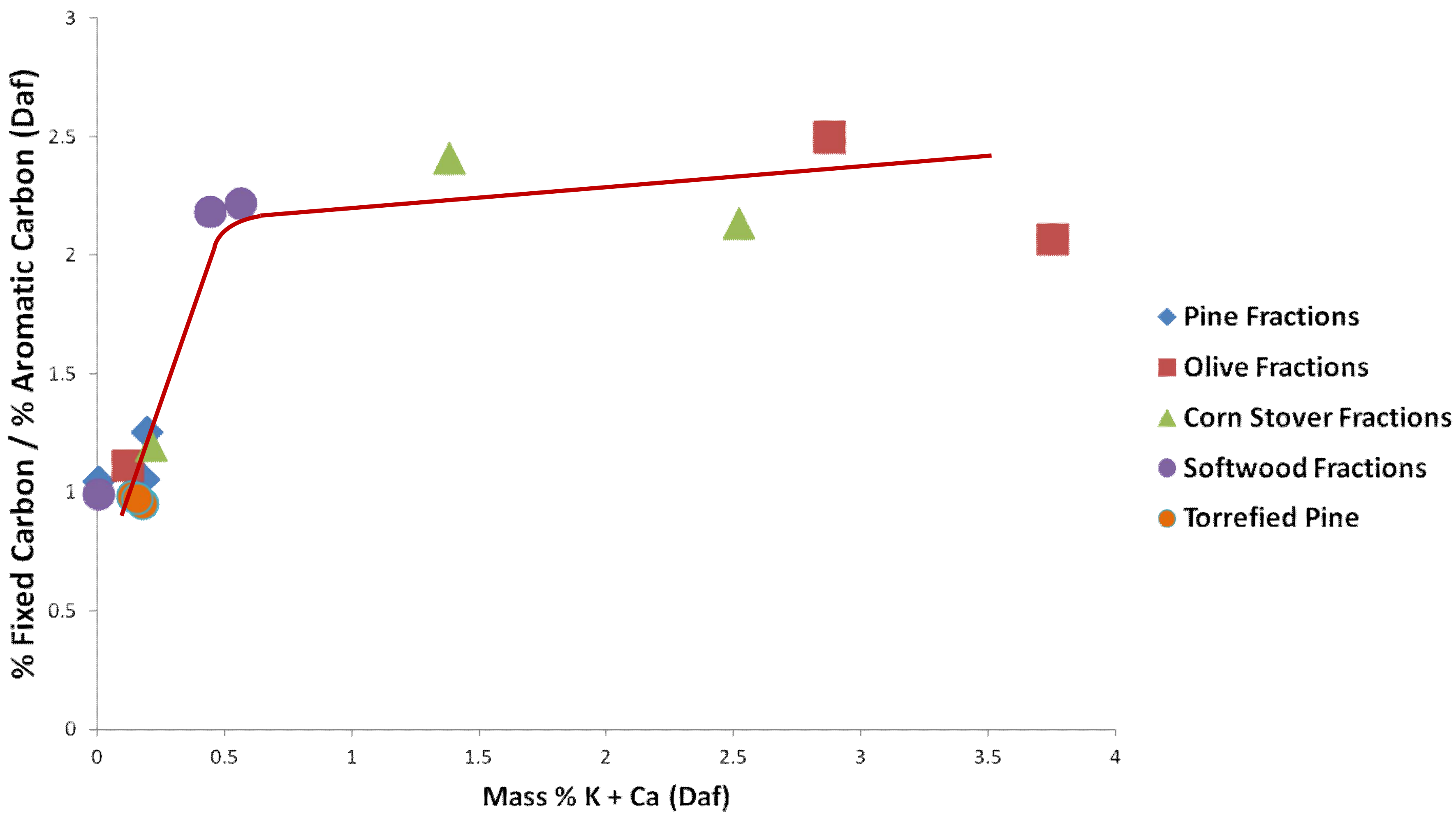
Influence of Inorganic Minerals (K+Ca)



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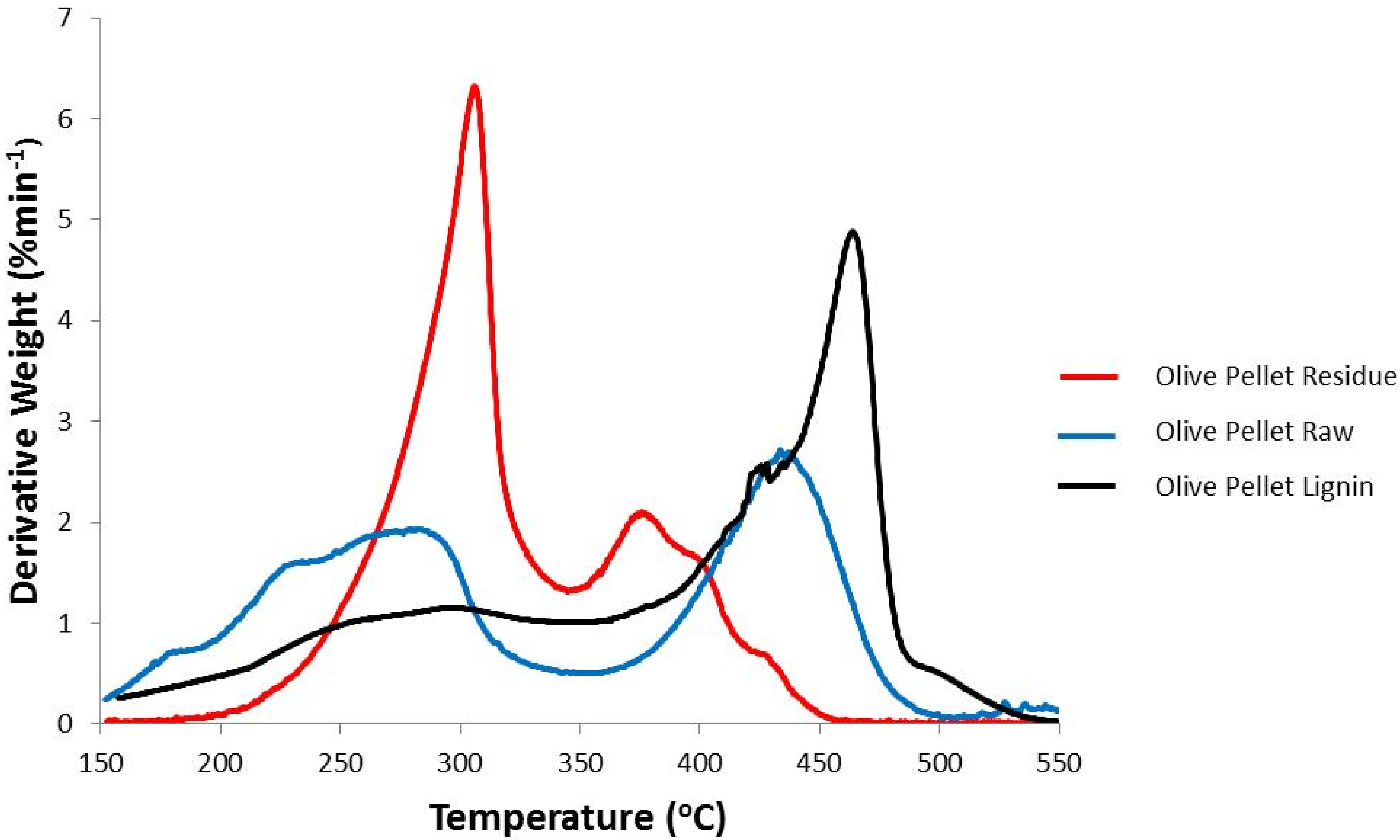
Non-Isothermal Combustion



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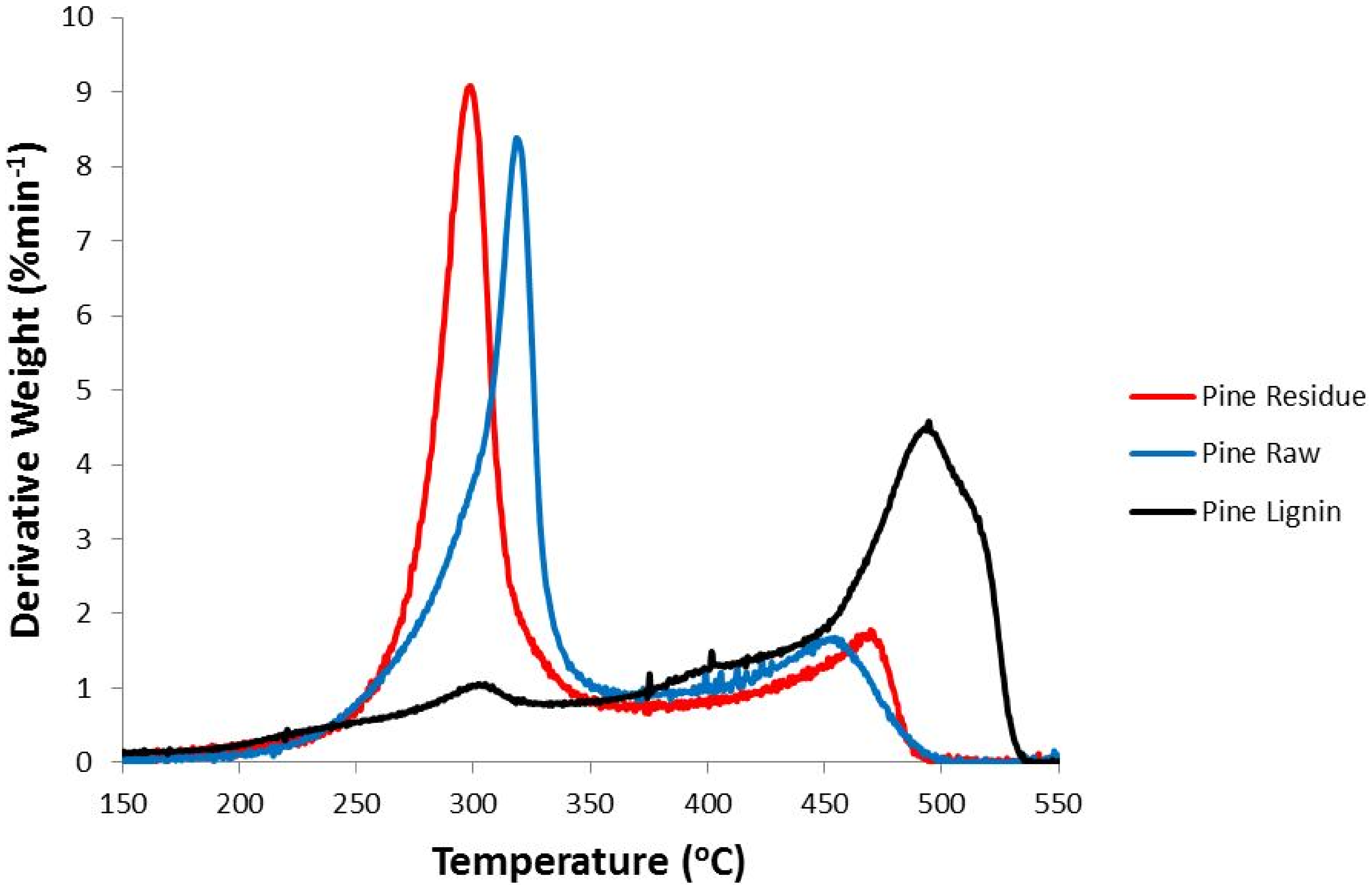

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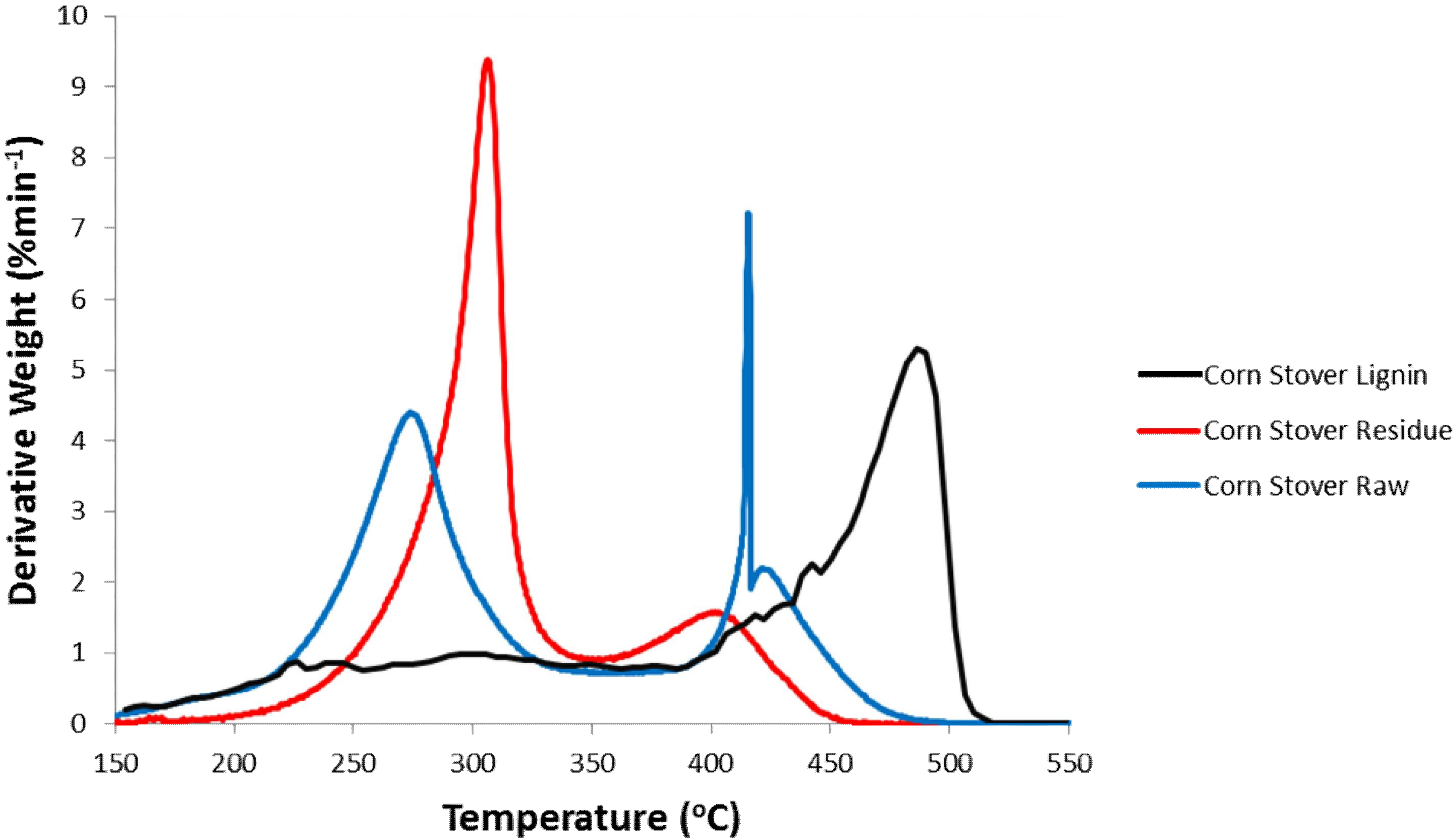
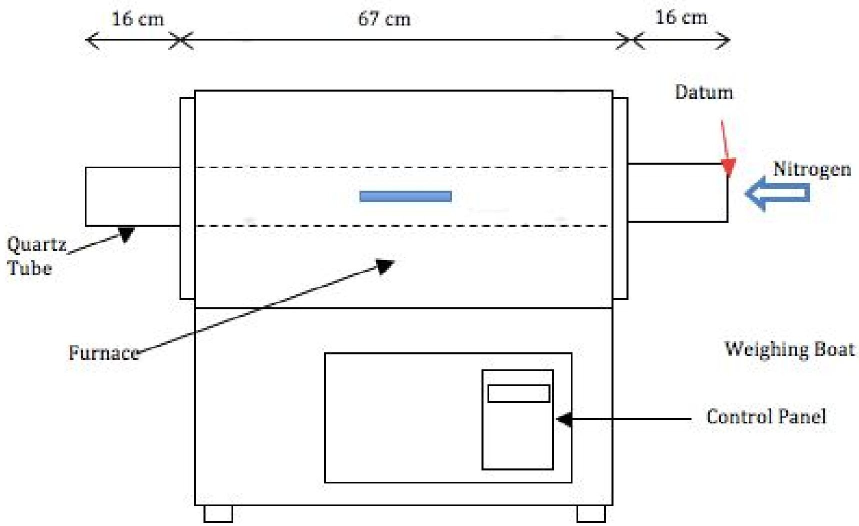


Derivative Weight (%min-1)
10
9
8
7
6
5
4
3
2
1
0
150
200
250
300
350
400
450
500
550
Temperature (°C)
Corn Stover Lignin
Corn Stover Residue
Corn Stover Raw

Slow Heating Char Preparation

- 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 $^{o}Cmin^{-1}$) 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^{o}C)

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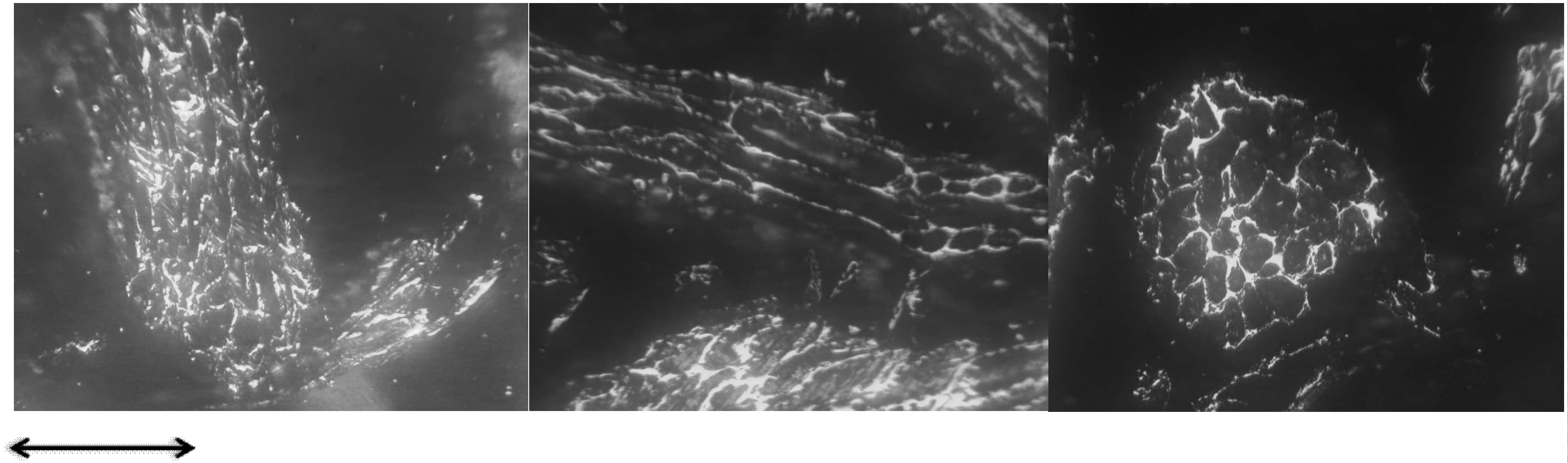
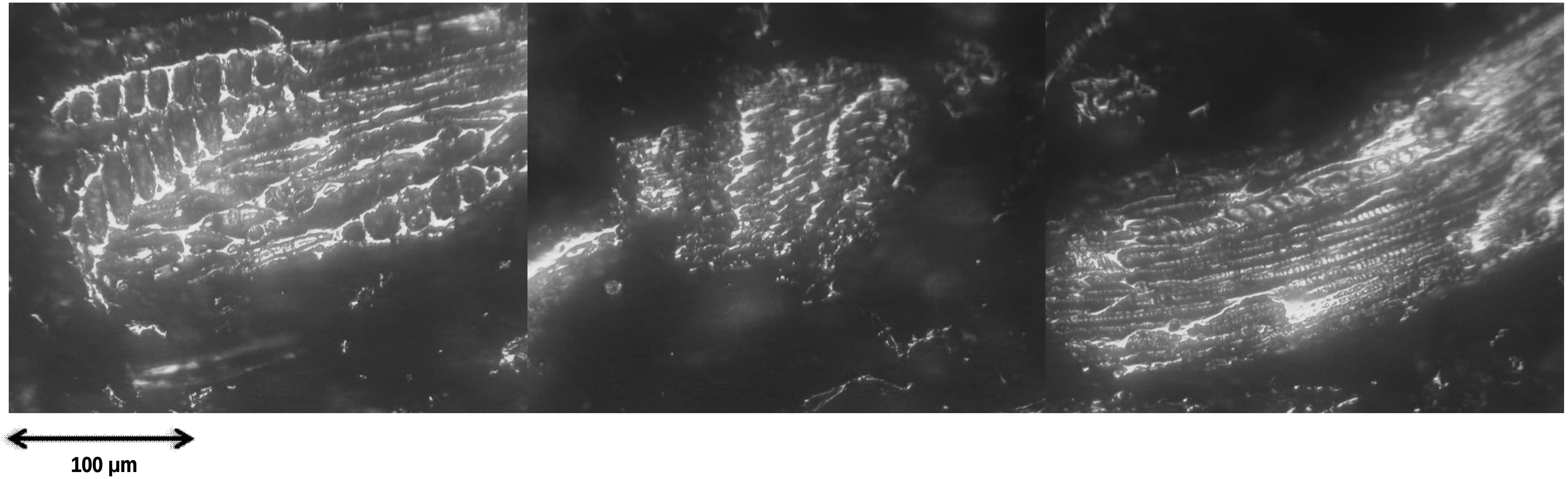
Pine Char Morphology: Raw



- 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 m^2/g (< 63 µm) and 376.40 m^2/g (125 – 250 µm)

Pine Char Morphology: Holocellulose



- 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)

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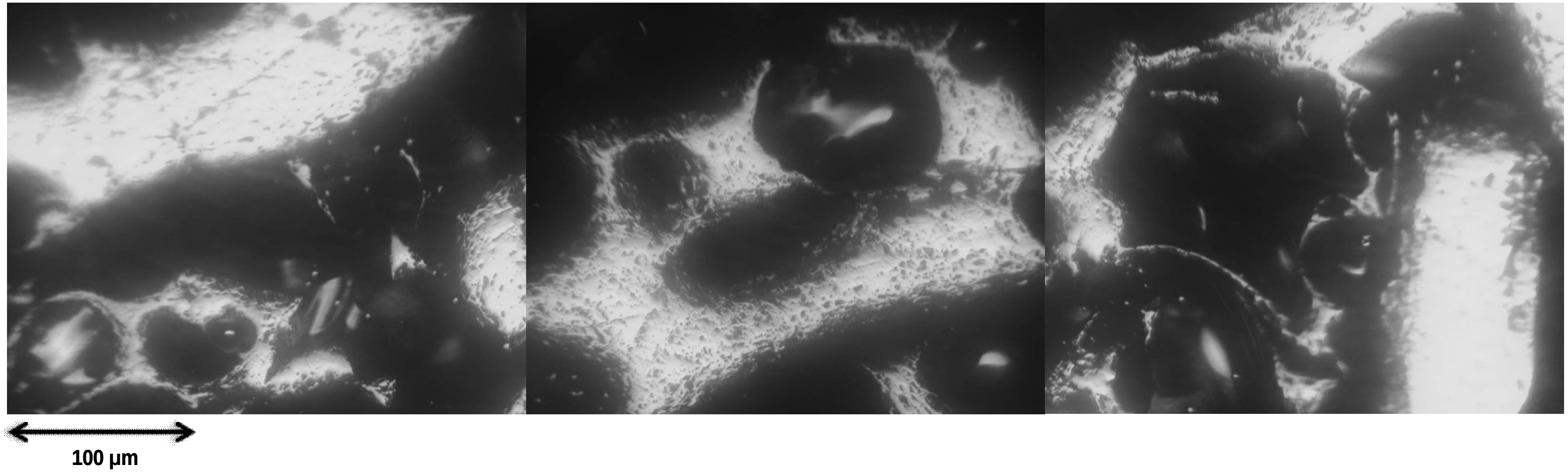
Pine Char Morphology: Lignin



- 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 m^2/g (< 63 µm) and 0.0121 m^2/g (125 – 250 µm) are thus likely to undergo slow char burnout

Slow Heating Char Burnout Reactivity

Sample	Ea (kJmol^{-1})	A (min^{-1})	1st Order Rate Constant at 400^{o}C (min^{-1})	90% Char Burnout Time at 400^{o}C (min)
Pine Raw Char	134.504	$4.09x10^{9}$	0.149	80.26
Pine Residue Char	143.079	$5.27x10^{9}$	0.044	271.2
Pine Lignin Char	163.105	$2.66x10^{10}$	0.017	557.72
Raw Olive Char	145.076	$3.05x10^{10}$	0.131	84.06
Olive Residue Char	85.352	$1.08x10^{6}$	0.263	42.05
Olive Lignin Char	103.978	$8.13x10^{7}$	0.051	246.89
Olive – Extractives Char	72.31	$1.02x10^{5}$	0.26	35.43
Raw Corn Stover Char	77.148	$3.12x10^{5}$	0.213	29.95
Corn Stover Residue Char	44.644	$1.37x10^{4}$	0.624	19.11
Corn Stover Lignin Char	109.268	$7.36x10^{7}$	0.238	51.72

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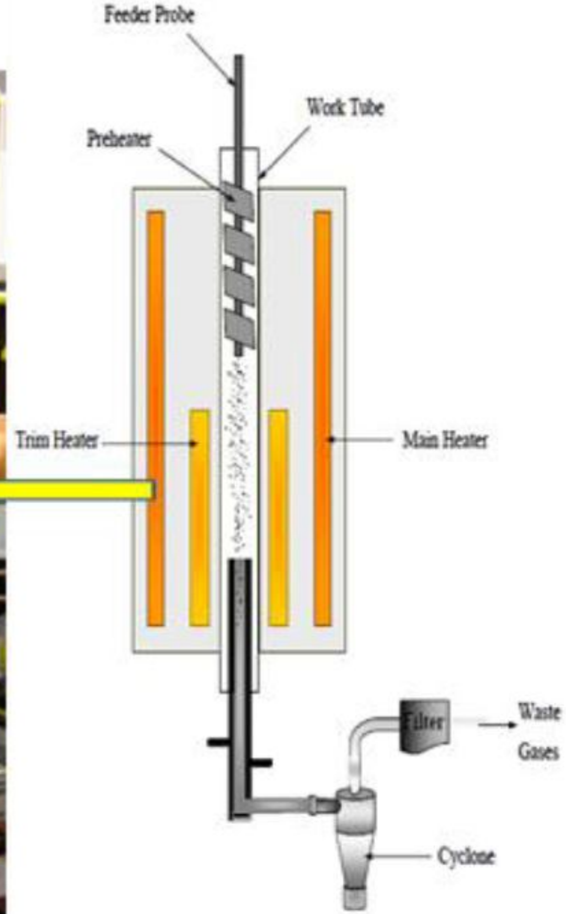
Drop Tube Furnace PF Simulation



Drop Tube Furnace (DTF) testing employed to generate char samples under simulated pulverised fuel combustion conditions with rapid heating rates (~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

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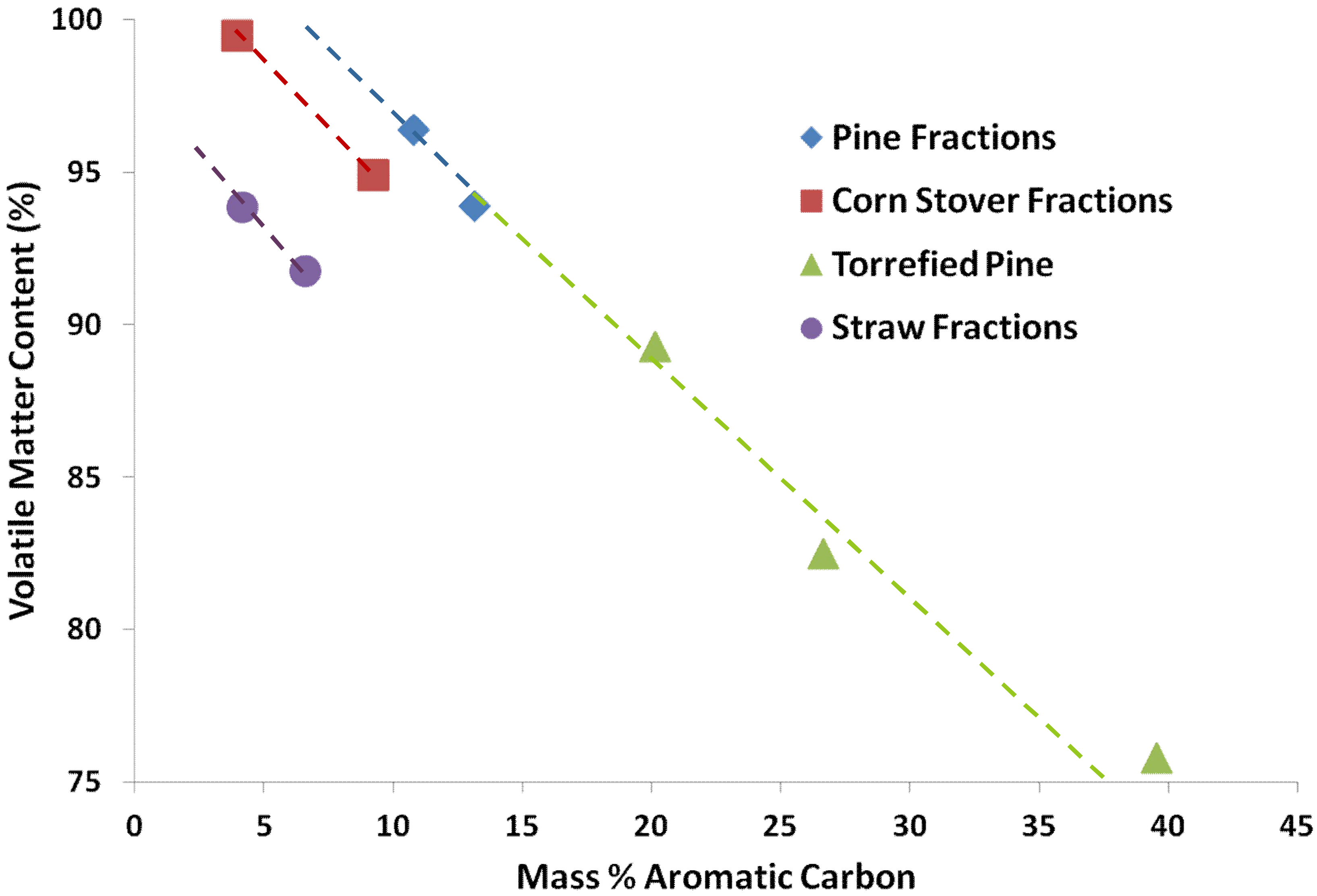
Simulated PF Volatile Yields



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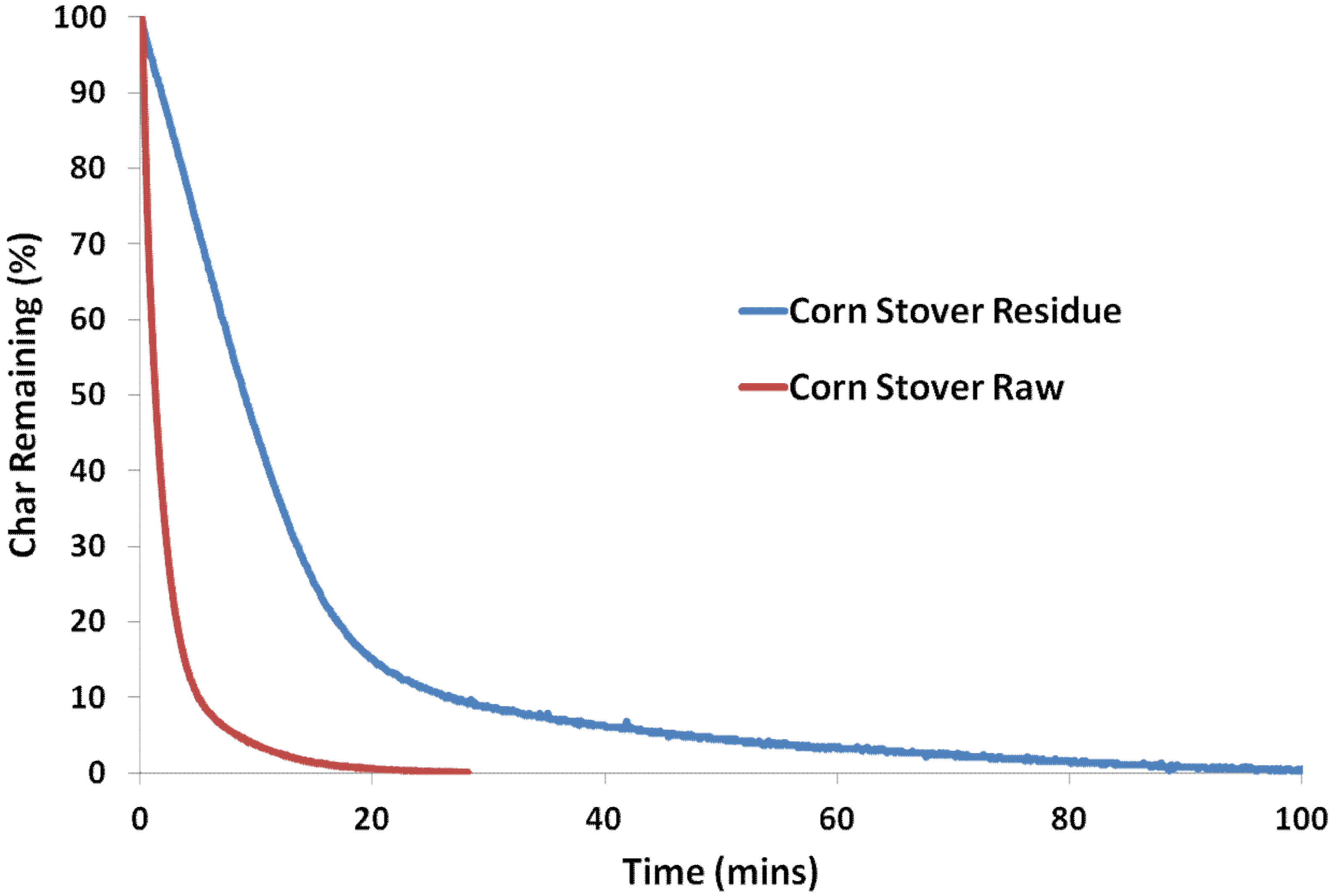
Burnout Profiles



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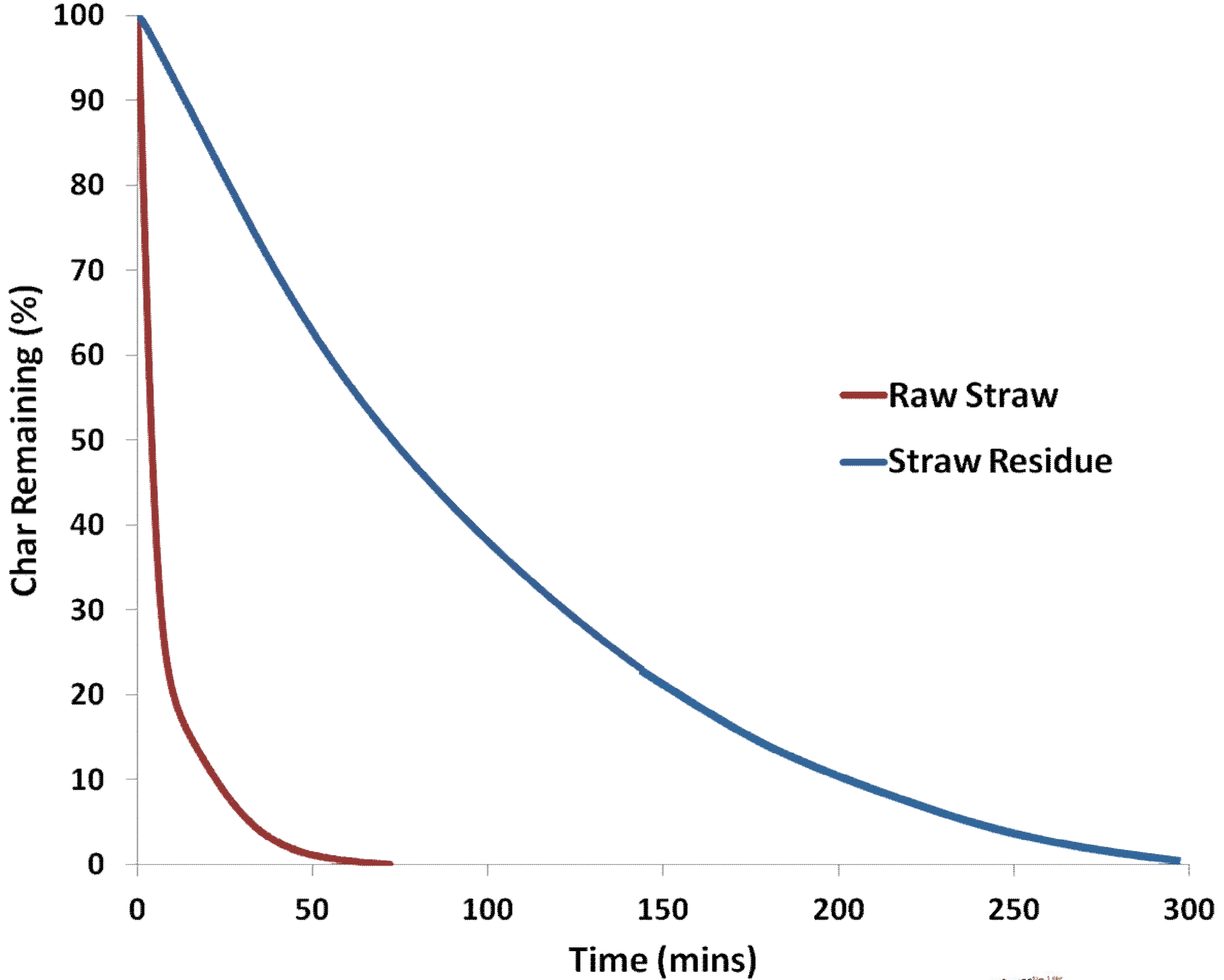

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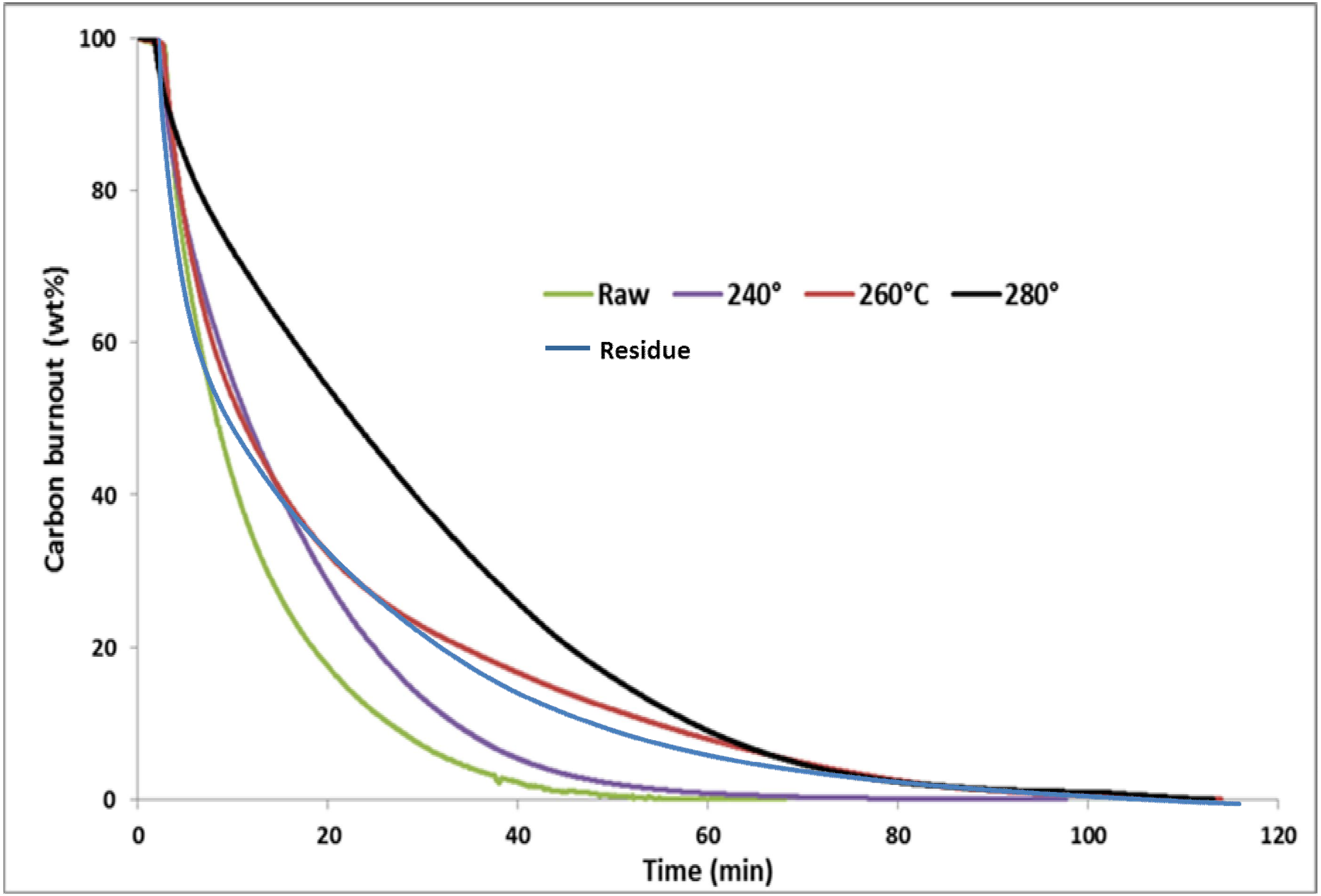
Raw
240°
260°C
280°
Residue
Carbon burnout (wt%)
Time (min)
0
20
40
60
80
100
120

Simulated PF Char Combustion

Sample	Ea ($kJmol^{-1}$)	A (min^{-1})	1st Order Rate Constant at 450ºc (min^{-1})	90% Burnout Time at 450ºC (min)
Raw Pine	82	3.7×10^5	0.056	28.4
Pine Residue	90.12	4.7×10^5	0.034	54.8
Torrefied Pine 240oC	93	1.8×10^6	0.044	34.7
Torrefied Pine 260oC	99	3.7×10^6	0.027	56.3
Torrefied Pine 280oC	107	1.3×10^7	0.015	61.1
Raw Corn Stover	87.43	3.85×10^6	0.364	4.9
Corn Stover Residue	82.26	2.9×10^5	0.068	26.1
Raw Straw	143.46	8.85×10^9	0.080	22.5
Straw Residue	157.34	2.00×10^{10}	0.021	179.75

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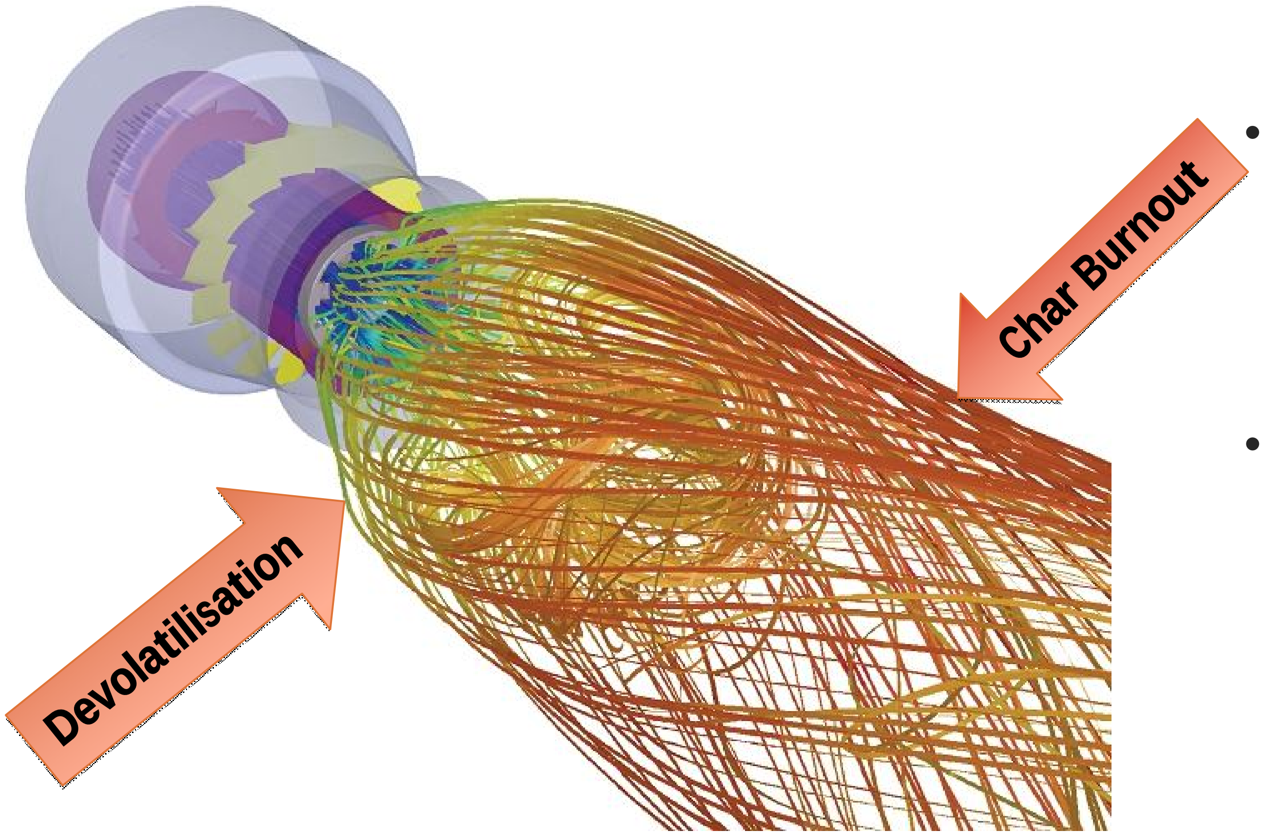
Implications



- 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 my 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