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Development of a carbon neutral process for producing renewable charcoal

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Scott Russell
Supervisors: Prof Colin Snape Dr Paul Langston

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Abstract

This thesis investigates the process conditions, charcoal composition and biomass sources for process development of BBQ charcoal briquette production. This aim has been achieved by three areas of investigation:

1. Experimental pyrolysis at lab and pilot scale, with the aim of determining optimal process conditions and if addition of low cost catalyst material is beneficial to slow pyrolysis.
2. BBQ charcoal combustion and modelling of the fire temperature history to determine the pyrolysis conditions and allowable concentrations of non-charcoal additive important to the final charcoal briquette.
3. Techno-economic and carbon analysis (TEA) of the various options for by-product utilisations and determination of important process conditions.

The novel findings from the experimental and modelling studies add to the literature on catalytic slow pyrolysis and lump char combustion, whilst applying these concepts to present optimal process flows and conditions for BBQ charcoal production.

1. The addition of low cost acidic and basic catalyst such as bentonite clay or dolomite to the slow pyrolysis of biomass can significantly increase the charcoal yield, and significantly improve the process economics. This also improves the quality of by-product liquid, high in low molecular weight phenolic compounds.
2. Lump charcoal combustion in a grate burner can be simulated by applying the analogy of a two first order chemical reactions in series model to the temperature profile of a simple combustion experiment. The model only requires proximate analysis of the charcoal briquette, and is valid up to briquette mixtures containing 30% inert or raw biomass additive.
3. Temperatures, around 450°C, are required. Lower temperature increases charcoal yield and therefore process economics and this is not too low to produce poor quality charcoal.
4. Processes either A) utilising the gas and liquid by-products in a combined heat and power engine or B) recovering the chemical stream as phenolic oils and using the gas stream to produce heat are the most economic and carbon efficient outcomes.
5. Addition of clay minerals are key to the economic success of both processes by increasing charcoal yield and producing better quality oil high in low molecular weight phenolic compounds.

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Publications and Presentations

Publications

Russell, S. H., Turrion-Gomez, J. L., Meredith, W., Langston, P., & Snape, C. E. (2017a). Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis, 124, 536-541.

Future Publications

- Journal publication of 'Development of a Model to Predict the Grate Burning Profile of Biomass Derived Char' study. Submission to Fuel Processing Technologies is pending as of writing.
- Publication focusing on comparison of type y zeolite and dolomite to the clay mineral study (published in Russell 2017). Target journal JAAP
- A techno-economic study on process selection and variables of interest in process development could be developed but this may run into IP issues with CPL and require large re-framing for external publication.
- **Conference Attendance and Publications**
- Poster presentation of 'Increased charcoal yield and production of lighter oils from the slow pyrolysis of biomass' at Pyro2016, Nancy France
- Oral presentation of 'Development of a Model to Predict the Grate Burning Profile of Biomass Derived Char' at European Biomass Conference and Exhibition 2017, Stockholm, Sweden.
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Glossary of Abbreviations

BBQ	Barbeque Grill
BM	Biomass
C	Concentration
CAPEX	Capital Expenditure
CFD	Computational Fluid Dynamics
CHP	Combined Heat and Power Boiler
CPL	Coal Products Limited
DAF	Dry Ash Free Basis
GC-FID/TCD	Gas Chromatography with Flame Ionisation Detector/Thermal Conductivity Detector
GC-MS	Gas Chromatography with Mass Spectrometry
LCA	Life Cycle Assessment
M	Mass
MC	Moisture Content
MCDA	Multi-Component Decision Analysis
NPV	Net Present Value
OPEX	Operational Expenditure
PAH	Poly cyclic Aromatic Hydrocarbon
T	Temperature
TEA	Techno-economic analysis
TGA	Thermogravimetric Analysis
VOC	Volatile Organic Compounds
wt%	Weight percent
Y	Yield
	Subscripts
A	Ash Content
add	Additive Addition to Briquette - Refers to Sand or Clay
al-C	Aliphatic Carbon Content
ar-C	Aromatic Carbon Content
Briq	Refers to content of briquette
Cat	Specific Additive which acts as a catalyst
fc	Fixed Carbon
M	Moisture Content
peak	peak temperature
pyro	Pyrolysis condition
vm	Volatile Matter
vol	Volatile Content
wet	Wet basis
	Biomass Types
EU	Eucalyptus Wood
HW	Hardwood
MS	Miscanthus
OC	Olive Cake
PW	Pinewood
ST	Straw

Glossary of Terms

Briquette	A small block of compressed peat, coal or charcoal. Comes in a variety of generally proprietary shapes for fuel use
Carbon Balance	Generally part of a life cycle analysis, but focuses on only the carbon emissions caused by a product or process
Life Cycle Analysis	Analysis aimed at modelling the environmental impact of a product or process
Multi-Component Decision Analysis	A weighted decision making tool which allows decision making between a wide number of options
Net Present Value	The value in todays money of investing in a process over its life time, weighing the **CAPEX (Capital Expenditure)** and **OPEX (Operational Expenditure)** against **Revenue (Income from sales of products or services)** from a project considering a required interest rate which must be met
Pyrolysis	Thermal decomposition brought on by high temperatures in an oxygen free environment. In this work, three types of pyrolysis are important: **Slow Pyrolysis:** Where the system is slowly heated with slow heating rates (<100°C/min) using large particles aimed at producing solid (charcoal) as a product **Fast Pyrolysis:** Where the system is slowly heated with fast heating rates (>1000°C/min) generally using small particles aimed at producing high yields of liquid and gas products **Catalytic Pyrolysis:** Where additives (generally zeolites) are added to the system to encourage produce of the desired product. Generally used in fast pyrolysis systems to produce higher quality liquid or gas streams
Techno-Economic Analysis	Analysis of a process encompassing a unit operation model of the process including equipment sizing, followed by costing. This is generally used to develop new technology or processes in a cost effective way

Chapter 1. Project introduction

1.1 Project background and aims

This project has been undertaken as a collaboration between CPL Industries (http://www.cplindustries.co.uk/cpl/) and the University of Nottingham.

CPL is one of the largest suppliers of coal and charcoal products to UK markets. Their home heating fuels division is the largest supplier of smokeless fuels by volume with various coal and coal/biomass products available. Most of coal based products are produced at CPL's briquetting works on the Immingham Docks, while in comparison most of their BBQ charcoal products are sourced from outside the EU.



Figure 1-1. Immingham briquetting process covered in snow January 2015

This project has been commissioned to develop charcoal production systems which utilise EU and UK fuel sources with the aim of reducing the CO_2 emissions (Johnson, 2009).

The push for this project then comes from two fronts:

- There is thought to be a high volume of biomass produced inside the EU which goes to waste and could be used for this purpose
- These CO_2 emissions lost from the processes represent a large proportion of the biomass introduced to the system, which could be better used either via by-product production or via system optimisation to encourage higher recovery as charcoal.

While this project aims to produce a system for BBQ charcoal, it is hoped that the implications could be applied to charcoal for heating fuel systems in the future as coal prices may be subject to increase due to increasing carbon floor prices which currently are set at £18/ton and may be required to be pushed higher (Ares *et al.*,

2016; DECC, 2013) to have an economic effect on fossil fuel use leading to a future where biomass products are similarly priced to coal.

These aims coincide with a global push to encourage low carbon technologies, with COP21 and 22 in 2015 and 2016 where the majority of the world's carbon polluters agreed to limit CO_2 production which would cause more than 1.5 °C global warming, with the aim of preventing irreversible climate change (Figure 1-2). While some global political movements may be aiming to turn away from these agreements, the uptake of renewable energy technologies has caused them to reach a maturity were they are cheaper and employ more people than coal based technologies (Casselman, 2017).

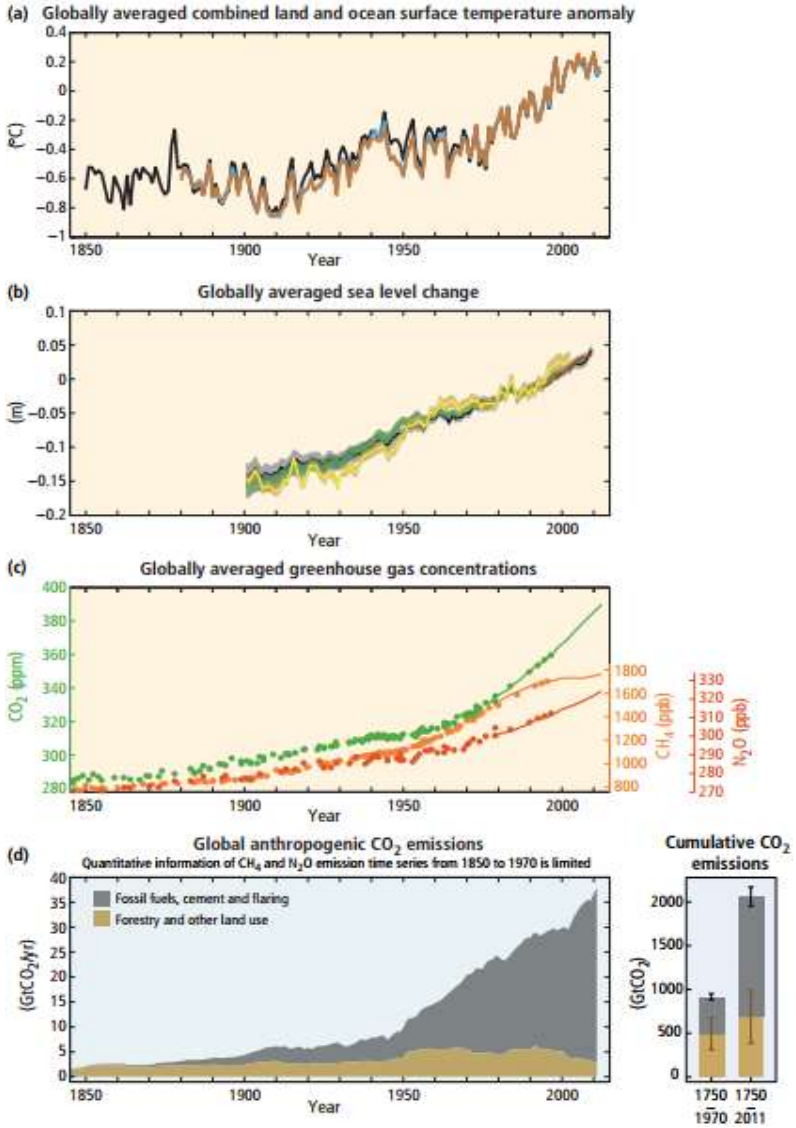


Figure 1-2. IPCC plots highlighting links between CO_2 emissions, temperature increase and the outcome of sea level rise (IPCC, 2014)

This research aims to provide concepts which can be applied to give CPL methods to decarbonise their products. These are:

- Carbonisation system process flows which lead to the most efficient uses of biomass in charcoal production processes.
- Simple tools to allow selection of biomass types which can be used in these systems, and methods of assessing their performance against existing products.

This chapter will now discuss the properties of BBQ and how it is made. Finally, the project scope undertaken to develop these ideas and outline of the thesis will be presented.

1.2 BBQ charcoal

Charcoal is used for many purposes: replacement of coke in steel production; art; and in many locations around the world as a common method for cooking food (Antal *et al.*, 2003) and shown in Figure 1-3.



Figure 1-3. Picture of burning BBQ charcoal

This project is developing charcoal with the purpose of cooking using barbeques, so this section will introduce the properties expected charcoal for this purpose.

Woody biomass and agricultural residues are converted to charcoal to increase the energy density and reduce the smoke produced from basic wood usage (Harris, 1999). Bhattacharya *et al.* (2002) show that there is an energy density increase from 19.5 MJ/kg to 28 MJ/kg when wood is carbonised, which brings the energy content of charcoal closer to that of coal, which is 24-35 MJ/kg depending on coal type.

This transformation is achieved by the pyrolysis process, which heats biomass under oxygen free conditions. This causes volatile fractions in the structure to be released and leaving a black carbon residue which is retained as the charcoal, as outlined in Figure 1-4.

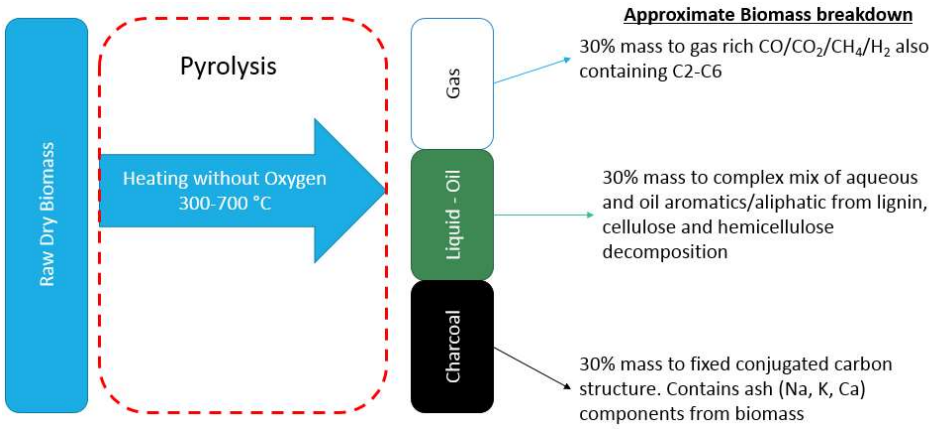


Figure 1-4. Outline of pyrolysis products. Constructed from various sources but Antal et al. (2003) provide a good review.

The conditions involved in pyrolysis will be discussed in more detail in section 2.4.1. The effect of this is that charcoal burns for longer and offers a more consistent product over fuel wood (Mwampamba *et al.*, 2013).

Personal communication with CPL has provided information regarding the UK charcoal market. It is estimated that the market for charcoal briquettes totals 30,000 ton/year, and they have aspirations for producing charcoal for a large proportion of this and therefore have requested that this study uses 20,000 ton/year as an expected scale for comparing charcoal production processes.

1.3 Project scope

To accomplish these aims, this project looked to three distinct areas:

- Experimental slow pyrolysis of various biomass sources, including catalytic pyrolysis, with the aim of observing charcoal yield. Properties of liquid and gas products will also be considered. Methods of modelling pyrolysis yields will be investigated.
- Experimental combustion of charcoal briquettes in a simulated grill for the determination of charcoal properties suitable for BBQ use. Again, methods of simulating these results will also be investigated.
- Techno-economic modelling of the charcoal process, to establish important process flows and variables for the production of charcoal. Optimal flow schemes and logistical requirements will be discussed.

1.4 Novel aspects of this project

There are several novel points to this project, with the main points centring on the areas of experimental pyrolysis and process development:

- Further development of work by Jenkinson (2016) to produce a simple method of determining the product yield from pure biomass pyrolysis.
- Work on assessing the usefulness of additives in slow pyrolysis. Particular focus has been placed on solid acid catalysts, with the presentation of the results on clay minerals at Pyro2016 and publication Russell *et al.* (2017a).
- Development of a method of assessing the charcoal combustion potential with the presentation at EUBCE 2017 and publication in the conference proceedings (Russell *et al.*, 2017b) and a paper submitted to Fuel processing technology.
- Outline of relevant ideas to consider when choosing process flows for a charcoal production process.
- Outline the process and economic effects of adding different additives to the charcoal production process, including clay as a tar reducing catalyst.
- Discussion of logistics effects on the economics of charcoal production, with the effect of various biomass types and locations of production discussed.

1.5 Thesis overview

This thesis will present the above concepts in 6 chapters, highlighting work previously done and gaps in pyrolysis and BBQ modelling literature to allow the process modelling work to be carried out.

1.5.1 Literature review

There are five main concepts to be taken from previous work around this project:

- The requirements of the UK BBQ charcoal market, including expected charcoal quality, cost, and consumer preferences on materials used.
- Slow pyrolysis of Biomass, specifically the effect of temperature on yields and charcoal quality.
- Catalytic slow pyrolysis using low cost materials.
- Methods of modelling charcoal fires.
- Process economic models used in other academic studies.

These ideas were used to frame the experimental and modelling work for this project to better achieve a more accurate process model, with experimental backing.

1.5.2 Slow pyrolysis of biomass and yield modelling

Chapter 2 aims to present the experimental work competed to determine the effect of temperature on charcoal, liquid and gas yields from various biomass sources. These results have then been compared to pilot plant work completed at CPL, which

proved a favourable comparison. The effect of biomass moisture content was also determined.

The results were then compared to previous work (namely Jenkinson (2016)) and synthesized into a simple algorithm to allow the estimation of yield breakdown (charcoal, gas and liquid) and quality of charcoal.

1.5.3 Catalytic slow pyrolysis of biomass

There are two main sections to chapter 3:

- A screen experiment comparing the effects of various additive types on the pyrolysis of biomass, which backed up the vast amount of literature present that solid acid catalyst are the most efficient additives for increasing charcoal
- Detailed characterisation of the clay mineral bentonite/montmorillonite. This was published as a paper presented at Pyro2016 and published this in the Journal of Analytical and Applied Pyrolysis.

Further equations are also presented to highlight the mechanism by which the clay catalytic pyrolysis may occur.

1.5.4 BBQ charcoal combustion modelling

Chapter 4 present the work done to produce and characterise pilot scale batches of charcoal. Charcoal combustion profiles are compared against commercially available BBQ charcoal. The effects of adding sand, raw clay, clay which has been through pyrolysis, and raw biomass have been assessed.

These results have been synthesised to generate a model to determine the expected combustion profile from charcoal briquettes, which has been presented at the 25th European Biomass Conference and Exhibition and has been submitted to Fuel.

The effect of combining the pyrolysis model with this BBQ model has also been assessed.

1.5.5 Development of a TEA model for BBQ charcoal production

Chapter 5 presents the work done in determining relevant process flows in charcoal production systems. This chapter initially assesses 18 potential process flows and discusses how these were narrowed down to two final concepts which have then been used for the final optimisations in chapter 6.

Methods to simulate the various unit operations and process integrations are outlined and discussed at the various stages.

1.5.6 Optimisation and key variables for charcoal production

Following selection of the optimal process flows, Chapter 6 presents a study which aims to determine the key variables on charcoal production. This includes study on:

- Biomass type and composition
- Effect of wet or dry biomass – drying cost vs. more expensive biomass cost
- Effect of temperature of pyrolysis
- Effect of changing briquette composition
- Study on the minimum scale of production, and finally
- Discussion of ideas surround location of production, including effect of multiple smaller plants, foreign charcoal production vs. biomass importing and maximum economic scale of production from various charcoal sources.

Chapter 2. Literature review

2.1 Scope of the literature review

There are five main areas which of literature which have been used to provide background to this project:

- Charcoal properties. This will cover requirements and considerations regarding charcoal quality
- A review of biomass supply in Europe which could be utilised by charcoal production process.
- Charcoal production. A review of variables and industrial equipment used for pyrolysis. This will include a review of catalytic pyrolysis and a brief overview of pyrolysis modelling methodology.
- Charcoal use. This will review charcoal combustion modelling methodology.
- Pyrolysis plant economics. A brief overview of other groups work into the modelling of pyrolysis plants will be added to establish methodology and process supply configurations which could be used for this work.

The review of these areas of literature provided three main outcomes:

- Present a list of relevant biomass types which are both economically relevant and available in quantities applicable for this study
- Aided experimental work by reducing the number of pyrolysis variables that needed to be studied; and aided in the selection of experimental methods for testing the combustion properties of BBQ charcoal
- Provided a framework for developing process modelling methods

2.2 BBQ charcoal quality

2.2.1 Consumers perspective & expectation

Consumers expect charcoal to come in either lump or briquette form, similar to the current product range of CPL, which can come impregnated with a fire starting compound or sold separately with lighter fluid (CPL, 2014). An internet search of a major online retailer and visits to high street retailers in May 2017 showed these have a selling price of between £1-5/kg. Information from CPL staff suggest that these costs are significantly inflated by mark up in the supply chain network and generally wholesale manufactured charcoal sells for £350/ton. Lump charcoal is made by pyrolysis of large pieces woody biomass, while briquettes are made by pyrolysis of particles of agricultural biomass which are then pressed and held

together by binders (EPA, 1976), a process which will be discussed in Section 2.4.6.3. Other agricultural by-products including grape residue and olive industry residue are also used industrially to make these charcoals.

Among home producers of charcoal, a preference exists for hardwood charcoal perhaps due to the slower heat release than softwood charcoal (Crossed Heart Forge, 2014; Levine, 2007; The Grilling Spot, 2014), which occurs due to the higher density of hardwood (US Forest Service, 1961), meaning a cleaner burning product exists. This project aims to look at a range of biomass types including agricultural residues such as straw which are not suitable for the lump wood process; therefore briquettes will be focused on. There are two main types of briquette in this market: roll pressed briquettes and extruded charcoal, as shown in Figure 2-1 and Figure 2-2. Due to greater availability of roll press briquettes in the BBQ industry (highlighted by availability in UK supermarkets), roll press briquettes will be the focus of this study.



Figure 2-1. Roll press briquettes (Agico Group, 2014)



Figure 2-2. Extruded briquettes (aFire, 2014)

2.2.2 Charcoal regulations

2.2.2.1 EU Regulations on charcoal

Standard EN 1860-2:2005 (Commission of European Communities, 2005) covers the regulations of barbeque charcoal and the testing methods for determining if this is met. This states that barbeque charcoal must be produced “from carbonisation of wood or vegetable matter” and the resulting charcoal cannot be “chemically treated or artificially prepared”. These can then be compressed into briquettes “with a suitable binder” and prepared for “lighting by addition of a lighting agent”. The relevant compositions for barbeque charcoal are presented in Table 2-1.

Table 2-1. Charcoal standards for grilling reproduced from Commission of European Communities, (2005)

	Lump wood Charcoal	Charcoal Briquettes
Fixed Carbon Content	>75%	>60%
Ash	<8%	<18%
Moisture	<8%	<8%
Granulation	[dia <80mm]<10% [dia <20mm]>80% [0-20mm]<7%	[dia <80mm] 0% [dia <20mm]<10%
Binder	-	No health effects, made of food grade compounds
Volatile Matter	No limits set – determined as part of fixed carbon	No limits set – determined as part of fixed carbon
Bulk Density	>130kg/m^3	-

However, this specification is only a guideline and does not need to be followed. From personal communication with CPL staff and testing on charcoal sourced from a major high street supermarket, it is clear that the ash limit is stretched where possible. This charcoal contained 28% ash, which opens the scope for some level of cheap inert material, such as sand, to be added to the mixture.

2.2.3 Food standards

On top of these regulations, there have been numerous studies which have shown that high levels of metals (Susaya *et al.*, 2010), and polycyclic aromatic hydrocarbons (PAH) and other volatile organic carbons (VOC) which can cause odour (Kabir *et al.*, 2010; Mahmudur Rahman *et al.*, 2012) can be emitted by the combustion of barbeque charcoal.

2.2.3.1 Metal concentration in charcoal

This literature search shows there are not any specific limitations on the metals concentrations allowed in charcoal for barbecuing, but will present the maximum levels for contaminants from European legislation and compounds shown to be in high levels from other studies.

European Standards (Commission of European Communities, 2006) set the maximum limit on some compounds and metals in food supplements in Table 2-2.

Table 2-2. Allowable concentrations of selected metals in food (Commission of European Communities, 2006)

Metal	Concentration (mg/kg)
Lead	3
Cadmium	3
Mercury	0.1

Susaya *et al.* (2010) studied the air contamination from charcoal combustion. They found that in some cases that Cd, Co, Ni, Pb and Mn exceed various US and World Health Organisation (WHO) standards for metals exposure, and more importantly that Cd emissions could be greater than some acute exposures standards, making this an important contaminant to consider. The average concentrations of these contaminants sited in this study are presented in Table 2-3. In the case of Cd, these concentrations are much lower than that outlined in the European Food Standards, and indicates levels of this in charcoal produced can be minimised.

Table 2-3 Concentration of air emitted contaminants (Susaya et al., 2010)

Metal	Concentration (mg/kg)
Pb	2.944
Co	0.0786
Cd	0.0594
Ni	0.0398
Mn	0.0268

To prevent these emissions, levels of metals in biomass to be converted to charcoal should be minimised where possible.

2.2.3.2 PAH emissions from charcoal

Some charcoal also release high concentrations of some odour compounds (Kabir *et al.*, 2010). Depending on the location of the charcoal produced, there are high concentrations of aldehydes, VOC and ammonia in particular which can lead to high odour intensity on the combustion. In Korea, ammonia emissions exceeded local air quality standards. The authors of that study concluded that this means that there should be warnings on charcoal packaging that it should be used in a ventilated

space, but this could also lead to foul tastes in food cooked with this charcoal, so quality control methods must be developed to ensure this product does not taint food.

These VOCs, namely benzene and toluene, produced can also have the toxic effects on humans as well as poor odour (Kabir *et al.*, 2010). Dioxin can also be formed if painted or treated wood is used in this process (Lavric *et al.*, 2004), affecting the amount of waste wood relevant for this process. Lavric et al (2004) recommends that carbonization processes should be done for longer on untreated or painted woods at higher temperatures to reduce the volatile component of the charcoal and to ensure that lighter fluids used should have low concentrations of VOCs.

It is expected however that these compounds come from:

- the addition of various compounds, including binders, from the charcoal production process;
- pyrolysis of waste materials including low grade waste wood, and;
- conducting pyrolysis at low temperatures to increase charcoal yield, leading to smoke effects.

These issues will be addressed in this study by focusing on clean agricultural residue, combustion testing of briquettes to ensure minimal smoke or odour is observed and determine pyrolysis temperatures which remove smoke producing volatiles.

2.3 Sources of biomass

The main sources of biomass of interest by CPL are biomass sources from the UK and Europe, as these have the potential to provide a stable supply chain. Therefore, this study will focus on outlining the properties and availability of:

- Forestry Residues;
- Agricultural Residues, and;
- Waste Wood

This project required 20-30,000 ton/year of charcoal to be produced, which assuming a yield of 25-30% by mass and the biomass contains an initial moisture content of 20% (Antal *et al.*, 2003) means that 30-50,000 ton/year of feedstock is required.

2.3.1 Forestry residues

Wood is generally presented as either soft or hard, which is a descriptor for the chemical structure of tree species. Typical compositions are in Table 2-4, though there is a wide range of different parts of the tree that can be used (Figure 2-4). Properties of fuels relevant to this study will be presented in Section 3.2.1.1.

Table 2-4 Generic properties of hard and softwood types

	Cellulose[a]	Hemicellulose[a]	Lignin[a]	Ash[b]	Moisture Content[b]
Hardwood	43-48	27-35	16-24	2.7	7.8
Softwood	40-44	24-29	26-33	1.7	8.8

a Dry ash free basis, average of source biomass types (wt%) (Demirbaş, 2009)

b Proximate analysis (wt%) (Demirbaş, 1997)

In Europe, there are a wide range of species of forestry plantations due the range of climatic and soil conditions (Figure 2-3). In 2012, the European forestry reserve produced approximately 200,000 ton of solid wood equivalent, of which approximately 120,000 ton (Mantau, 2012; Mantau *et al.*, 2010) was used for household energy production, though this includes a wide range of different parts of the tree (Figure 2-4) which can have a wide range of different properties. IRENA (2014) also suggests that imported biomass may be more cost effective than these sources (Table 2-5).

This market study indicates that there are a wide range of costs for forest residue available, therefore this study will present four case studies of interest to the operations CPL currently has. These are:

- Pinewood residues in the UK, Northern, Central and Eastern Europe
- Eucalyptus in Northern Spain and Portugal
- Eucalyptus & pinewood pellets on the world commodity market

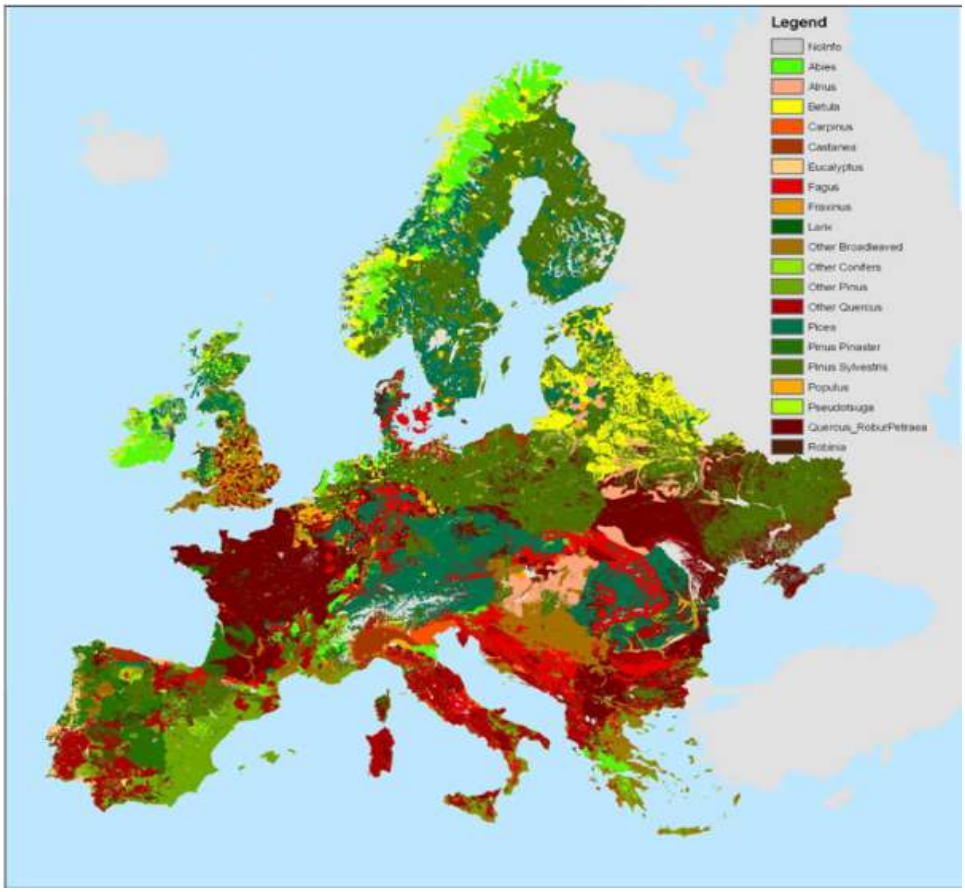


Figure 2-3. Distribution of tree varieties over Europe reproduced from Brus et al. (2012)

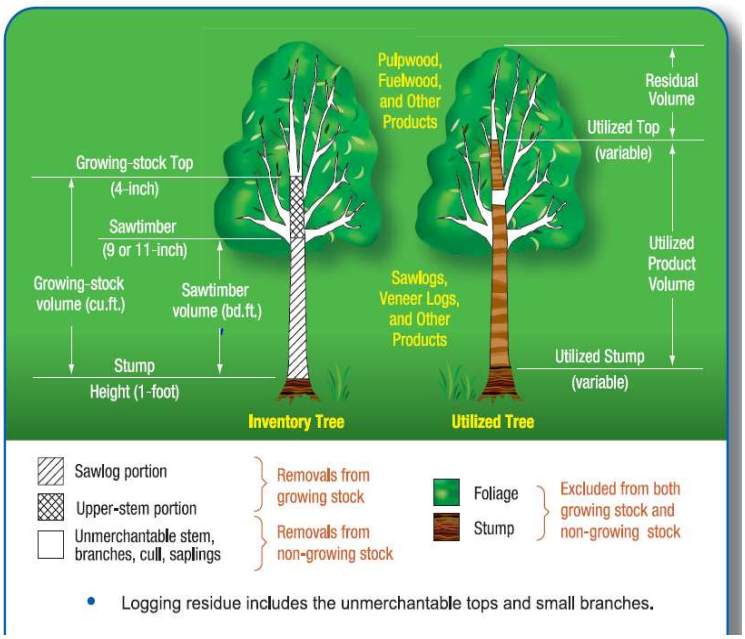


Figure 2-4. Parts of a tree and uses of the biomass reproduced from Perlack et al. (2005)

Table 2-5. Cost comparison between International and US biomass including shipping to Europe reproduced from IRENA (2014)

Feedstock	Transport		Total Cost			
	USD/GJ	USD/Ton	USD/GJ	USD/Ton	USD/GJ	USD/Ton
Woodchips from UK Energy Crops	5.2-8.2	60-94			5.2-8.2	60-94
Woodchips from Scandinavia	5.6-6.7	64-77	3.0-3.4	34-38	8.6-10.1	98-115
Local Agricultural Residues	4.8-6.0	55-68			4.8-6.0	55-68
Pellets Imported from USA	6.0-7.1	100-119	3.3-3.7	57-63	9.3-10.8	157-182

2.3.1.1 European Pine chip residues

A wide range of costs exist inside the EU for pinewood chips, which is best indicated by Figure 2-5 produced by the S2Biom (2017) project. Prices here represent those at the 'road side', which means that they are raw wood cost, before transport, chipping or drying occurs which explains why they are so low. The countries where these products are available in the largest quantities are Latvia, Sweden and Germany (Evans, 2014).

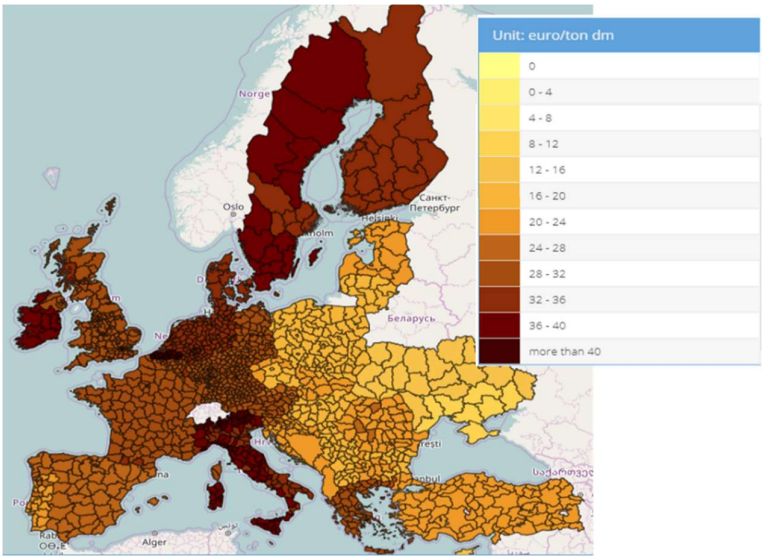


Figure 2-5. Range of conifer tree cost (Euro/dry ton) throughout Europe. Roadside Cost (therefore raw wood moisture content 45-50%, before milling in 2012). Reproduced from S2Biom (2017)

For wood residues available in the UK for actual chipped wood, Table 2-6 presents a range of expected costs for woodchips based on the expected moisture content of the wood.

Table 2-6. Range of costs for woodchips in the UK, 2012 prices

Moisture Content	Cost (£/ton)	References
50% Moisture	25-40	(Carbon Trust, 2012)
30% Moisture	60-110	(Carbon Trust, 2012)
Dry	70-130	(Carbon Trust, 2012)

With these costs in mind looking at the S2Biom (2017) cost for pinewood in 2012 of approximately £25/ton, the cost of chipping can be estimated to be approximately £10/ton, and drying down to 30% moisture costing approximate £40/ton. These costs agree with those presented by (Suchomel *et al.*, 2012) which suggest that these woodchips are approximately £65 ton in Austria and the costs provided by IRENA (2014) in Table 2-5.

2.3.1.2 Spanish eucalyptus

Eucalyptus globulus plantations are considered short rotation crops in Northern Spain (Galicia region) and Portugal and grow well to the climatic conditions (Diaz-Balteiro *et al.*, 2009). This crop has good credentials as an energy crop as it has greater forest productivity, uses water more efficiently than some other species. Eucalyptus is also fast growing and because of this can sequester more CO_2 than other tree species, with 0.14 Tonne CO_2/year/tree absorption compared to Oak with 0.025 tonne/year/tree (ENCE, N.D.). In 2009, 4.2 million m^3 is produced in Spain (Cremades, 2012), with the main market being pulp and paper production.

2.3.1.3 Wood pellets on world commodity market

While Spain produces a significant amount of Eucalypts, significant amounts are produced in Brazil, India and China (GIT Forestry, 2009), however the species thrives in Australia and in 2008 Plantation Energy began to export scale volumes of Eucalyptus pellets annually to Europe.

As discussed, wood chips from the USA are available in large quantities in Europe, with large scalable volumes being used by UK power stations (Evans, 2014).

Table 2-7. Properties of commodity wood pellets

Biomass Source	Moisture Content	Availability (Ton/year)	Cost	Reference
Spanish Eucalyptus	55%	4,200,000	45	(S2Biom, 2017)
Australian Eucalyptus Pellets	5%	250,000	100	(Smith, 2013)
US Softwood Chips	N/A	(UK Power stations import grid scale quantities)	110	(Argus Media, 2016)

2.3.2 Agricultural residue

There are a diverse range of agricultural residues throughout Europe however as with forestry biomass review will focus on the available agricultural residues in sites relevant to CPL's plants.

Therefore, agricultural residues that are of initial interest are:

- Straw from wheat and canola produced in the Lincolnshire area near the Immingham processing plant.
- Miscanthus grown in the UK, which is predicted to be the largest energy crop in the UK
- Olive vines and by products produced in Spain and Southern Europe

2.3.2.1 Lincolnshire straw residue

The two main straw residues produced in Lincolnshire are wheat and canola. Wheat is grown for food or bioethanol; while canola is grown for bio-diesel production. In 2010, Lincolnshire produced 12% and 13% of the total wheat and canola oil in the UK, highlighting that this is a significant feedstock for this region and are the most significant crops in this region (DEFRA, 2014). This straw is used as animal feed and bedding, but a study showed that in 2007 there was a potential for a 2-3 million tonne surplus (Copeland *et al.*, 2008).

Straw residues have higher levels of chlorine and sulphur than wood which could lead to emissions problems at the pyrolysis site or during barbecue use (Eriksson *et*

al., 2012). However, several experimental studies do not cite this as a potential issue of pyrolysis of wheat (de Wild *et al.*, 2012; Mohanty *et al.*, 2013; Zhao *et al.*, 2014) but this could be because they were looking at production of bio char for soil amendment and sequestration and bio-oil chemicals.

2.3.2.2 UK miscanthus

Miscanthus (sp. Miscanthus Giganteus) is a woody perennial grass crop, with shoots resembling bamboo, used in the UK energy crop. It can be grown yielding up to 10-13 tonnes/hectare at 20% moisture content after three years of cropping, with the East Midlands and Humberside regions having the potential to grow half of the UK's miscanthus (DEFRA, 2007). Initiatives such as the Energy Crop Scheme, where the UK Government covers half the crop establishment costs (International Energy Crops, N.D.) more farms may begin to produce this crop. Like other agricultural products, miscanthus is considered carbon neutral but requires less fertiliser inputs and the root structure has the potential to sequester a significant amount of CO_2 compared to other crops over the plants life (Felten *et al.*, 2013).

On harvesting, miscanthus can be chipped to 30-40 mm then bailed, reducing the number of unit operations required before pyrolysis (ADFDA and AFBI, 2011).

2.3.2.3 Olive residue

Spain is the worlds largest producer of olives (FAO, 2012b) producing 362,660 M tonnes in 2012. This also represents 10% of the agricultural output of Spain. Unlike wine, olive oil production is focused in the south of the country, with the Andalucía region producing 75% of the total volume of olive oil (Olive Oil from Spain, N.D.). For one tonne of olive fruit into a processing mill, 200 kg – 140 kg of fibre and 60 kg of stones is produced providing a significant energy stream to be utilised. The properties of this husk are highlighted in Table 2-8.

Encinar *et al.* (1996) highlight that the yield of charcoal is expected to be over 35% charcoal in a system designed to produce bio-oil, indicating this biomass could produce significantly greater levels of charcoal than wood sources which are expected to have charcoal yields around 20%. Jahirul *et al.* (2012) suggest that the high lignin in olive means that it favours charcoal production compared to woods.

2.3.2.4 Grape residue

Spain is the fifth largest producer of grapes in the world, producing 5,340,000 M Tonnes of grapes in 2012. This produces a significant amount of residue (FAO, 2012a) with of vineyards producing 1 t(dry)/ha of residue. Until recently, this was seen as a waste but more often as an opportunity for bioenergy (Spinelli *et al.*, 2010). This

residue is distributed over the country into several wine areas, meaning there may be a case for distributed charcoal production, rather than centralised processing.
On Italian vineyards, (Spinelli *et al.*, 2010) studied the most effective ways to collect grape vine pruning. They found shredding at source was the most effective way to do so, and estimate the extra handling, equipment to cost 30-40 €/t when picked up from the farm gate. This system would produce a product suited to input to this pyrolysis system, properties of this outlined in Table 2-8. These properties appear to be very similar to hardwood, which is expected as grape vines are a woody biomass, although ash has shown to be higher in other sources (Encinar *et al.*, 1996).

Table 2-8. Summary of agricultural residue properties

	Vol Availability (t/y)	Cost (£/ton 2014)	References
Lincoln Wheat Straw	2-3,000,000 (surplus)	50	(Eriksson *et al.*, 2012), (Hosseinpour *et al.*, 2010), (DEFRA, 2014b)
Lincoln Canola Straw			
UK Miscanthus	80,000	50 (20% moisture)	(ADFDA and AFBI, 2011), (Brosse *et al.*, 2012)
Spanish Grape Bagasse	10,00,000	20-40	(Demiral *et al.*, 2011), (Spain, 2014), (Spinelli *et al.*, 2010)
Spanish Olive Cake	94,000,000	100	(Olive Oil from Spain, N.D.), (Jahirul *et al.*, 2012)

2.3.2.5 Waste wood

The UK classifies waste wood into three categories, which breakdown the wood based on the level and type of coatings (for example sealants or paint) and metal content (DEFRA, 2012). Potential issues using the higher grades will be included here.

- Grade A: can still include some coatings or paint, and nails/metal fixings. Wood is likely to come from distribution or retail packing.

- Grade B: fibre board included at this point. Contaminants with grade A but including glass, plastic, binders and glue. Some treated wood, although there are limits on this as defined by the waste incineration directive (Carbon Trust, 2012).

The use of waste wood generally comes with low cost, around £25-50/ton for chipped 20% moisture content wood (Carbon Trust, 2012). However, even though these wood classes mentioned are still considered fine for combustion use, because the final product is to be used in conjunction with food sources it has been decided that these sources are not suitable for the scope of this project.

2.3.2.6 Summary

From this analysis, it has been determined that there are four major sources of biomass that should be taken forward for experimental analysis. These are:

- Softwood, due to their wide availability, range of price and traditional use as a charcoal component. UK sourced pinewood has been chosen as the representative species for analysis
- Hardwood, for the same reason. Spanish Eucalyptus and Mixed UK hardwood are the likely sources.
- Straw residue, for the high volume and potential for low cost in Lincolnshire.
- Spanish Olive Cake. For the high volume and potential for integration into other CPL processes.

In terms of modelling the costs of this process, there is one other consideration for these biomass types: transportation to a processing site. Transport costs for biomass around Europe can then be estimated in various ways. For example, Argus Media (2016) can then provide costs of shipping woodchips around Europe, and US DOE (2014) provide estimates of the cost per kilometre per ton for various shipping methods, which have been presented in Table 2-9 and Figure 2-6.

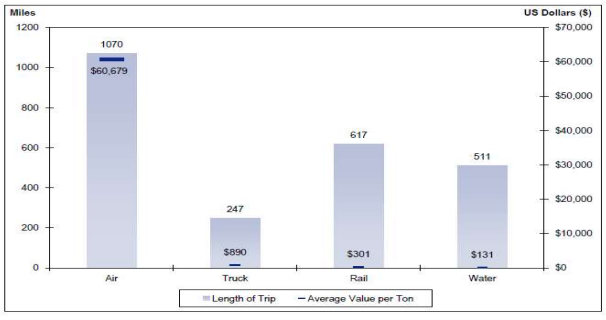


Figure 2-6. Transport costs via different shipping mechanisms, reproduced from US DOE (2014)

Table 2-9. Estimation of transport costs of biomass reproduced from Argus Media (2016)

Argus wood pellet freight indications, spot cargo				
Route	Tonnage	Units	Rate	±
Aveiro-ARA	3,500	€/t	14.00	nc
Aveiro-Copenhagen	3,500	€/t	16.00	nc
Aveiro-Hull (UK)	3,500	€/t	14.00	nc
Riga-ARA	5,000	€/t	17.00	+0.25
Riga-Copenhagen	5,000	€/t	12.00	nc
Riga-Stockholm	5,000	€/t	11.50	nc
St Petersburg-ARA	3,500	€/t	23.00	-0.50
St Petersburg-Copenhagen	3,500	€/t	15.00	nc
St Petersburg-Stockholm	3,500	€/t	13.75	-0.25
Mobile-ARA	25,000	$/t	15.20	nc
Mobile-ARA	45,000	$/t	11.40	nc
Savannah-ARA	25,000	$/t	14.50	nc
Savannah-ARA	45,000	$/t	10.80	nc
Vancouver-ARA	45,000	$/t	19.50	nc

2.4 Charcoal production process

Charcoal has been produced for centuries by the process of pyrolysis, with several levels of technological intensity to produce charcoal as domestic fuel (Antal *et al.*, 2003; Bridgwater, 2003). Charcoal use is still widely employed today for fuel purposes, as it is a more consistent, cleaner burning product with higher energy density than raw biomass. There is also a reduction in smoke output due to the increased fixed carbon content (Bhattacharya *et al.*, 2002; Harris, 1999; Mwampamba *et al.*, 2013). Cha *et al.* (2016) have reviewed more modern uses of charcoal, which range from soil amendment for increased fertility and carbon sequestration to replacement of fossil fuel absorbents.

These areas outline that charcoal production is important, but charcoal yields of biomass processes are quite low due to the relatively high atomic H/C ratio (Antal *et al.*, 1996). Greater recovery of biomass as charcoal could lower the cost of production for these applications which is the purpose of this study. Many studies have investigated how to increase this conversion through modifying the process conditions and with use of additive in the pyrolysis, particularly through the use of alkaline/alkali earth metals, transition metal oxides and alumino silicates such as zeolite and clay minerals.

This section will outline the background theory on pyrolysis, yield modelling and catalytic pyrolysis. From this, suggestions will be made as to the important variables, additives for study experimentally and methods for modelling pyrolysis yield.

2.4.1 General mechanisms of pyrolysis

Pyrolysis has been around for many centuries, and charcoal from this process used as a soil modifier, increasing productivity with increased water and nutrient holding, most notably in Terra Petra soils in the Amazon (Kleiner, 2009). Traditionally, charcoal is produced in low oxygen environments in mounds or pits as in Figure 2-7 and Figure 2-8.

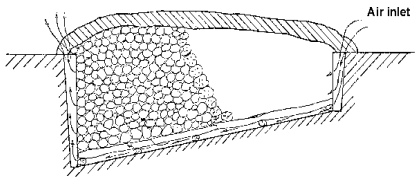


Figure 2-7 Earth pit for charcoal production (FAO, 1987)

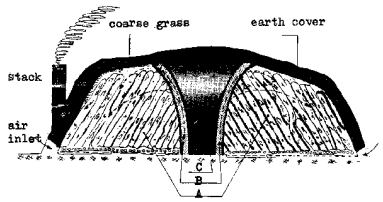


Figure 2-8. Mounds for charcoal production (FAO, 1987)

Modern charcoal processes use many different types of industrial equipment: from batch kilns to continuous systems where many further variables can be controlled, such as heating rate, feed rate, peak temperature, pressure, and swept gas flow rate (and Figure 2-10).

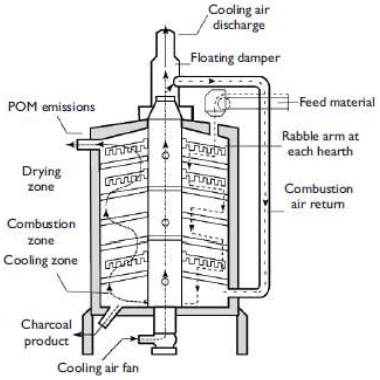


Figure 2-9 Continuous multiple hearth kiln for charcoal production. Reproduced from Radian Corporation (1988) in Brown (2012)

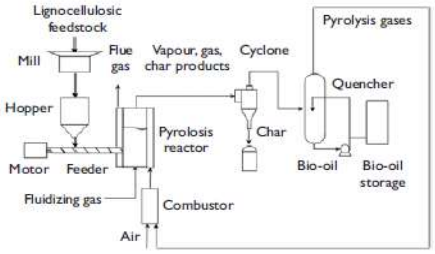


Figure 2-10 Fluidized bed reactor for bio-oil production. Reproduced from Brown (2012)

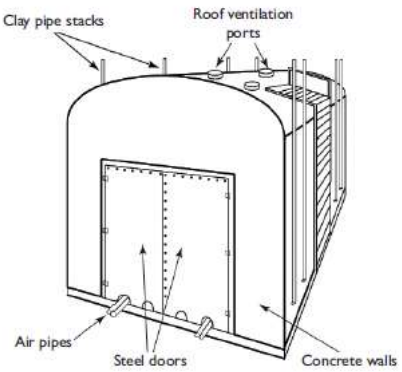


Figure 2-11. Missouri style batch kiln for charcoal production. Reproduced from Maxwell (1976) in Brown (2012)

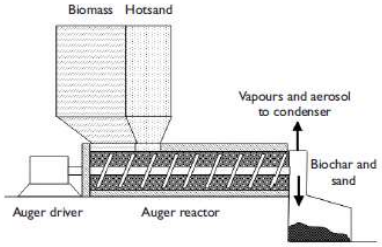


Figure 2-12. Screw auger kiln for charcoal production. Reproduced from Brown (2012)

The general process of pyrolysis is described by (FAO, 2008) in the following temperature steps:

- 20 – 110°C
    - Water inside the biomass is completely volatised, leaving dry biomass.
- 110-280°C
    - Wood components (hemicellulose, cellulose and lignin) begin to decompose, releasing water CO and CO_2. At the higher end of this range (+250°C (Antal *et al.*, 2003)) acetic acid, methanol and aromatic carbon structure starts to develop. Torrefaction occurs between 250-290°C, which causes the biomass to turn black(Antal *et al.*, 2003). The temperature is held at 280°C to ensure that carbonisation is uniform throughout the reactor (Payakkawan *et al.*, 2014).
- 290-400°C
    - Hemicellulose is fully decomposed, and cellulose begins to decompose faster. Vapours are released, beginning the production of acetic acid, methanol in higher concentrations (Payakkawan *et al.*, 2014)
- 400-550°C
    - At 400°C transformation to charcoal complete; further heating drives off tar raising fixed carbon content to ~75%

- At higher temperatures, polycyclic aromatics still held in the charcoal which are carcinogenic upon combustion, are broken down into smaller ones, and production of gaseous products, namely CO is greatly increased (Antal *et al.*, 2003; Balat *et al.*, 2009; Payakkawan *et al.*, 2014).

Pyrolysis cannot begin until the biomass is completely dry, which can require a lot of energy input, especially with green wood (FAO, 2008). The product mix differences from this process (presented in (Antal *et al.*, 2003)) are controlled by the heating rate, residence time, particle size and peak temperature. These general conditions are illustrated in Table 2-10.

Table 2-10 Operating conditions for each of the pyrolysis processes. Reproduced from Balat et al. (2009)

Pyrolysis	Solids Residence Time (s)	Heating Rate (K/s)	Particle Size (mm)	Temperature (K)
Conventional Slow pyrolysis	450-550	0.1-1	5-50	550-950
Fast	0.5-10	10-20	<1	850-1250
Flash	<0.5	>1000	<0.2	1050-1300

According to Balat et al. (2009) temperature is the most important parameter in pyrolysis as production of charcoal reduces with temperature increasing. Because of this, the review will now focus on the slow pyrolysis systems which operate at low temperatures so a maximum amount of charcoal is obtained from operation. A short discussion on each of the effect of the parameters presented in Table 2-10, gas residence time and pressure and the effect on charcoal yields will now be presented.

2.4.1.1 Effect of conditions on pyrolysis

Peak temperature

Generally, the most important process condition to modify in order to increase the charcoal yield is to lower peak pyrolysis temperature (Balat *et al.*, 2009) because lower levels of volatile compounds are released as gas and tar.

Heating rate

Increases in charcoal yield can also be made by controlling the heating rate – decreasing heating rates mean that there is a longer residence time of volatile compounds in the fixed carbon structure, so more of these volatiles are fixed and retained (Angın, 2013; Strezov *et al.*, 2007).

Biomass pre-drying

Pre-drying of the biomass so that moisture removal does not strip volatile matter and increasing the vapour phase residence time to allow for more secondary tar conversion to charcoal (Antal *et al.*, 2003) are also well known techniques to increase charcoal yield.

Pressure effects

Aside from temperature however, the most promising operating conditions to increase charcoal yield are to increase operational pressure (Antal *et al.*, 2003; Van Wesenbeeck *et al.*, 2016)and increase the particle size (Wang *et al.*, 2013). The issue with these systems is that they require good process control and high capital cost equipment, and cannot be retrofitted to current production systems cheaply. Large biomass particles also generally require the use of virgin wood stocks, rather than chips or pellets which can utilise waste.

Particle size

The size of particles affects the rate of heat transfer and therefore the particle centre temperature. Asadullah *et al.* (2010) showed that increasing particle size from 1 to 6mm can increase the charcoal yield by up to 5%. They speculate this is because intra-particle mass transfer is higher in larger particles, meaning that the tar caught up in the charcoal has a higher residence time so secondary recombination reactions allow it to be retained.

2.4.2 Pyrolysis yield modelling

This project requires a tool which can be implemented in a process model of a pyrolysis system to determine the effects of various operating conditions, so a brief review of pyrolysis modelling methodology has been completed. A wide range of processes occur drying pyrolysis, as summarised by Figure 2-13.

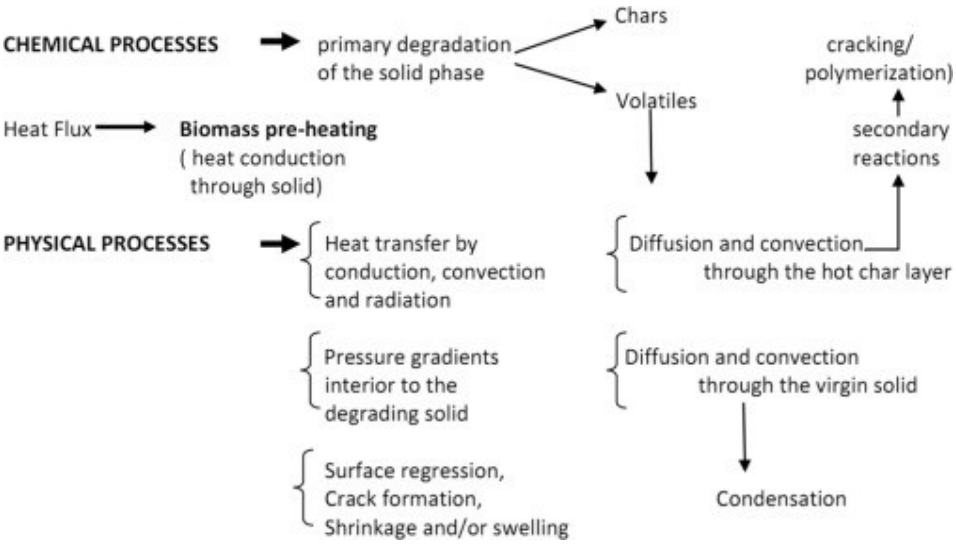


Figure 2-13. Summary of processes involved in pyrolysis of biomass reproduced from Di Blasi (1993). This figure shows the interaction between chemical reaction and physical processes occurring during pyrolysis in the biomass structure.

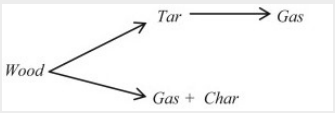
Sharma *et al.* (2015) have published a review of methods which aim to simulate pyrolysis. These models start at low levels of detail, focusing on the reaction kinetics of the pyrolysis reactions. Particle levels models then have been developed which look at how these reactions interact with the biomass structure, so parameters such as secondary char condensation can be further estimated. Reactor level models then use these findings to see how the individual particles interact inside a larger system. Further details on these methods are summarised in Table 2-11.

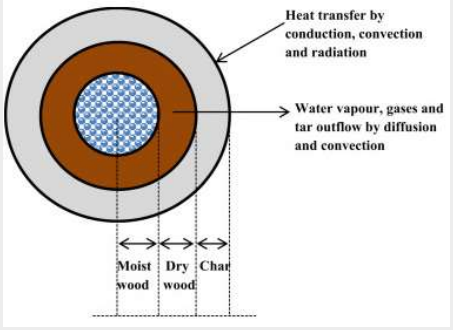
As further observed by Sharma *et al.* (2015), methods require a varying level of detail, but generally rely require at least the lignocellulosic structure of the biomass, but can also require: specific properties of biomass and char shape and heat transfer properties; reactor conditions including temperature, residence time, pressure and potentially require measurement of the specific heat transfer properties of the reactor.

Other routes to allow the estimation of charcoal yield based solely on the biomass properties have been presented, based on observations that lignin content and alkali metal/alkaline earth metal concentrations are key predictors in the charcoal yield of a coal or biomass (Fahmi *et al.*, 2007; Sharma *et al.*, 2004). These observations have been applied by Jenkinson (2016) to determine correlations to use lignin and calcium (Ca) and potassium (K) metal concentrations as predictors to determine the charcoal yield. This method has lower accuracy than methods presented in Table 2-11, but also requires less experimental inputs for the result. Demirbaş (2003) has determined

there is a near linear relationship between the lignin content of the biomass fixed carbon concentration. As Ca/K also make up a significant proportion of the biomass ash this research speculates that a model using inputs from the simple proximate analysis can be formulated.

Table 2-11. Summary of various pyrolysis modelling mechanisms (Sharma et al., 2015). This table highlights how fundamental kinetic models are developed then incorporated to show how the physical properties of the biomass are accounted for and how these reaction and particle models are incorporated into a larger system model to represent how a chemical reactor can be modelled.

Model groups	Model type	Description
Kinetic models	Lumped models	Products are lumped into classes: tar, char and gas; and char; and looks at the biomass as either a whole degrading or the effects of the individual lignocellulosic components, and require fitting activation energies to each reaction. For example, a simple model is presented in Figure 2-14.  Figure 2-14. Example of Lumped framework reproduced from Linen et al (1988) in Sharma *et al.* (2015)
	Distributed models	These assume pyrolysis products are '…formed by infinite number of parallel reactions with different activation energies given using a Gaussian distribution function.' (Sharma et al., 2015) and are generally based on coal pyrolysis models. Require more pseudo-components than lumped models.
Particle models		Developed to look into the effect of heat propagation throughout biomass particle, which is neglected by above schemes, and indicated in Figure 2-15.

		 Figure 2-15. Particle pyrolysis model Galgano and Di Blasi (2004) in Sharma *et al.* (2015)
Reactor models	Phenomenological models	Looks into including the effect of the reactor environment, applying kinetic or particle models inside a reactor system
	CFD	As above, but with the increased processing power and more varied calculation effects of using multi-phase CFD solvers.

2.4.3 Catalytic pyrolysis

Fast pyrolysis systems generally exist to produce gas and oil from biomass, however the pyrolysis process produces gas and oil with relatively poor quality compared with conventional fossil fuels (Bridgwater, 2003), with considerable refining required to improve these products (Bridgewater, 2012), as will be discussed in section 2.4.5.1. Catalysts have been extensively studied using: impregnated or raw zeolites or similar low cost alumino-silicate materials clay minerals; increasing the level of natural alkali/alkaline earth metals (generally acidic, e.g. K, Ca) or adding generally basic transition metal oxides (e.g. MgO) (Bru *et al.*, 2007; Samolada *et al.*, 2000; Stefanidis *et al.*, 2011; Stefanidis *et al.*, 2016; Veses *et al.*, 2015; Veses *et al.*, 2014). These are added to the pyrolysis reactor with the aim of cracking heavy oils in the oil, reducing the amount of oxygenation present in the resulting oil, or changing the resulting pyrolysis product mixture. Each of these systems impact the pyrolysis in a different way; minerals and zeolites generally involve reactions in the gas phase, between the de-volatised compounds and the catalyst; while atomic earth metal addition can be of great effect to changing how the lignin and cellulose interact and decompose. The issue with metal addition to the pyrolysis is that it limits the use of the final charcoal potentially due to remaining toxicity from the metals. Therefore, this study will investigate mineral catalysis.

Alumino-silicate minerals and zeolites that have a high concentration of Lewis acid sites, relatively high surface area and mesopores and have been identified in the literature as increasing cracking (Antal *et al.*, 1990; French *et al.*, 2010; Gollakota *et al.*, 2016; Li *et al.*, 2010; Min *et al.*, 2011b; Mortensen *et al.*, 2011). These cracking reactions are a wide mixture of dehydration reactions which break down and decarboxylate the ring structures present in the oils (Domine *et al.*, 2008). Studies have shown that zeolites can produce higher concentration of valuable aromatic compounds than non-catalytic runs too opening up the potential of investigation of specialty chemical refining from the process (Mendes *et al.*, 2016). If the decomposition products are not small enough to be released as gas, then fouling of the catalyst can occur as the fragments recombine and deposit on the surface as coke. In the case of this study, this is being considered as extra char yield, as it is assumed that this will behave as charcoal.

Rutkowski (2012) and Solak *et al.* (2014) have looked into applying these effects to fast pyrolysis of plastic wastes with several types of clay mineral (montmorillonite and bentonite) under fast pyrolysis conditions. They found oil quality was improved but yield was reduced, as oil was cracked into gas and coke which fouled the catalyst. High coke deposits were observed, especially using bentonite. From these studies, it appears that bentonite could be promising for the purposes of this work on biomass. Some groups have already looked at applying these concepts to slow pyrolysis. For example Gerçel (2011); Veses *et al.* (2014) showed that slow pyrolysis systems can be modified in a similar way using the mineral sepiolite, which can mimic the properties of basic transition metal oxides, while other studies have showed that atomic earth metal addition can also applied to slow pyrolysis (Durak *et al.*, 2015; Veses *et al.*, 2014). Gerçel (2011) also showed findings that agreed with Rutkowski (2012) that sepiolite lowers the yield of charcoal, so it could be expected that the effects using bentonite may translate to slow pyrolysis as well. Bentonite was looked at by Veses *et al.* (2015), who studied the effects of it at 450°C. This study provides evidence that with pinewood liquid yield is reduced and tar cracking reactions are happening, but have not characterised the results over a temperature range or catalyst concentration as they have done with sepiolite.

2.4.4 Industrial equipment for pyrolysis

As presented, in Figure 2-7 to Figure 2-12, there are a number of ways that charcoal has been produced by pyrolysis, with a wide range of operating and system capital costs. Jahirul *et al.* (2012) present a review of the different types of reactor systems

(Figure 2-132). They also present recommendations of the different types of reactor to use for each product type in Table 2-14.

So, how does the process to be developed by this project fit in with the analysis by Jahirul *et al.* (2012)? A brief system sizing is presented in Table 2-12. Based on these constrains and with equipment available to trail at pilot scale at CPL, fixed bed reactor systems, such as those presented in Figure 2-12 will be used as the pyrolysis reactor for this project. These systems are also standard continuous pyrolysis system for charcoal production (Brown, 2012).

Table 2-12. Basic system sizing considerations

Plant scale	20-30,000	ton/y
Initial biomass moisture content	20	wt%
Charcoal yield	30	wt%
Operation time	7000	Hours/year
Biomass input rate required	2800-4500	kg/h

2.4.5 Properties of syngas and bio-oil produced

Slow pyrolysis still has a large amount of loss of carbon to bio-oil and syngas (~60%), which can have a negative environmental effect (Antal *et al.*, 2003), therefore must be collected and utilised by the process to be developed in this project.

2.4.5.1 Bio-oil

Bio-oil is a two phase emulsion of oxygenated hydrocarbons from the decomposition of cellulose, hemicellulose and lignin, with water from the original biomass and reaction products (Bridgwater, 2003). The composition of the liquid organic phase is related to the original biomass that was used in the process (Bridgwater, 2003). Bio-oil has an energy density of 17.2 MJ/kg (Bridgwater, 2003; FAO, 2008) though the high water content means it cannot be directly be blended with diesel other or other hydrocarbons. According to (Bridgwater, 2003) it also contains residual char, and oxygenated compounds which gives the oil a high viscosity and chemical instability. With hot gas filtration, the charcoal content can be reduced, and the emulsion can be removed by several processes which increase the stability, which is again summarised in Bridgwater (2003). The potential pathways for bio-oil use are summarised in Figure 2-16.

If enough bio-oil is produced by the process to be developed, it can be upgraded to produce various chemicals which could be sold or developed chemicals (charcoal

binder or ignition fluid), however the use of bio-oil for process heat or combustion with syn-gas for electricity is the most likely outcome (Kim *et al.*, 2014; Liaw *et al.*, 2012).

Table 2-13. Review of types of pyrolysis system, reproduced from Jahirul et al. (2012)

Reactor type	Advantages	Disadvantages	Bio-Oil Yield
Fixed bed	Simple design Reliable Biomass size independent	High carbon conservation Long solid residence time Low ash carry over Difficult to remove char	35%–50%
Bubbling fluidised bed	Simple design Easy operation Good temperature control Suitable for large scale	Small particle sizes are needed	70%–75%
Circulating fluidised bed	Well-understood technology Good thermal control Large particle sizes can be used	Unlikely to be suitable for large scale Complex hydrodynamics Char is finer	70%–75%
Rotating cone	Centrifugal force moves heated sand and biomass No carrier gas required Less wear	Complex process Small particle sizes needed Not proven yet for large scale	65%
Vacuum	Produces clean oil Can process larger particles of 3–5 cm No carrier gas required Lower temperature required Easier liquid product condensation	Slow process Solid residence time is too high Require large scale equipment Poor heat and mass transfer rate Generates more water	35%–50%
Ablative	Inert gas is not required Large particle sizes can be processed System is more intensive Moderate temperature required	Reactor is costly Low reaction rate Low reaction rate	70%
Auger	Compact No carrier gas required Lower process temperature	Moving parts in hot zone Heat transfer in large scale is not suitable	30%–50%
PyRos	Compact and low cost High heat transfer Short gas residence time	Complex design Solids in the oil Alkali dissolved in the oil High temperature required	70%–75%
Plasma	High energy density High heat transfer High temperature Very good control	High electrical power consumption High operating costs Small particle sizes required	30%–40%
Microwave	Efficient heat transfer Exponential control Compact High heating rate Large size biomass can be processed Uniform temperature distribution High temperature	High electrical power consumption High operating costs	60%–70%
Solar	Use renewable energy High heating rate High temperature	High costs Weather dependant	40%–60%

Table 2-14. Best technologies for pyrolysis reproduced from Jahirul et al. (2012)

Product		Pyrolysis Type	Reactor	Heating Method	Temp. (°C)	Biomass
Bio-char		Slow	Fixed bed	Furnace or kilns	<300	Walnut shell, olive husk, hazelnut shell
Bio-oil	Large scale	Fast	Bubbling fluidised bed	Heated recycle gas	450–550	Agriculture residue, wood chip, fruit shell
	Medium scale	Fast	Circulating fluidised bed	Wall and sand heating	450–550	Forest residue, municipal waste, dry wood, waste tyres
	Small scale	Flash	PyRos	PyRos heating	450–550	Grass, husk, wood dust
Syngas		Slow/Fast	Microwave	Electromagnetic	>800	Rice husk, wood dust

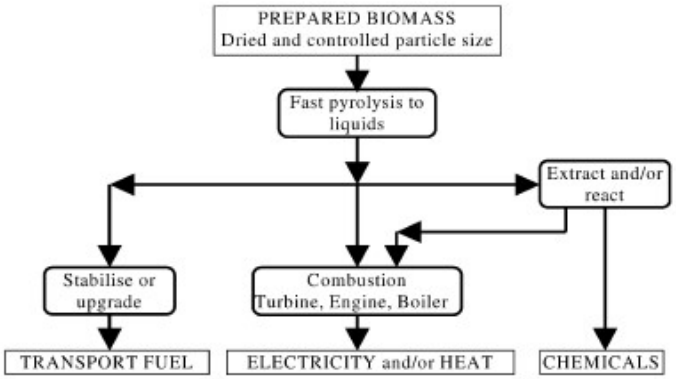


Figure 2-16 Potential uses for bio-oil reproduced from Bridgwater (2003)

2.4.5.2 Syngas

According to (Bridgwater, 2003) the main constituents of syn-gas from pyrolysis are CO, CO_2, H_2, CH_4 and has a likely energy content of 15-20 MJ/m^3. Like bio-oil, there are a range of uses for syn-gas, outlined in Figure 2-17.

While Figure 2-17 applies to a gasification process, the syn-gas produced is very similar though as the quantity of syn-gas produced from pyrolysis is much lower, and the plant size being considered is much smaller, the economic route for use of syn-gas appears to be combustion for process heat or incorporation into an electricity generation system with the bio-oil.

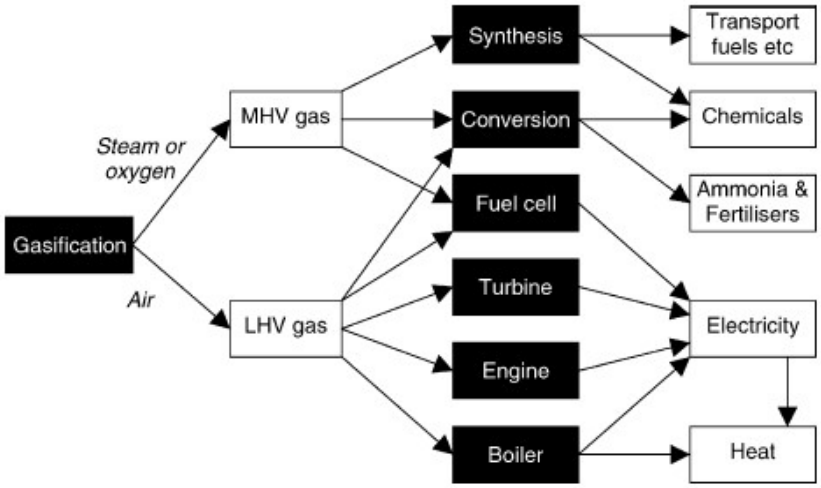


Figure 2-17. Outcomes for syn-gas from gasification. Reproduced from Bridgwater (2003)

2.4.6 Pre-treatment & post-treatment steps for biomass processing

This section has defined that three other unit operations are required by the carbonization process for this project:

- Moisture reduction
- Size reduction – to pre-process biomass when it is collected
- Briquetting of biomass, to be done either:
    - Pre-pyrolysis, through densification of processed biomass
    - Post-pyrolysis, through extrusion or briquetting of the charcoal

This is only a subset of biomass pre-treatments used in industry, however, as the feed stocks for this process are likely woody biomass, processes such as washing the biomass for metals content (Long *et al.*, 2012; Vassilev *et al.*, 2012) are likely to be too expensive for a process selling charcoal.

Considerations will need to be made in this unit operation for biomass quality changing for various reasons throughout the year, for example: degradation in storage, changing growing patterns throughout the year and changing mix due to biomass costs.

2.4.6.1 Particle size reduction

It is speculated that a process taking wood chips will require size reduction post pyrolysis, before the final densification of the charcoal for sale. According to Cummer *et al.* (2002), the most common devices for size reduction for gasification processes (which have similar specifications to pyrolysis systems) are knife chippers and hammer mills.

Chippers work by using rotating and stationary blades to cut the biomass. These work best on wood though require a clean feedstock (i.e. no nails or metal) or the blades can be damaged (Cummer *et al.*, 2002). Hammer mills work by using metal hammers to pulverise biomass through a screen, which controls the particle size. These work best when the biomass is smaller than 4 cm or a pre-crusher may be required, and can be used to process wood and agricultural residues (Cummer *et al.*, 2002).

A further option is a tub grinder, which is "becoming an alternative to chippers and hammer mills… particularly for forestry residues" (Cummer *et al.*, 2002) and have a rotating tub which feeds into a hammer mill. These are designed to be portable which means they can be used to encourage grinding on site, potentially reducing transport costs to the pyrolysis plant.

From this quick analysis, further research into the energy and sizing of hammer mills will be conducted for the economics section of this thesis.

2.4.6.2 Biomass drying

(Antal *et al.*, 2003; Cummer *et al.*, 2002), and Jahirul *et al.* (2012) suggest that biomass is likely to arrive at processing plants with a moisture content exceeding 20 wt%, while the ideal moisture content is in the range of 10-15 wt%. Therefore drying is required.

This can be a costly process, and reduce plant energy efficiency, though if done as part of the pyrolysis or size reduction process rather than offsite this could utilise waste heat from the system to pre-heat the biomass (Cummer *et al.*, 2002). Cummer *et al.* (2002) suggest that the cheapest method of drying is through a perforated floor bin process, as shown in Figure 2-18. However, these systems are large and batch-wise processes. More continuous systems include rotary cascade dryers which "are the most common device for drying large-scale biomass…" (Cummer *et al.*, 2002) but these systems are likely to require a lot of external heat and much higher capital cost, so may not appear as attractive in financial modelling of the process.

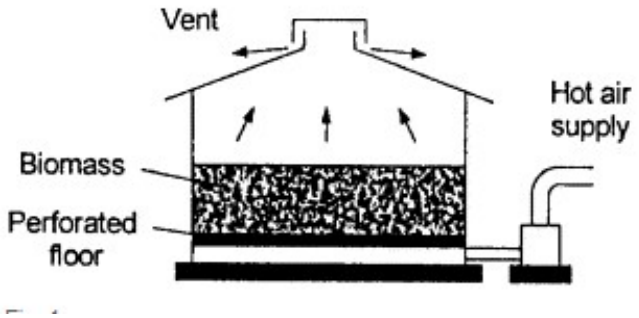


Figure 2-18. Perforated floor bin dryer reproduced from Brammer and Bridgwater (2009), initially published in Drying in a biomass gasification plant for power or cogeneration. Proceedings of the Fourth Biomass Conference of the Americas, Oakland, CA, USA, p291-7 in Cummer et al. (2002)

2.4.6.3 Briquetting

Briquetting of biomass is done in several ways: via screw extrusion, piston pressing, roll pressing (or pillow briquetting) or pelletisation (Mwampamba *et al.*, 2013), each of which can give the resulting briquettes different combustion properties (Grover *et al.*, 1996). In most cases, a binding agent is added to the charcoal which aids the adhesion of the charcoal particles, and generally is a starchy substance (EPA, 1976).

In terms of capital cost, (Mwampamba *et al.*, 2013) suggests that screw extruders have lower capital cost than pillow briquetting, though agglomeration (which product pellets) are the least expensive in systems which carbonize biomass then briquette it. The advantage of densification post carbonisation is that the biomass is of a consistent specification, with similar moisture content, particle size and agglomeration properties which can affect the quality of the process (Grover *et al.*, 1996). This arrangement can also allow densification to be done while the charcoal is hot which has the effect of helping many binders set and is required for most applications of briquetting to set the particles in place (Grover *et al.*, 1996).

The size of particles and moisture content of charcoal into the briquetting process has an effect on the quality of the final product. EPA (1976) and Grover et al. (1996) suggest that the ideal particle size is between 3-6 mm and moisture content of around 5-10%.

Due to CPL's expertise in roll press briquetting, this will be the only option considered for the production of briquetting process. This may not provide economic advantage to the process, but allows for leverage of intellectual property CPL has built up around coal briquette production, and integration into the traditional coal production process CPL uses.

2.5 Pyrolysis char combustion modelling

Before charcoal can be used widely as a solid fuel, its properties must be further understood. In terms of this project, tools are required to determine if the charcoal made can be used for purpose as well as meeting the economic goals of the project. This will be done by developing a set of equations predict charcoal combustion profile, based its chemical properties.

According to Saidur *et al.* (2011) much work has been put into this understanding, focusing on the experimental comparison of charcoal and coal combustion and modelling differences between the properties of coal and charcoal. The scope these modelling studies have undertaken have focused on: kinetic schemes, and; modelling combustion based on char structure via CFD modelling systems (Barranco *et al.*, 2009; De Lepeleire *et al.*, 1983; Eghlimi *et al.*, 1999; Hurt *et al.*, 2001; Wang *et al.*, 2016a). The current status of these modelling methods will now be outlined.

2.5.1 Kinetic modelling strategies

Several studies into kinetic modelling of biomass combustion have been carried out, with several methods favoured.

2.5.1.1 Modelling of TGA char combustion experimental results

One common method which has a lot of interest is combustion of charcoal in thermogravimetric (TGA) studies which allows the rate of heating to be controlled so parameters such as ignition temperature, activation energy and reaction order can be observed. Di Blasi (2009) provided a good review of the subject, which was then updated by Wang *et al.* (2016a). These analysis methods are based around Eq. 2-1.

$$\frac{d\alpha}{dt} = A\ exp\left(-\frac{E_a}{RT}\right)F(\alpha) \qquad \textit{Eq. 2-1}$$

Symbol	***Description***	***Units***
$\boldsymbol{\alpha}$	***Reacted fraction as predicted by chemical model***	***Concentration***
$\boldsymbol{F(\alpha)}$	Reaction model function including information on reaction pathway and order	Concentration
$\boldsymbol{t}$	***Time***	$\boldsymbol{s^{-1}}$
$\boldsymbol{A}$	***Pre-exponential factor***	***Concentration***
$\boldsymbol{E_a}$	***Activation Energy***	$\boldsymbol{s^{-1}}$
$\boldsymbol{RT}$	***Gas constant * Temperature***	***Concentration***

Wang *et al.* (2016a) has observed that there a wide range of experimental properties which can affect the results of these experiments including:

- Too much mass in the TGA, and high carrier gas flow which can have implications regarding combustion being mass transfer limited
- Poor assumptions by other studies regarding the order of reaction chosen, which is represented by the model chosen for F(α).

These issues mean that there has been a wide range in activation energy and reaction order reported for some char combustion systems.

The results from these studies have been reported to be influenced by factors regarding the char structure and porosity (Morin *et al.*, 2017) and that the model results have shown that there are differences due to the pyrolysis conditions used (Guerrero *et al.*, 2005; Morin *et al.*, 2017; Vorobiev *et al.*, 2016). These ideas suggest that a large number of properties of the charcoal are required to get accurate results for this method of analysis can apply.

2.5.1.2 Reaction kinetics

Several studies have related various properties of char from coal and biomass to the kinetic decomposition.

The literature for coal combustion is large, (Hurt *et al.*, 2001) have reviewed and built on reaction kinetic models on coal based on the carbon and oxygen concertation in the combustion system. Several studies have built on these reaction kinetics for example, several studies have looked further into incorporating the mass transfer and mineral composition of biomass, which has been done nicely by studies by Barranco *et al.* (2009), Rojas *et al.* (2012) and (Mitchell *et al.*, 2007). Lobo (2013); Lobo *et al.* (2016) and Tilghman *et al.* (2017) have reviewed the recent advances in these modelling techniques, which has led to complex reaction schemes and require more and more processing power to solve.

Tilghman *et al.* (2015) then looked at applying these ideas to charcoal combustion, requiring more complex information about the surface area and porosity of the charcoal to be known so the mass transfer effects which control how the kinetic pathways are affected can be considered.

2.5.1.3 CFD modelling

Bibrzycki *et al.* (2016); Eghlimi *et al.* (1999); Tabet *et al.* (2015); Zhang *et al.* (2016); and Zhou *et al.* (2017) among other studies have looked into CFD of various coal char boiler systems, while Centeno-González *et al.* (2017); Ma *et al.* (2007); Woodfield *et al.* (2000) have completed similar studies on biomass and biomass derived charcoals.

Common points about these studies are that they require detailed knowledge of the geometry and system the substrate is to be combusted in; and in many cases require the utilisation of a detailed kinetic systems, mentioned in section 2.5.1.2.

2.5.2 Summary from combustion modelling review

The issue with these studies is that present models that they require detailed information about charcoal into the system, which may not be available when screening a wide range of charcoal types and briquette structures. The charcoal briquettes are also likely to be required to contain sand and raw biomass for process financial stability, due to the lower cost of raw biomass and sand compared to charcoal and to be similar to other commercial briquettes, which may be difficult to include into some of these more in-depth modelling methods. Several of these methods also focus on complex combustion systems which have controlled airflow or char feeding systems which introduce too much complication for the simple grill system which the charcoal produced in this project will eventually end up. This work has tried to approach the simulation of charcoal combustion behaviour from a different direction – start with the most basic method of characterization of biomass types, proximate analysis. There were two methods that could have been chosen to do this:

- Develop an empirical model based on the temperature time profile obtained from experimental work.
- Consider a BBQ fire as the simplest system its – a system which heats rapidly due to fire, then cools over a period of time.

This simple fire containing a heating and cooling step can be compared to a two reactions in series, mechanisms for which have been developed thoroughly, as presented in the textbook by (Levenspiel, 1998). As opposed to the methods outlined in section 2.5.1.1, this method would focus on modelling the temperature output rather than the change in mass. The method of deriving this analogous method will be presented later in this thesis, in Chapter 5.

2.6 Process modelling

To this point in the literature review, it is clear that a process to produce charcoal is likely to follow a process as suggested by Figure 2-19.

The core charcoal process appears to be a well-studied factor, with advances likely to come in the addition of catalyst and reduction of the temperature range for pyrolysis based on expected product quality prediction.

The two areas which will affect the process the most in terms of economics are:

- Biomass choice: will change process conditions and process economics , with different charcoal quality and product yield
- Use of gas and oil by-products from pyrolysis. These can represent a significant proportion (over 80%) of the original biomass, and as discussed in section 2.4, have value which needs to be utilised.

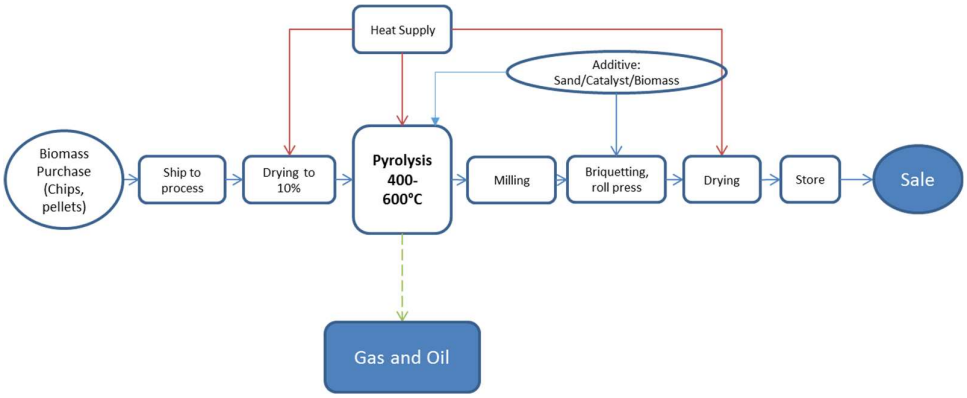


Figure 2-19. Process flows as suggested by literature search

Therefore this project will require a process economic tool, designed to assess both of these cases. Effects of the process on a carbon balance will be assessed as part of this process as well.

A model covering the aspects of the process outlined in Figure 2-20 is required. This section will discuss the required steps, including carbon balance and costing. Finally, a discussion around other case studies of pyrolysis processes in literature will be discussed looking at methodologies or tools that were relevant to this project.

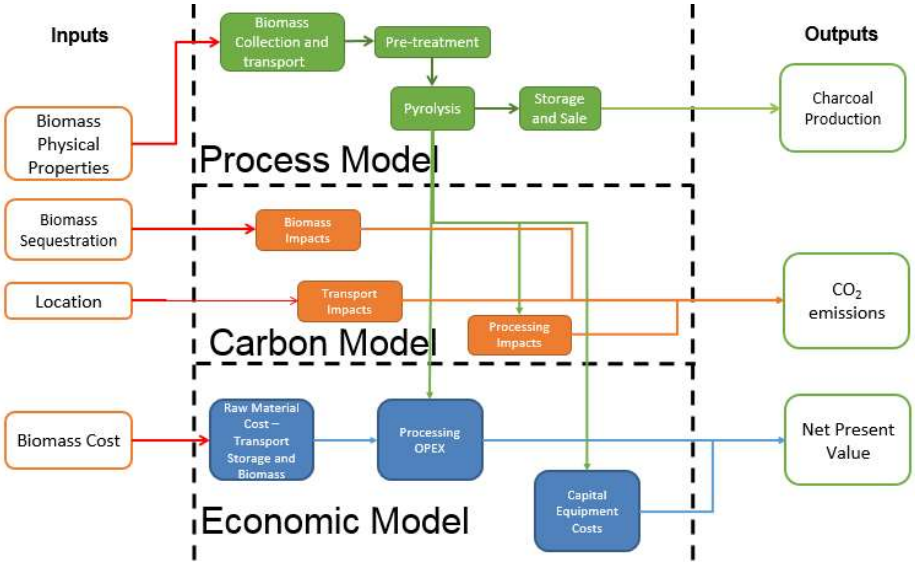


Figure 2-20. Outline of process modelling stages expected to satisfy project requirements. A process, economic and carbon model are required for this purpose, with the interactions between these as suggested here.

2.6.1 CO_2 emissions calculations

Methods of charcoal production from biomass are seen by many as being environmentally friendly. However, Johnson (2009) questions the CO_2 emissions credentials of charcoal as the most sustainable style of grilling, indicating that it potentially produces three times as much CO_2 as LPG grilling. Delving into this study, one of the largest issues with Life Cycle Analysis (LCA) presents its self – what feedstock can be considered carbon neutral? This study indicates that if woody biomass used to produce charcoal is considered a waste by product or not diverted from any other source of use, then the emissions are significantly lower and comparable to LPG.

The effect of this reduction by using waste resources in the UK (European Climate Foundation, 2010) is indicated by Figure 2-21. Bailis *et al.* (2013) also shows that utilising produced syngas and tar from pyrolysis is likely to be a significant source of emissions reductions for this project.

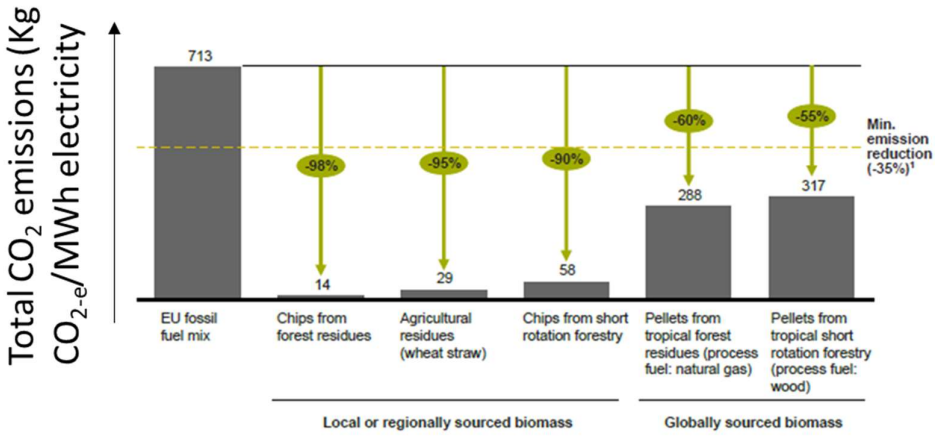


Figure 2-21. Potential for CO_2 off setting by fuel type reproduced from European Climate Foundation (2010). This shows that forestry and agricultural residues sourced from inside the EU can provide the largest offset for CO_2 emissions compared to the current paradigm.

Therefore, to reduce emissions from charcoal production, it is expected that the system chosen will need to generate the highest yield of charcoal from a feedstock that is considered a residue or that is not offsetting a current use. To measure these emissions, a clear methodology must be followed to allow comparison with other processes.

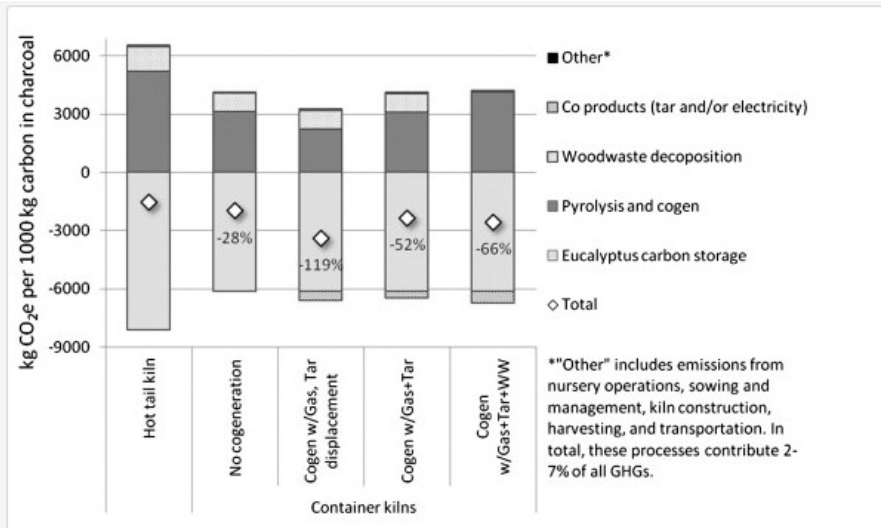


Figure 2-22. Effect of use of syngas and tar reproduced from Bailis et al. (2013)

Numerous software packages exist which can calculate the life cycle of different processes, including effects of acidification, eutrophication and land use changes which result from an activity. If costs and CO_2 emissions alone do not allow the

selection of one biomass type or mix, this extra level of detail may be required for this study. However, before this level of detail is required CO_2 emissions calculations following a method presented by the (Carbon Trust, 2012b) can be used:

- Choosing the scope of the analysis as defined by the Greenhouse Gas Protocol Standard:
    - Scope one: direct emissions resulting from a process
    - Scope two: including indirect emissions inside the business's control from steam, heat, power and fuel a process may use
    - Scope three: inclusion of indirect emissions outside the business's control, including waste disposal, water consumption
- Define system boundaries
- Collect data
- Apply emissions factors
- Verify results and reduce emissions

For this study, Scope two emissions will be considered, as the effects of the biomass and use of the oil and gas by-products as heat and power against electricity and natural gas will be assessed.

2.6.2 Project cost modelling

Once the process model has been built, it will need to be costed. The method this will be done by is largely taken from (Sinnott *et al.*, 2005), and will be considered a basic front end costing package. Statements of total capital expenditure (CAPEX), operating expenditure (OPEX) and project revenue will be produced using the methodology provided by Sinnott.

For comparison between options, (Sinnott *et al.*, 2005) recommends that a Net Present Value is calculated.

2.6.2.1 Net Present Value (NPV) method

NPV is calculated by Eq. 2-2.

$$\boldsymbol{NPV = \sum_{n=1}^{total\ life} \frac{Cash\ Flow_n}{(1+i)^n}} \qquad \textbf{Eq. 2-2}$$

Symbol	Description	Units
NPV	Net present value calculated in 2015	£
n	Project year number	-
Cash flow	Cash position for year n	£
i	Interest rate for the project	%

Total Life	Project length	-

This method requires assumptions to be made around the life of project and interest rate. Project life and interest rates will be updated in consultation with CPL, but initial values used will be 15 years at an interest rate of 10%, using estimates from similar projects (Sarkar and Kumar 2010 and Braimakis, Atsonios et al. 2014).

This process modelling comprises use of Microsoft Excel and Aspen Hysys, with the specific methodology used outlined in Chapter 6.

2.6.3 Case studies

Several cases studies will be presented to highlight various issues and potential analysis methods for this analysis. They do not have to produce charcoal as the key product, but do have pyrolysis as the main processing step.

2.6.3.1 Bio-char production in the UK (Shackley et al., 2011)

This study examines the production of bio-char for CO_2 sequestration in soil in the UK. This is done to both improve the soil quality of farm land for agricultural purposes and to offset CO_2 emission. The authors base their process in the flow scheme presented in Figure 2-23, over three scales as 2,000, 16,000, and 184,800 tonnes per year biomass. The medium scale plant here is comparable to the potential size for this project.

Each of these plants produce electricity, which the authors believe are eligible for Renewable Obligation Certificates (ROCs), which provide an extra revenue stream if syn-gas and bio-oil are used to produce power. However, ROCs no longer are available, so have been ignored from this project and may bring into question the economics for these processes.

The cost of bio-char production in each of these scenarios is presented in Table 2-15. This appears strongly related to the cost of biomass. Figure 2-24 shows that again the definition of something as a waste feed stock is highly important – with wood waste being cost negative in terms of required revenue from CO_2 sequestration.

Table 2-15. Cost breakdown for the medium scale production of charcoal with different types of biomass. Reproduced from Shackley et al. (2011).

	Straw	SRC+FRs	*Miscanthus*	Sawmill Residues	SRF	Canadian FRs	Waste Wood	Green waste & sewage sludge	C&I veg and animal waste
Sales of electricity	-37	-37	-37	-37	-37	-37	-37	-37	-37
Renewable obligation certificatess	-74	-74	-74	-74	-74	-74	-74	-74	-74
Avoided gate fee	0	0	0	0	0	0	-124	-89	-96
Capital cost	101	101	101	101	101	101	101	101	101
Feedstock	147	166	176	157	176	247	0	0	0
Transport	22	29	62	-8	39	13	12	12	12
Storage	15	15	15	15	15	15	15	15	15
Natural gas	11	11	11	11	11	11	11	11	11
Labor	48	48	48	48	48	48	48	48	48
Plant costs	60	60	60	60	60	60	60	60	60
Application to field	5	5	5	5	5	5	5	5	5
Net cost	298	323	366	277	344	389	17	51	44

C&I: Commercial and industrial; FR: Forestry residue; SRC: Short rotation coppice; SRF: Short rotation forestry.

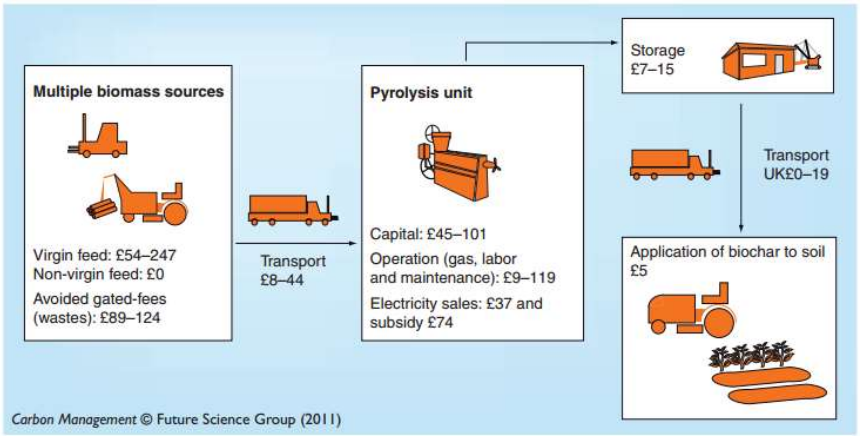


Figure 2-23 Process examined by Shackley et al. (2011) for producing charcoal for carbon for sequestration and soil quality improvement. Reproduced from Shackley et al. (2011)

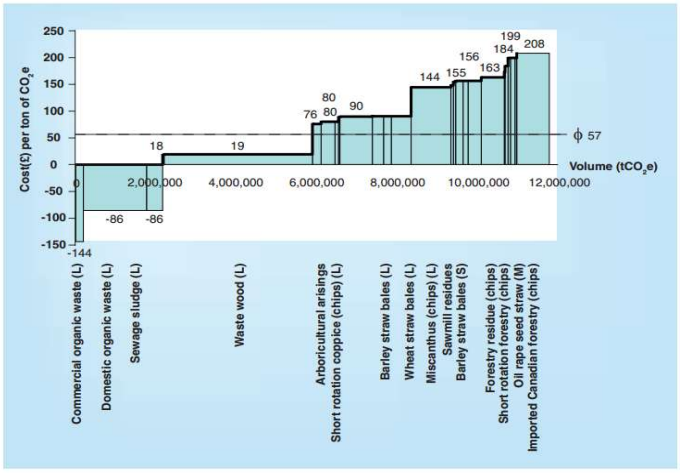


Figure 2-24. Comparison of the abatement of CO_2 for each feedstock type. Reproduced from Shackley et al. (2011). Indicates that waste biomass types have the largest effect at abating emissions compared to specifically grown energy crops.

2.6.3.2 Bio-oil to bio hydrogen processing plant (Sarkar et al., 2010)

This project looks at converting whole trees, forest residues and wheat straw crops to bio-oil at 2,000 ton biomass/day for bio-hydrogen production in Canada. One interesting observation of this process is that the plant profitability is almost directly proportional to the yield – feed stocks with a high yield are going to have better profitability.

From the cost breakdown of this process, a significant percentage of the plant budget goes into the handling and preparation of biomass from raw trees. This could be an economic advantage for methods using pre-processed biomass pellets rather than investing in biomass pre-treatment unit operations. However, the study by Sarkar et al. (2010) considers a significantly larger biomass input to any process developed by this project to the process differences in scale required for economic production of oil and gas compared to charcoal.

2.6.3.3 Evaluation of decentralised pyrolysis for centralised gasification (Braimakis et al., 2014)

This study set out to compare the economics of distributed or centralised production, summarised in Figure 2-25. To do this, they are utilising an 80 ton biomass/h fast pyrolysis system, which is considerably larger than the scenarios presented in this project.

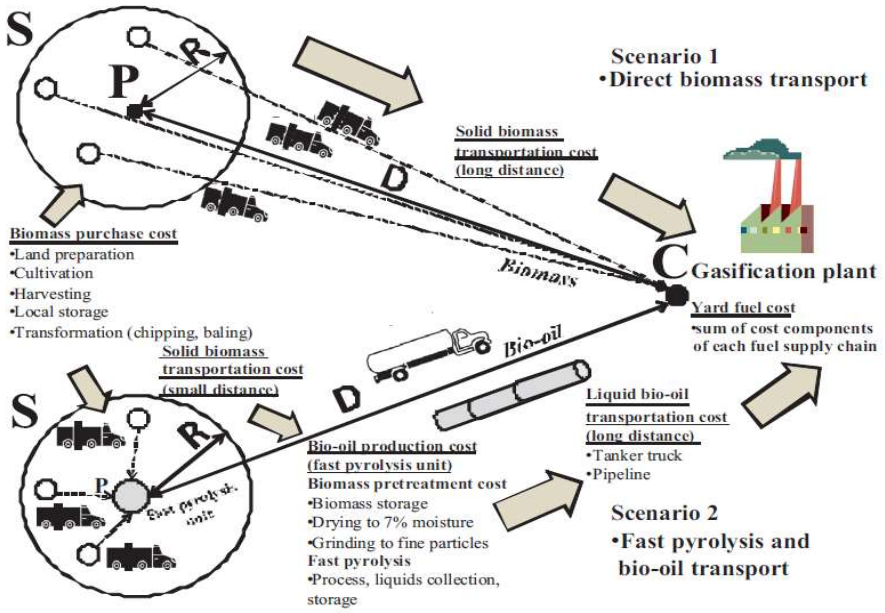


Figure 2-25. Visualisation of the two options compared in Braimakis et al. (2014). Reproduced from Braimakis et al. (2014). Option 1 indicates the variables involved in the transport of biomass from distributed logging operations to a centralised oil

gasification plant. Option 2 shows that the biomass is processed at localised processing operations to bio-oil then gasified for heat.

For this study, they speculated that the transport costs of un-refined bio-oil to a centralised location where the biomass or oil is gasified for heat would be much lower than that of the raw biomass to the same central location.
However, they found that the extra capital and operating costs of the additional number of plants negated this effect.

2.6.4 Case studies summary

Three main considerations have been taken from these case studies, which can be tested during the process modelling phase of this thesis.

- Biomass cost is an important determinant on the profitability of a process
- Yield of key products from this biomass source and the cost of biomass improvements to the biomass (e.g. sizing and drying) are also important considerations
- Economies of scale at centralised processing locations for pyrolysis upgrading projects are more significant than reductions in transport cost.

These ideas will be developed into case studies which will be used to determine areas of interest and limitations around the charcoal pyrolysis plant system and supply chain.

2.7 Summary of literature review

Previous literature has helped shape the project in several important ways:

- Biomass types important to the project have been identified and narrowed down to:
    - Raw wood: pinewood, mixed hardwood, and eucalyptus sourced from the UK, EU and international locations Australia and the USA.
    - Agricultural residues from the UK and EU; including olive cake, grape industry residue, straw and miscanthus.
- Process conditions and reactor systems have been reviewed which have indicated that this process should be carried out under slow pyrolysis conditions involving slow heating in an atmospheric pressure fixed bed system. There is a potential that low cost solid acid catalysis can also improve the process. This is done to maximise charcoal yield from the process.

- An outline of the usefulness of pyrolysis oil and gas as either electricity, heat and chemical by-products has been presented. This can now be compared in the process modelling component of this project to determine which of these is the most optimal use of by-products.
- Methods of modelling the charcoal yield and BBQ charcoal combustion have been reviewed. The conclusion of both of these reviews is that high accuracy can be obtained but at the expense of complex model building and high computational resources to solve them. This project has stipulated that it requires simple tools which can be implemented into a process model, so suggestions of how these tools can be developed have been made.
- Previous modelling studies have been reviewed which provide both an outline of how the important process characteristics can be calculated including carbon emissions and economic parameters of the process.

Chapter 3. Experimental biomass pyrolysis and yield prediction

3.1 Introduction

Two main concepts will be outlined here:

- Section 3.2 and 3.3 presents the characterisation of scale up effects between lab pure pyrolysis experiments and pilot plant pyrolysis.
- Section 3.4 presents the development of a model to predict the charcoal, liquid and gas yield from pyrolysis based on the simple proximate analysis of the raw biomass

Further discussion of the liquid and gas properties of the pyrolysis products and how the composition of these change will be outlined in Chapter 4, while this chapter will focus on presenting the effect of temperature on overall yields and charcoal quality (in terms of proximate analysis). The incorporation of this yield model into the larger process and economic modelling task of this report will be outlined.

3.2 Methods

3.2.1 Materials and methods

3.2.1.1 Biomass types used

To improve the error and make any modelling task more universal, a wide range of biomass types with different proximate analysis have been analysed, as presented in Table 3-1.

Biomass types were sourced from several commercial suppliers, proprietary information of CPL. The pinewood/hardwood/straw and miscanthus came from UK based companies, while the remaining (olive cake/eucalyptus and olive stone) came from Spanish companies.

Moisture content experiments

Biomass is available on the market at various prices which influences the moisture content (MC) that the biomass will come with, as has been discussed in the literature review, some experiments were performed to determine the influence of moisture content on pyrolysis yields. These were performed on olive cake and pinewood.

Wet biomass was made by submerging biomass in water for 3 days then placing the biomass on a strainer a day before experiments were performed, so free water was removed. This meant that the remaining moisture was associated with the biomass structure.

Dry biomass was made by storing biomass in a drying oven and removing at most 5 mins before experiments were performed.

MC achieved in each case is outlined in Table 3-2.

Table 3-1. Database of biomass types analysed and included in pyrolysis yield model

	Proximate analysis			Ultimate analysis			
Type and size delivered	Moisture content (wt%)	Volatiles content (wt%)	Ash content (wt%)	C (wt%)	N (wt%)	H (wt%)	O (wt%)
Pinewood G50 Chips	16-18	81.9	0.6	43.9	0.29	6.85	48.9
Olive Cake Pellets	15	66.3	6.7	47.7	6.0	1.5	44.7
Straw Pellets	13	75.1	6.8	43.6	6.3	1.0	49.1
Eucalyptus G50 Chips	11	68.0	0.55				
Olive Stone Stone	11.3	78.9	0.4	45.1	0.20	6.76	47.9
Miscanthus Pellets	12	69.9	8.4	42.9	6.0	0.8	50.3

Biomass used in lab testing was milled to fit through a 3 mm circular screen, while pilot plant runs were done with as received particle sizes.

Table 3-2. MC of biomass for MC effects experiments

	Dry MC (wt%)	'As received' MC (wt%)	Wet MC (wt%)
Pinewood	3	16	52
Olive Cake	0	15	32

3.2.2 Pyrolysis method

3.2.2.1 Gray-King assay

Gray-King pyrolysis is performed in a quartz tube inside a horizontal tube furnace (Figure 3-1). This is a standard measurement technique for determining the coking

potential for coals (Davis *et al.*, 1928; van Krevelen, 1993), where no carrier or sweep gas was used. Screen experiments have indicated this does not affect the charcoal yield, as indicated in Appendix 1.2.

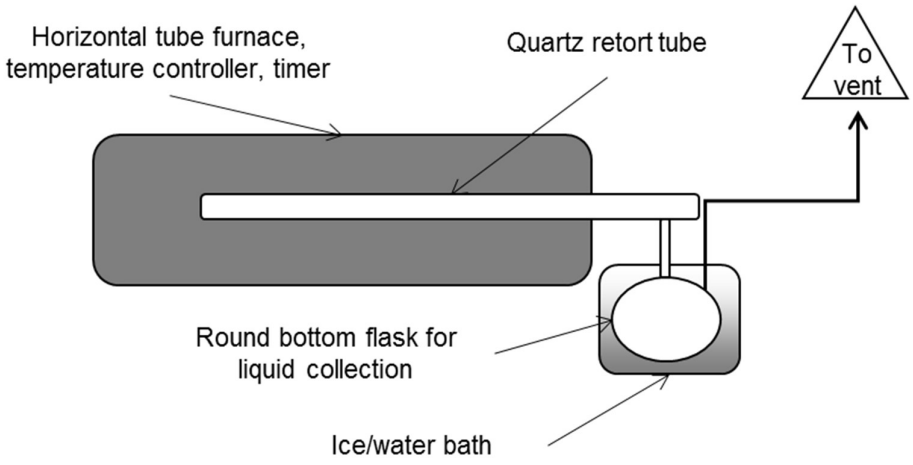


Figure 3-1. Gray King pyrolysis system. A quartz retort tube (300 mm long, 10 mm diameter) was inserted into a horizontal tube furnace (Carbolite). Biomass fill was kept below 150 mm (halfway into oven) to ensure biomass sample could be kept in the hot part of the oven.

For the bulk of experiments, gas and liquid products escaped due to natural flow from a side arm into a round bottom flask in an ice water bath. Liquid products were collected by condensation in a round bottom flask in an ice bath, while non-condensable fractions were sent to vent. A further set of experiments were completed with gas collection, but these results and method modifications will be discussed in Chapter 4.

10-20g of biomass was added to the retort tube, ensuring that the tube was no more than half filled. This was done to ensure that the biomass sample was kept in the hot part of the furnace.

The HTF was pre-heated to 250°C, to prevent effects on uncontrolled heating due to the furnace setup, then the biomass sample was introduced and heated to peak temperatures between 300-700°C at a heating rate of 20°C/min. Dwell time at the peak temperature was 1 hour to ensure complete and repeatable pyrolysis. These experimental conditions were selected based on preliminary experiments which are presented in Appendix 1.1.

The charcoal was left to cool in the furnace until below 300°C, when the quartz tube was removed for natural cooling. The round bottom flask and quartz tube were weighed for yield calculations.

Lists of experiments conducted can be found in Appendix 1.2 and 1.3

3.2.2.2 Pilot plant pyrolysis methodology

This technique has been outlined by both Lenthall (2016) and Gill (2017) The purpose of the testing for this thesis is to confirm that the findings from the laboratory experimentation could be repeated at scale, and to produce charcoal which can be used for the charcoal combustion experimental section of this experiment presented in Chapter 5. A short method and brief details of the kiln and operating procedure will be provided here, and a list of experimental runs can be found in Appendix 1.5.

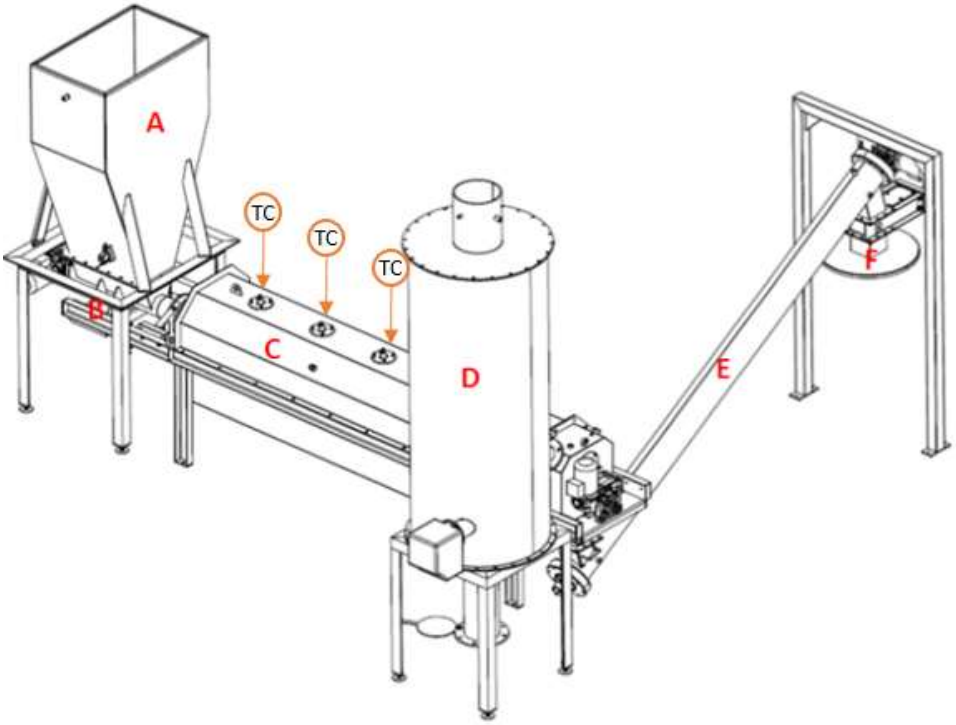


Figure 3-2. Ansac Rotary Kiln HK250E pyrolysis kiln. A = feed hopper; B = feed screw; C = rotating heat tube: 3 m length, 0.25 m diameter,1.5° of incline; D = after burner; E = cooling screw; F = discharge slight gate. TC are temperature control and indication points. Modified from Lenthall (2016).

A schematic of the pilot plant system is indicated in Figure 3-2. Several aspects of this system can be controlled:

- Rate of biomass feed from hopper, based on feed screw set point, kept at 2 RPM throughout experimental runs. This corresponded to a feeding rate of 15 kg/h for wood chips and 45 kg/h for pellets.
- Heat tube speed, which controls the residence time of biomass was kept in the kiln and was set at 2 RPM.

- Temperature of the kiln, which is controlled by thermocouples indicated in Figure 3-2. Set temperatures of 400/550/750 were selected, which have an error of ±75 °C due to pilot plant controller settings.

These operational conditions were set after consultation with A. Gill, whose experimental work (presented in (Gill, 2017)) required a more detailed characterisation of pilot plant effects. The conditions were selected to get full carbonisation.

The limitation of keeping these factors constant is that the residence time of the different biomass types varied, but this will be discussed in greater detail in the results Section 3.3.3.

3.2.3 Analysis techniques

The following section outlines the analytical techniques performed to determine the quality of the charcoal produced from the pyrolysis.

3.2.3.1 Proximate analysis

Proximate analysis were carried out according to ASTM standard procedure:

- Moisture (ASTM D2016), Volatile matter (ASTM E872-82) and Ash (ASTM D1102-84).
- Moisture (reported as total basis, as received) (charcoal: 1 g heated for 2 h in a 115 °C oxygen free oven, then cooled in an oxygen free dissector, biomass 24 hours in a 105 °C oven), ash (reported as dry basis) (1 g heated slowly from 515 -815 °C and held at 815 for 1.5 hours), and volatile (reported as dry basis) (1 g heated in sealed crucibles at 900 °C for 7 mins, then cooled for 7 mins on a table and then cooled for 7 mins in a desiccator).

3.2.3.2 Elemental analysis

Elemental analysis was completed on a LECO elemental analyser at the University of Nottingham. This gave the carbon, nitrogen, hydrogen composition of the raw biomass and charcoal. Oxygen content was assumed to be the remainder.

3.2.4 Yield calculation outline

3.2.4.1 Total yield

Total dry yields of liquid, charcoal and gas were then calculated by equations Eq. 3-1 to Eq. 3-3.

$$Y_{charcoal,total} = \frac{M_{charcoal}}{M_{biomass,wet}(1 - C_{m,bm})} \quad \textit{Eq. 3-1}$$

Symbol	Description	Units
$Y_{charcoal,total}$	Yield of charcoal, total dry basis	g/g
$M_{charcoal}$	Mass of dry charcoal recovered from pyrolysis	g
$M_{biomass,wet}$	Mass of wet biomass added to pyrolysis	g
$C_{m,bm}$	Initial Concentration of moisture in raw biomass	g/g

$$Y_{liquid,total,dry} = \frac{M_{liquid} - M_{biomass,wet}C_{m,bm}}{M_{biomass,wet}(1 - C_{m,bm})} \quad \textit{Eq. 3-2}$$

Symbol	Description	Units
$Y_{liquid,total,dry}$	Yield of liquid (assumed to be reaction moisture + oil)	g/g
M_{liquid}	Mass of Liquid collected from pyrolysis	g
NOTE: $M_{biomass,wet}C_{m,bm}$ indicates that moisture into the pyrolysis is removed therefore all remaining moisture is from pyrolysis reaction. Allows dry basis assumption to be made.		

$$Y_{gas,total} = 1 - Y_{charcoal,total} - Y_{liquid,total} \quad \textit{Eq. 3-3}$$

Symbol	Description	Units
$Y_{gas,total}$	Total yield of gas, dry basis	g/g

These equations are subject to the following assumptions:

- It is assumed that the charcoal is dry on recovery from pyrolysis. Inspection via proximate analysis suggests that the moisture content of charcoal is negligible.
- This calculation aims to calculate the yield of liquid from the pyrolysis of biomass only – moisture content is ignored as while this is collected as liquid it is irrelevant. This liquid comprises the chemical water produced from biomass pyrolysis reactions and pyrolysis oil.

3.2.5 Dry ash free yield

The yield on a dry ash free basis (DAF) was then calculated, shown in Eq. 3-4 to Eq. 3-6. This allow the fate of carbon from the raw biomass to be monitored.

$$Y_{charcoal,DAF} = \frac{M_{charcoal}(1 - C_{a,charcoal})}{M_{biomass,wet}(1 - C_{m,bm})(1 - C_{a,bm})} \quad \textit{Eq. 3-4}$$

Symbol	Description	Units
$Y_{charcoal,DAF}$	Yield of charcoal from biomass pyrolysis on a DAF	g/g
$C_{a,charcoal}$	Ash content of charcoal from proximate analysis	g
$C_{a,bm}$	Ash content of biomass from proximate analysis	g

$$Y_{liquid,DAF} = \frac{M_{liquid} - M_{biomass,wet}C_{m,bm}}{M_{biomass,wet}(1 - C_{m,bm})(1 - C_{a,bm})} \quad \textit{Eq. 3-5}$$

Symbol	Description	Units
$Y_{liquid,DAF}$	Yield of liquid, DAF basis	g/g

$$Y_{gas,DAF} = 1 - Y_{charcoal,DAF} - Y_{liquid,DAF} \quad \textit{Eq. 3-6}$$

Symbol	Description	Units
$Y_{gas,DAF}$	Total yield of gas, DAF basis	g/g

3.3 Results of lab pyrolysis yields

Some results have been included here for the pyrolysis of biomass. Indicative results will be provided for pinewood and olive cake which were considered the standard biomass for these experiments. Results on further biomass types can be found in Appendix 1.3.

The key results that will be discussed are

- Total yield vs. dry ash free yield for pinewood and olive cake
- Volatiles content vs. elemental analysis for pinewood
- Total yield vs. dry ash free yield

Total and DAF yields for pinewood and olive cake are presented in Figure 3-3. The main trends seen here are well known – increased temperature leads to lower charcoal yield with increasing liquid and gas yield references. The nature of the biomass types is different also, as higher levels of char can be obtained from the olive cake.

The most interesting point to note is the difference between the dry ash free and total yields for each of the biomass. The high ash content of the olive cake compared to the pinewood (Table 3-1) causes a large difference between the total and DAF

yields. The trend observed in the olive cake results further highlights that at high temperatures production of liquid and gas products are favoured due to their relative increases compared to the total basis results.

3.3.1 Proximate analysis and elemental analysis of charcoal

The quality of the charcoal has been broken down and for pinewood and olive cake is presented in Figure 3-4.

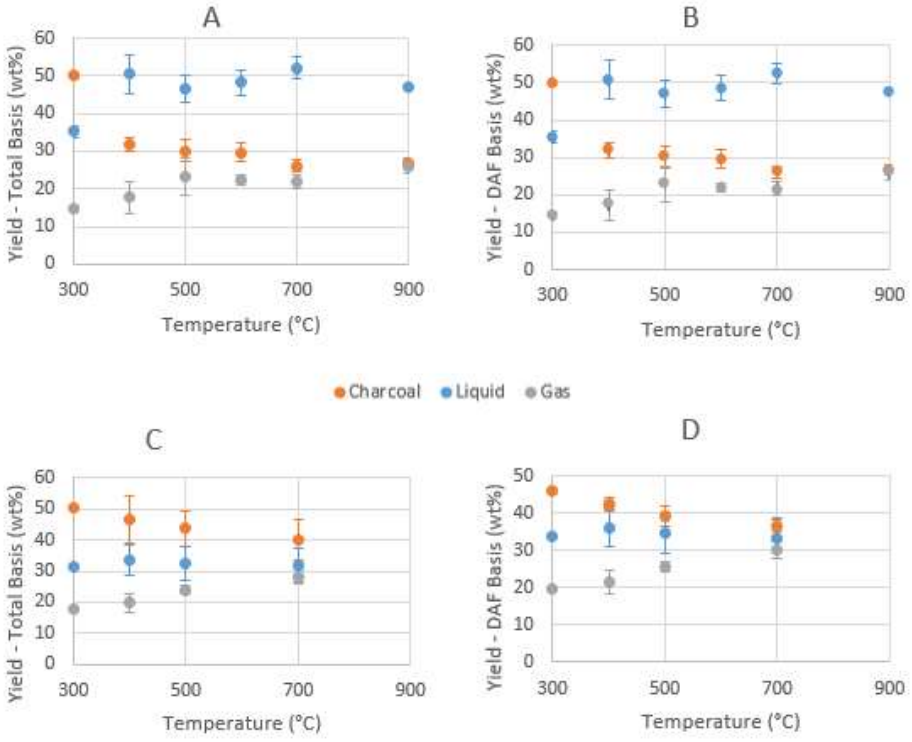


Figure 3-3 A) Total basis yield A) and B) Dry Ash Free Basis yield for pinewood and C) total basis yield and D) dry ash free yield for olive cake, as a function of pyrolysis temperature.

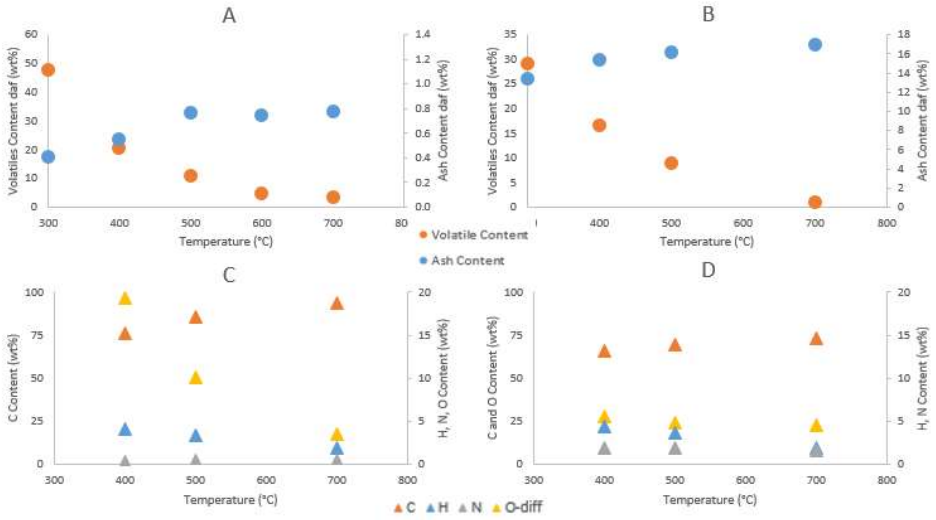


Figure 3-4. Proximate and Elemental Analysis of charcoal from pinewood (A,C) and olive cake (B,D) as a function of pyrolysis temperature.

From Figure 3-4, with increasing temperature carbon and ash content increases while volatiles content, hydrogen, nitrogen and oxygen decrease. This is explained because as the volatile components, generally containing H, N and O, are removed in increasing amounts with higher temperatures, which leaves a more conjugated carbon structure agreeing with previous literature (Antal *et al.*, 2003). Ash is also concentrated at higher temperatures as it is not degraded at higher temperature. This will have implications when the effect of the quality of charcoal as a BBQ fuel us considered, as will be discussed in Chapter 5.

3.3.2 Effect of moisture content on pyrolysis yields

The effect MC has on pyrolysis yield is outlined in Figure 3-5.

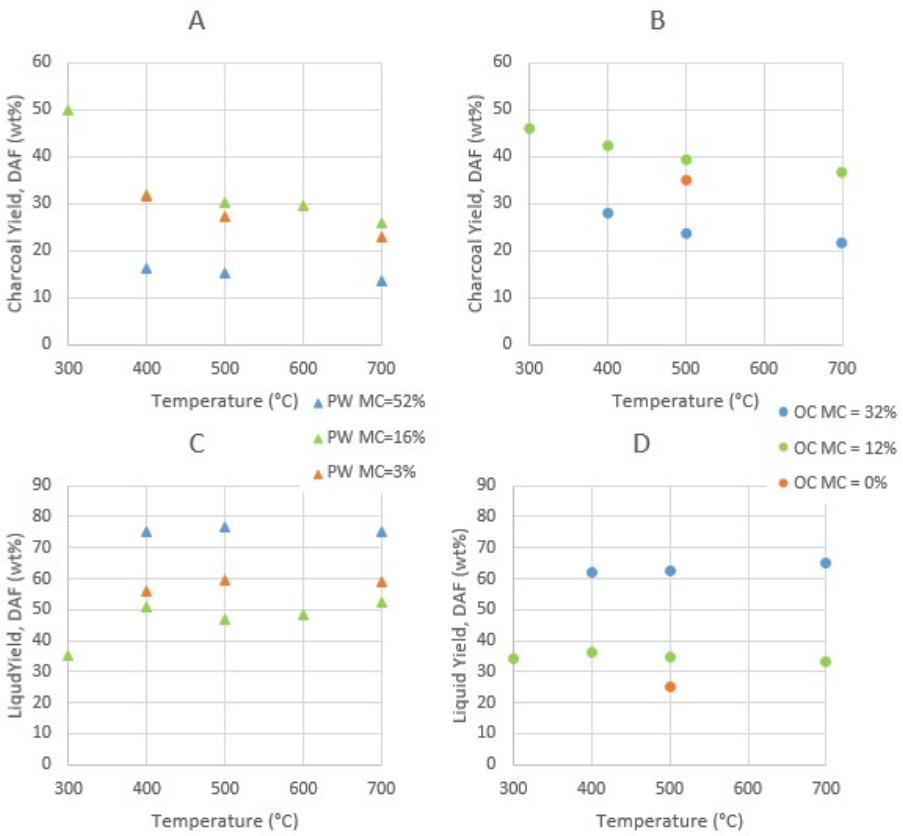


Figure 3-5. Charcoal and liquid yield results, dry ash free basis from MC experiments. A) Charcoal yield from pinewood B) Charcoal yield from olive cake C) Liquid yield from pinewood D) Liquid yield from olive cake.

These results agree with literature that high moisture content biomass has a very negative effect on the charcoal yield and a great increase in liquid, due to the mechanisms which water escapes as steam from the biomass structure during heating (Antal *et al.*, 2003). This steam acts to extract compounds in the carbon structure. Also in agreement with previous literature is that ultra-dry biomass has little effect on changing charcoal yield.

The implications from this will be used in a modelling study to determine the financial trade-off between cheaper biomass and using pre-drying processes (Section 7.2).

3.3.3 Pilot plant pyrolysis – scale up effects

Pilot plant results have been compared to the lab results and a simple inspection shows they compare poorly, as indicated by Figure 3-6

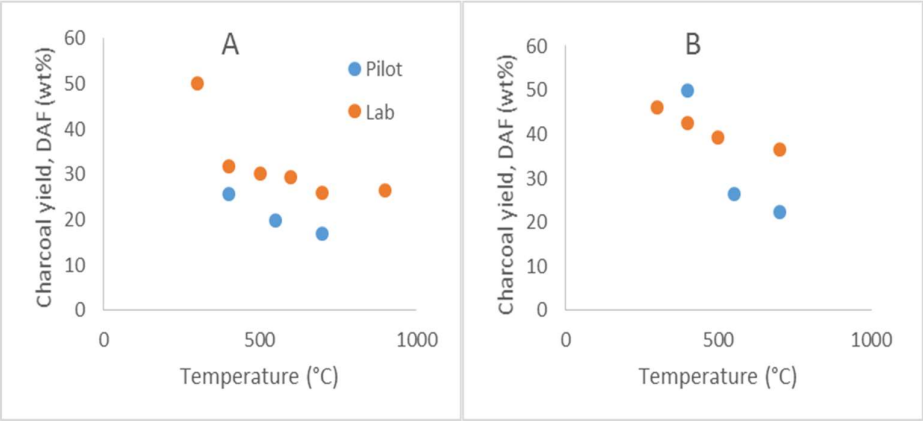


Figure 3-6 Lab vs. pilot plant charcoal yield results for A) Pinewood and B) Olive cake

However, as alluded to in the pilot plant method (Section 3.2.2.2), there are likely to be issues with the temperature control strategy which may mean that the biomass does not experience the set temperature:

- Temperature in the pilot plant is controlled by thermocouples outside the heat tube where the biomass travels as indicated by Figure 3-7. Because of this, the thermocouples may read higher than what the biomass is experiencing.
- Biomass types will pass through this system at different rates. This is because, for example, olive cake pellets and wood chips will pass through the feed screw at different flow rates due to their size, and then reside in the heat tube for different lengths of time – regular shaped pellets may roll through the kiln more quickly than chips which may accumulate and need the natural rolling of the kiln to push them through.

This second point is further highlighted that wood chips (both pine and mixed hardwood) were fed into the kiln at approximately 15 kg/h and pellets (both straw and olive cake) fed in at approximately 45 kg/h. Because of these points which combine to give a lower residence time than the lab experiments, an apparent temperature correction to account for the average temperature seen by each of the biomass types. Quantification of the residence time once this discrepancy was noticed was not possible as in prior projects due to changes in pilot plant.

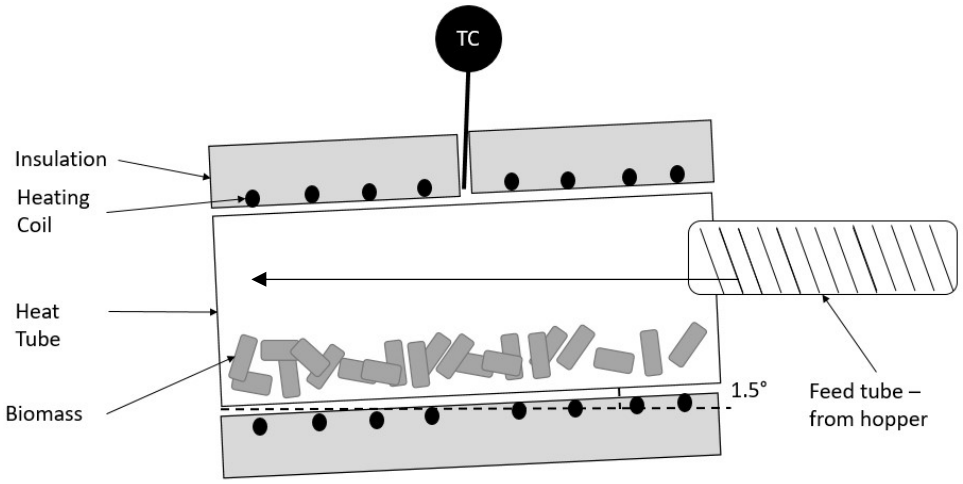


Figure 3-7. Pilot plant kiln cross section - indicating the heat tube, heating and temperature control points inside the reactor, and the feed tube containing the screw conveyor used to feed the biomass to the kiln

This correction was made based on the observed volatiles content of the charcoals, presented in Figure 3-8, as corrections based on yield could be subject to charcoal loss at various points in the system. The resulting charcoal yield comparison in Figure 3-9. To construct this plot, a 6.00% correction has been added to the total yield results, representing average losses due to grinding through the feed an product screws, losses to the pilot plant after burner, and losses of some particles in the base of the pilot plant product screw which could not be avoided. This correction is based on the average difference between all pilot plant points and their expected position on the lab trend line. Apparent temperatures during woody biomass pilot runs were approximately 50 °C lower than the set point temperature; while olive and straw runs were 100 °C lower than set point.

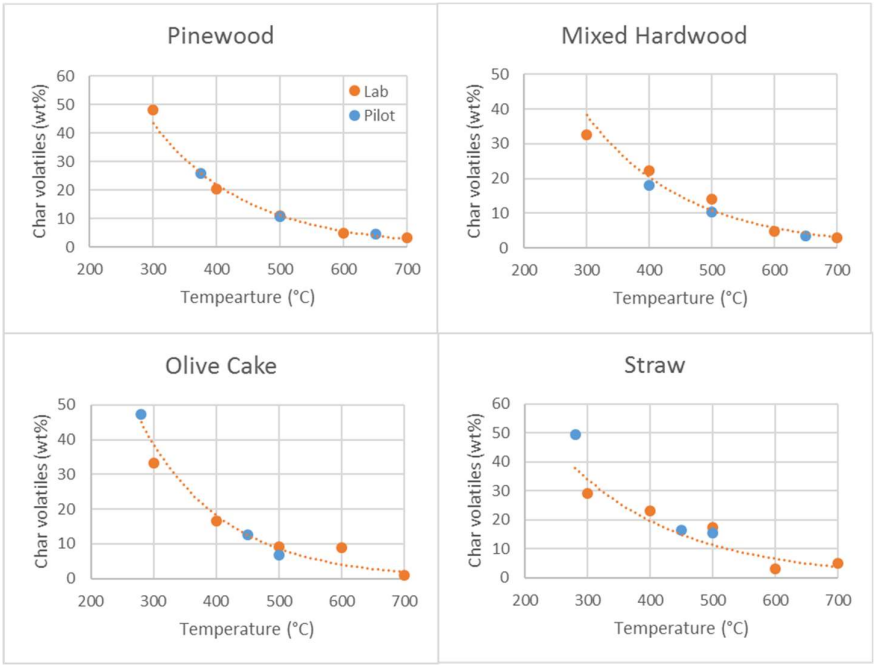


Figure 3-8. Correction of pilot plant temperatures to match the charcoal volatiles content in the pilot plant with lab data

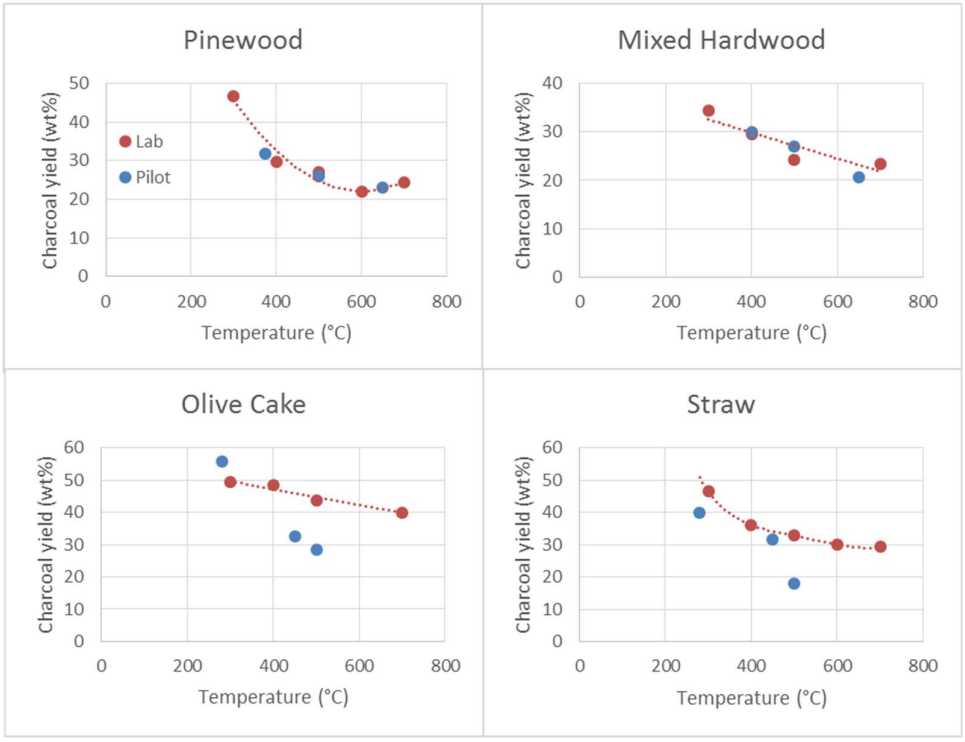


Figure 3-9. Charcoal yield – lab vs pilot plant with corrected temperatures and 6% yield correction added to the pilot plant data to account for losses due to grinding and transport in the pilot plant process.

The corrected temperatures have been made clear in Table 3-3, and from this it can be seen that there are expected trends due to the residence time effects as suggested on pg 57.

Table 3-3. Temperature corrections for volatiles consistency (all in °C)

Set Temperature	Pine	Hardwood	Olive Cake	Straw
400	375	400	280	280
550	500	500	450	450
700	650	650	500	500

3.4 Pyrolysis yield prediction

Previous work by Jenkinson (2016) has related the yield of charcoal and volatiles loss from charcoal to the aromatic carbon content (as a proxy for lignin content) and alkali metals (Ca, K) at the specific condition of 700°C, as presented in Eq. 3-7and Eq. 3-8. Jenkinson's previous work has shown that this model is universal to biomass types for complete carbonisation in a thermogravimetric analysis (TGA) system with slow heating to 850 °C, with very high (>0.99) correlation coefficients.

This work requires a model which can predict the product distribution and charcoal properties for a wide range of biomass types (which the work by Jenkinson does) and adds a temperature dependence term to this model.

$$Y_{char} = (C_{ar-C}) + (T_{d,y}\,(C_K + C_{Ca})) \qquad \textit{Eq. 3-7}$$

Symbol	Description	Units
Y_{char}	Charcoal yield, dry ash free	g/g
C_{ar-C}	Concentration of aromatic carbon in raw biomass, dry ash free basis	g/g
C_K	Concentration of potassium in raw biomass, dry basis	g/g
C_{Ca}	Concentration of calcium in raw biomass, dry basis	g/g
$T_{d,y}$	Temperature dependency of the model. In Jenkinson (2016) for 850 °C the value of this is 15.91	wt% char yield/wt% K + Ca

$$Y_{VM} = (C_{al-C}) - (16.22 * (C_K + C_{Ca})) \qquad \textit{Eq. 3-8}$$

Symbol	Description	Units

Y_{VM}	Yield of volatile matter in charcoal from raw biomass, dry ash free basis	Mass Frac.
C_{al-C}	Concentration of aliphatic carbon in raw biomass, dry ash free basis	g/g

It is expected that the constant in equation 3.7 will increase with decreasing temperature, as higher temperatures reduce charcoal yields, presented in Figure 3-10.

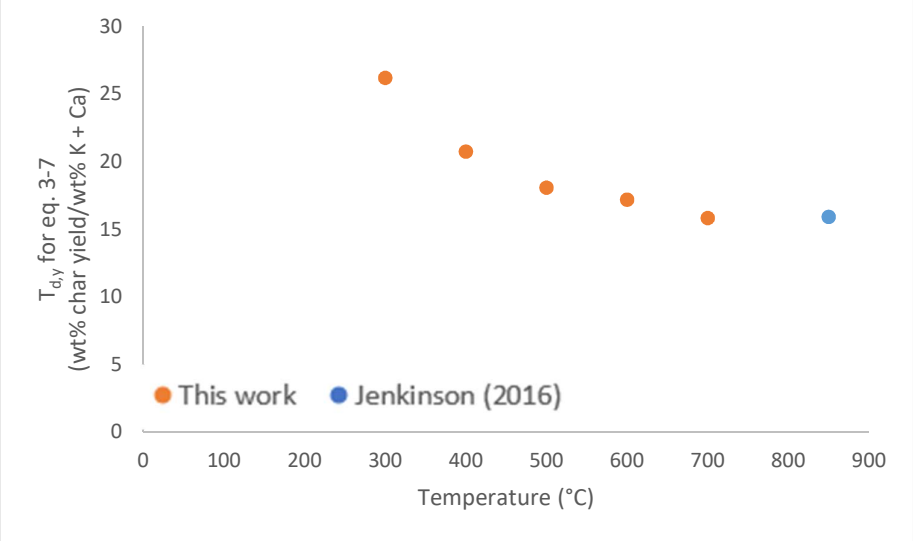


Figure 3-10. Constant $T_{d,y}$ for equation 3.7 vs temperature, highlighting how this value changes with temperature.

However, Figure 3-10 is made using K, Ca and aromatic carbon concentrations for the biomass types found by the experimental work of Jenkinson (2016) and not for the biomass used by this work. Therefore there may be some differences with the biomass batches, which means that the correlation coefficients for each of these points are very low, so while it appears there is some trends which conform to the expected theory there is high error.

The tool used to characterise biomass that has been used by this study is the method of proximate analysis, and it has been attempted to relate this biomass characterisation in a similar way to Jenkinson (2016) by adapting equations 3.7 and 3.8 to fit this framework. Overall, it would be expected that this should lead to a higher error in the yield prediction if this was expanded to a similar sized data set to Jenkinson (2016) but if error can be kept to 5% then it can match the bounds found in this experimental work. To do this it has been assumed that the aromatic carbon

and aliphatic carbon content are analogous to the volatile content; while the concentrations of K and Ca can be represented by the ash content.

The model framework was set up using a least squares model to reduce the r^2 between the experimental vs. calculated yield of all the biomass types and temperatures presented. 300 and 900 °C runs were removed from the model; 300 °C because these produced high errors and 900 °C, because there are limited data points.

3.4.1 Charcoal yield

To match the equation framework presented in Eq. 3-7, the charcoal yield model was modified to the form presented in Eq. 3-9.

Extra factors (x_1 to x_4) were added to allow the temperature dependence to be examined in more detail than the previous version of this model. x_1 and $_3$ allowed for differences in the temperature dependence to be seen independently from the effect of volatiles and as concentration which are highlighted by x_2 and x_3 . The least squares solver was run, and the resulting equation is presented in Eq. 3-10 and correlation is shown in Figure 3-11.

$$Y_{char,DAF,m} = \left(x_1 T_{pyro} + x_2\right) C_{bm_v} + \left(x_3 T_{pyro} + x_4\right) C_{bm_a} \qquad \textit{Eq. 3-9}$$

Symbol	Description	Units
$Y_{char,DAF,m}$	Charcoal yield from pyrolysis, dry ash free basis, modelled	g/g
T_{pyro}	Temperature of Pyrolysis	°C
C_{bm_v}	Concentration of volatiles in raw biomass	g/g
C_{bm_a}	Concentration of ash in raw biomass	g/g
x_{1-4}	Constants to be set by r^2 minimisation	Various

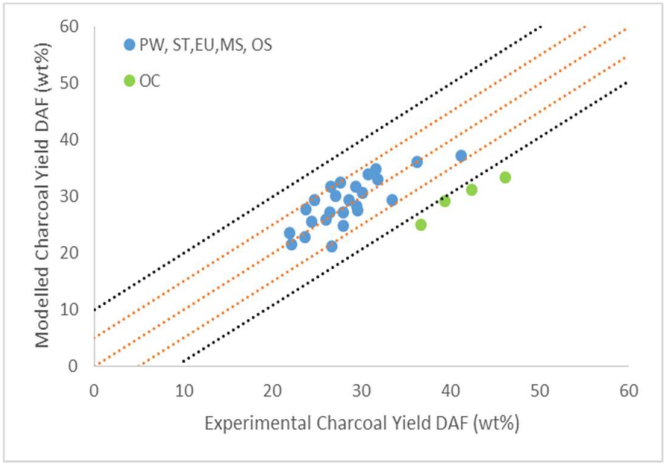


Figure 3-11 Model vs experimental fits for charcoal yield model. +/- 5 and 10% error shown

$$Y_{char,DAF,m} = \left(-3 * 10^{-4} * T_{pyro} + 0.51\right) C_{bm_v} + \left(-3 * 10^{-4} * T_{pyro} + 0.83\right) * C_{bm_a} \quad \textit{Eq. 3-10}$$

This model fits all the biomass types well, excluding olive cake. It is assumed that this is because the olive cake is quite different in terms of structure compared to other biomass types. The ash multipliers need to increase greatly to fit the olive cake data set. This error could be reduced if elemental and aromatic carbon was used instead of proximate analysis, but this highlights the trade off between simple and complex biomass analysis and is still considered acceptable for this work.

3.4.2 Liquid and Gas Yield

As this work has aimed to determine the best uses of the liquid and gas fraction of the biomass, the experimental data has been analysed to determine if similar trends can be used to generate correlations to find liquid and gas yields.

The total liquid and gas yield is then calculated by 1- charcoal yield. It was then decided that determining the fraction of these which go between liquid and gas should be calculated to determine the yield of each of these. This was done to reduce error by focusing calculation solely on either the liquid or gas concentrations.

There are assumed to be three important parts to this breakdown, as indicated in Eq. 3-11 which calculates the yield of liquid from the pyrolysis.

$$Y_{V-L} = (x_1 T_{pyro} + x_2) C_{bm_v} + (x_3 T_{pyro} + x_4) * C_{bm_a} + x_5 T_{pyro} \quad \textit{Eq. 3-11}$$

Symbol	Description	Units
Y_{V-L}	Yield of volatile fraction from pyrolysis as liquid.	g/g

The first factor $(x_1 T_{pyro} + x_2) C_{bm_v}$ looks at the amount of volatiles converted to liquid from the pyrolysis. The second $(x_3 T_{pyro} + x_4) C_{bm_a}$ looks at the effect ash has on the production of liquid, due to the catalytic cracking that can occur which can convert heavy oil produced to lighter oils and gases. $x_5 T_{pyro}$ is added on the end to account for the large effect temperature will have on this process as increased energy will mean more gas is produced relative to liquid.

The equation and fit produced are presented in Eq. 3-12 and Figure 3-12. Indication of the fit over the temperature range is show in Figure 3-14.

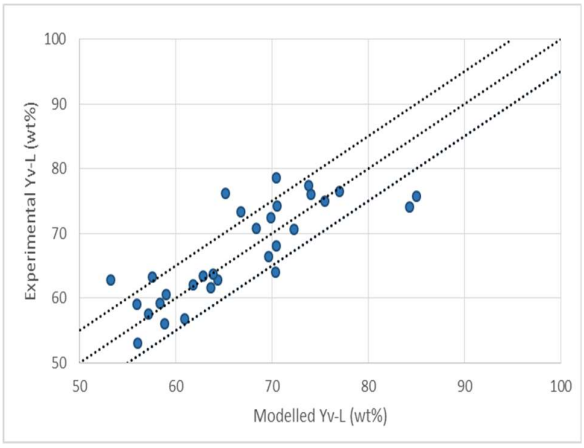


Figure 3-12 Experimental vs modelled liquid and gas ratio. Error lines showing +/- 5% deviation from the mean.

$$Y_{V-L} = (-2 * 10^{-2} T_{pyro} + 1.06) C_{bm_v} + (-2 * 10^{-2} T_{pyro} - 0.91) * C_{bm_a} + 0.0018 T_{pyro} \quad \textit{Eq. 3-12}$$

The liquid and gas yield can then be found by:

$$Y_{L,DAF} = Y_{V-L} * (1 - Y_{char,DAF}) \quad \textit{Eq. 3-13}$$

Symbol	Description	Units
$Y_{L,DAF}$	Dry ash free liquid yield – including water from pyrolysis reaction and oil – from pyrolysis	g/g

$$Y_{G,DAF} = (1 - Y_{V-L}) * (1 - Y_{char,DAF}) \qquad \textit{Eq. 3-14}$$

Symbol	Description	Units
$Y_{G,DAF}$	Dry ash free gas yield	g/g

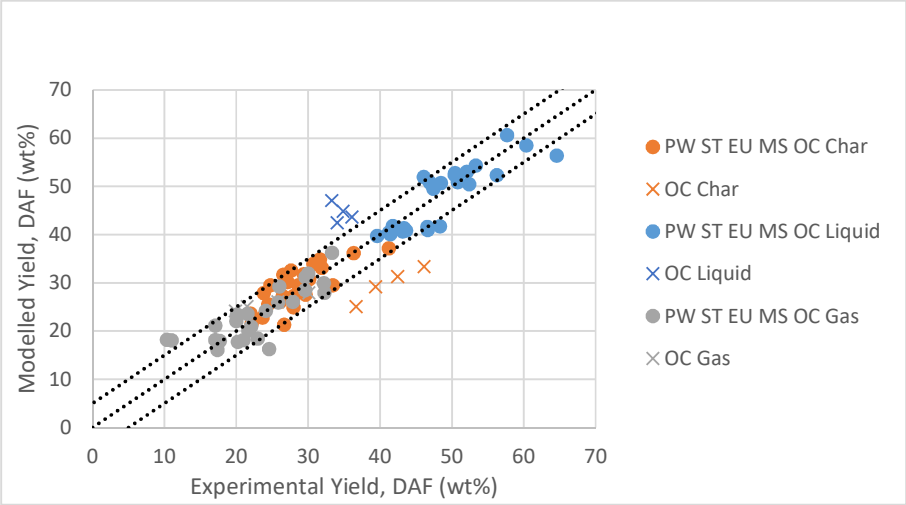


Figure 3-13. Breakdown of char, liquid and gas yield on a dry ash free basis. Error lines showing +/- 5%. Can see that Olive cake does not conform to this model.

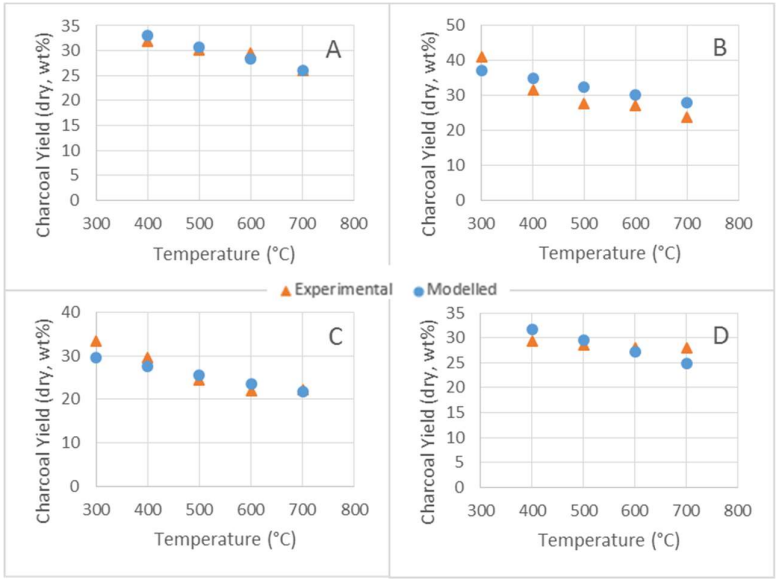


Figure 3-14. Comparison of experimental and modelled charcoal yield over the temperature range for A) pinewood B) straw C) hardwood D) olive stone

3.4.3 Charcoal quality – proximate analysis

3.4.3.1 Volatile content

Volatile content loss from charcoal is expected to have a higher rate of loss at higher temperatures, as discussed in Section 3.3.1.

Therefore, it can be read from this that the volatiles content decreases by an exponential or power law rate. It has been assumed that this can be corrected over each of the biomass types by taking into account the charcoal yield and initial biomass concentration, as outlined in Eq. 3-15. This is a different form of equation than presented in Eq. 3-8 as it is expected that temperature will dominate the effect produced by ash constituents.

$$C_{char_{v,m}} = \frac{\left(1 - x_1 T_{peak}^{x_2}\right) C_{bm_v}}{1 - Y_{char,m}} \qquad \textit{Eq. 3-15}$$

Symbol	Description	Units
$C_{char_{v,m}}$	Concentration of volatile matter in charcoal, modelled	g/g

The constants have been solved to reduce the r^2 as with before, and the equation and fit are presented in Eq. 3-16 and Figure 3-15.

$$C_{char_{v,m}} = \frac{\left(1 - 0.14\, T_{peak}^{0.29}\right) C_{bm_v}}{1 - Y_{char,m}} \qquad \textit{Eq. 3-16}$$

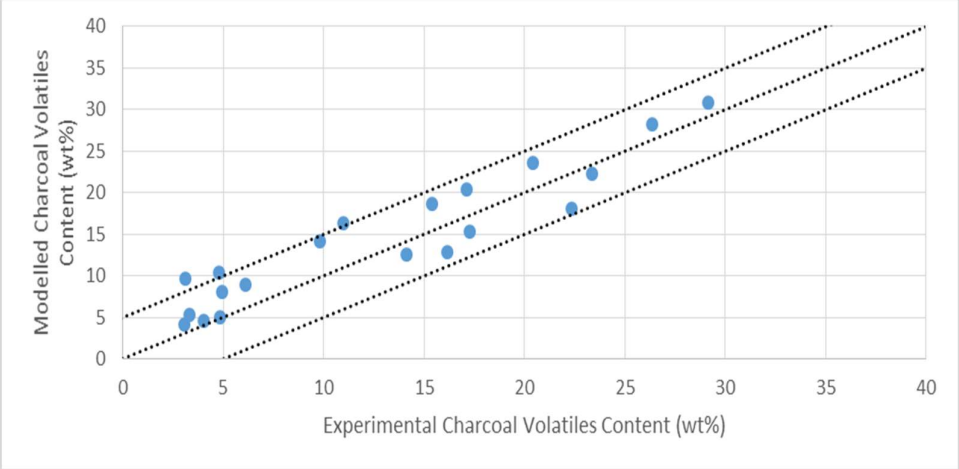


Figure 3-15. Modelled vs experimental charcoal volatiles content, wt%. Error lines showing +/- 5% error. Olive cake fits inside this model.

The fit appears good, against the 5% error threshold, but the actual useful of this model will be determined in Chapter 5 when the model will be used to predict BBQ charcoal quality which for the purposes of this project is to be the main use.

3.4.3.2 Ash content

As above, ash is assumed to be fully conserved, which would mean that Eq. 3-17 applies.

However, there appear to be some issues with this in terms of the fit, as indicated by Figure 3-16 and an extra factor (Eq. 3-18) is required to ensure a improved fit. Physically this factor could represent parts of the biomass ash which remains through the oxygen-free pyrolysis process, but are then volatised off during the oxygen rich ash process.

$$C_{char_{ash,m}} = \frac{C_{bm_{ash}}}{Y_{c,DAF}} \qquad \textit{Eq. 3-17}$$

Symbol	Description	Units
$C_{char_{ash,m}}$	Concentration of ash in charcoal, Modelled	g/g

$$C_{char_{ash,m}} = \frac{0.70\ C_{bm_{ash}}}{Y_{c,DAF}} \qquad \textit{Eq. 3-18}$$

Symbol	Description	Units
$C_{char_{ash,m}}$	Concentration of ash in charcoal, Modelled	g/g

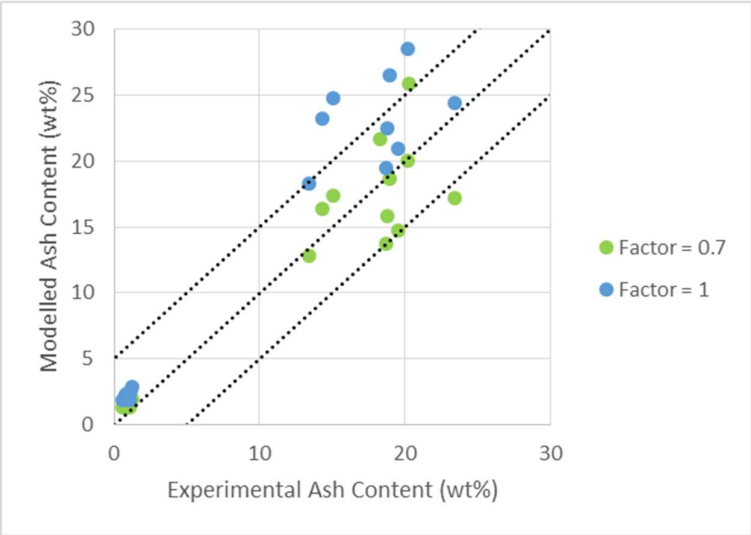


Figure 3-16 Experimental vs modelled ash content of the biomass charcoal. Shown with two modelling methods, Factor = 1 applying Eq. 3-17 and Factor = 0.7 applying Eq. 3-18.

3.4.4 Total basis yield calculations

Conversion of all yield results from dry ash free basis to total yield is performed by the process indicated in Eq. 3-19.

This method was then applied to the modelled dry ash free yields then compared to the experimentally measured total yields, as indicated in Figure 3-17. Further testing will need to be performed regarding the product yields in the economic model to

determine if this model is significant enough to be used for all biomass types, which is done in chapter 5 when the outputs of this model are used as input for the BBQ model calculation. Woody biomass appears to fit the model well, but miscanthus and straw do not.

$$Y_{x,total} = \frac{Y_{x,DAF}}{1 - C_{char_{ash}}} \qquad \textit{Eq. 3-19}$$

Symbol	Description	Units
$Y_{x,total}$	Yield on a total basis where x = gas, liquid or charcoal	g/g
$Y_{x,DAF}$	Yield on a dry ash free basis where x = gas, liquid or charcoal	g/g

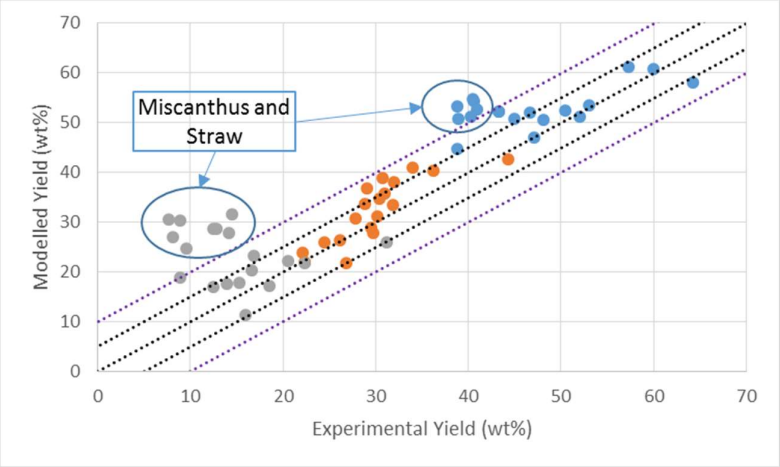


Figure 3-17. Breakdown of char, liquid and gas yield on a dry ash free basis. Error lines showing +/- 5% and 10% error. Can see that Straw and Miscanthus Liquid and Gas Yields provide high sources of error.

3.5 Conclusions

This chapter has presented the following information regarding biomass pyrolysis:

- Gray King and CPL rotary kiln pilot plant pyrolysis yields for a wide range of biomass types.
- Presented a reasoning why the lab and pilot pyrolysis results are different.

The other major deliverable achieved has been a framework of equations for biomass pyrolysis based on the simple proximate analysis of biomass, using a theory developed by Jenkinson (2016) using more complex inputs of elemental analysis and aromatic carbon concentration. This model appears to fit well for woody biomass but straw types seem to provide inaccurate liquid and gas total yield results, and olive cake appears to provide poor dry ash yield fits.

Chapter 4. Experimental catalytic pyrolysis and yield prediction

4.1 Introduction

This chapter outlines the experimental catalytic pyrolysis and reaction yield modelling work that has been completed. The aim of this work was to identify and characterise additives to pyrolysis which could increase the biomass conversion to charcoal, while also being low cost. To meet these aims, the following experimental results will be presented:

- Preliminary screening of catalyst types to determine their effect on pyrolysis yields from biomass. The catalysts screened here include:
    - Sand, HZM-5 zeolite, bentonite/montmorillonite clay minerals of both lab and industrial grade, dolomite ore, and type Y zeolite
- Detailed characterisation of bentonite/montmorillonite clay reactions during pyrolysis has then been performed to outline the effect of product yield and quality.
- Presentation of pilot plant pyrolysis experiments to determine if in situ clay pyrolysis could work at scale
- Experiments to determine if pyrolysis oils could react directly with clay minerals.

These results will then be summarised to develop a set of equations which will be used later in the project to determine the effect clay mineral addition could have on pyrolysis system design and charcoal quality.

4.2 Materials and methods

4.2.1 Biomass types used

The biomass types used for these experiments have been described in Chapter 3. The main biomass used has been pinewood, with supplementary data from olive cake, straw, eucalyptus, miscanthus and olive stone. Experiments using bentonite clay were also completed using the wet and dried pinewood and olive cake.

4.2.2 Catalyst types used

Several types of catalyst have been sourced and screened as part of this study, outlined in Table 4-1.

Table 4-1. Outline of types of catalytic material used, acid base properties and biomass source

		Acid/Base Properties	Source
1	Kiln Dried Sand	None	CPL trade supplier
2	Cement	Mixed	CPL trade supplier
3	Lab Grade Bentonite Clay	Acid	Sigma Aldrich
4	Industrial Grade Bentonite	Acid	CPL trade supplier
4A	Industrial Grade Bentonite (milled)	Acid	CPL trade supplier
5	Dolomite	Base	SKA minerals
6	HSM 5 Zeolite	Acid	Sigma Aldrich
7	Type Y Zeolite	Acid	BASF

4.2.3 Pyrolysis method

4.2.3.1 Gray-King Assay with Catalyst Addition

The method used here is the same as in Section 3.2.2.1 of this thesis, with the following changes:

- Biomass and catalyst material were weighed, then mixed together in a beaker to ensure distribution of the catalyst over the biomass.
- The mixture was then transferred to the quartz retort tube, and pyrolysis was conducted as in Section 3.2.2.1, using the heating rate of 20 °C/min and residence time at peak temperature of 60 mins.

For the detailed characterisation of some of the catalyst effects:

- Liquid was collected for moisture content and composition analysis by GC-MS, which have been included in Appendix 2 (method outlined in Section 4.2.4).

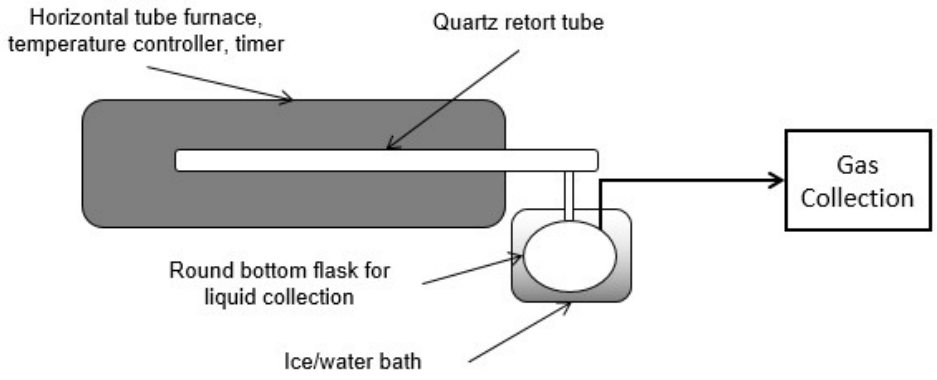


Figure 4-1. Gray King lab pyrolysis system with gas collection method added

- Gas was collected by attaching a 1 L tedlar gas bag to the outlet of the round bottom flask, as shown in Figure 4-1. This was then analysed by GC-FID/TCD as outlined in method 4.2.4.1.

A full list of the experimental runs performed and the analytics done on each experiment in this section can be found in Appendix 2.1, 2.2 and 2.3.

[redacted]

4.2.3.3 Pilot plant pyrolysis methodology

The pilot plant pyrolysis method that was used is the similar to that has been outlined in section 3.2.2.2 of this thesis. Clay was added with the biomass at the desired concentrations by adding it to the vessel used to add biomass into the hopper. Mixing was ensured by shaking of the clay into the biomass transport vessel and due to the mixing action in the hopper. Charcoal collection and analytics where performed using the same method as done previously.

4.2.4 Analysis techniques

Analysis techniques used with catalytic pyrolysis are the same as those listed in section 3.2.3, with the addition of techniques to analyse the quality of the liquid and gas produced.

4.2.4.1 Gas collection and analysis

The gas bag was sealed following pyrolysis, then using a 5 ml sample was taken via gas syringe and analysed. This was done by Gas Chromatography (GC) (Clarus 580N) with Flame-Ionisation Detector (FID) and a Thermal Conductivity Detector (TCD) operating at 200°C using the method developed by Uguna *et al.* (2016). Samples were injected in split mode (split ratio 10:1). The injector temperature for the FID and TCD was 250 °C and 165 °C respectively. The oven temperature was held at 60 °C for 13 minutes before increasing to 80ºC at a heating rate of 10 °C/min with a hold time of 10 minutes. Argon was used as the carrier gas. The analysis was looking for alkanes and alkenes C1-C5, CO_2 and CO. The remaining sample volume was determined via gas syringe and used to determine the weight percentage of the gas components

4.2.4.2 Liquid analysis

Oil samples were weighed into a sample tube and diluted with dichloromethane. Gas Chromatography with Mass Spectrometry (GC-MS) in full scan mode (m/z 40-450) was performed on the samples with a Varian CP-3800 gas chromatograph, interfaced to a Varian 1200 mass spectrometer (EI mode, 70 eV). Separation was made using a ZB-1701 fused silica capillary column (60 m x 0.25 mm i.d., 0.25 mm thickness), with helium as the carrier gas, and an oven programme of 50°C (hold for 2 min) to 300°C (hold for 33 min) at 5°C/min. GC-MS output covers the range up to number of carbon atoms (NC) 35.

The chromatograms where then split into heavy and light fractions based on the retention time of 4 methyl phenol (boiling point 201°C, molecular weight 108.13g/mol, approximately NC-13). The relative peak area before and after this compound were then compared to get a qualitative measure of oil cracking.

4.2.4.3 Dean-Stark titration

Dean-Stark titration (Dean *et al.*, 1920) was used to determine the moisture content of the pyrolysis oils. This was done using toluene as a higher boiling solvent than water. Water was boiled off the oil and collected in a dean stark tube.

4.2.4.4 Dry ash free yield calculation outline

Due to the additives used, the yield calculations have been modified to reflect this. The dry ash free yield in this allows the calculation of the biomass breakdown alone. This is because there are no carbon or large volatile components, apart from the chemical moisture in the structure of these additives.

$$Y_{charcoal,DAF,Cat} = \frac{M_{charcoal}(1 - C_{a,charcoal})}{M_{biomass,wet}(1 - C_{m,bm})(1 - C_{a,bm})} \quad \textit{Eq. 4-1}$$

Symbol	Description	Units
$Y_{charcoal,DAF}$	Yield of charcoal from biomass pyrolysis on a DAF	g/g
$C_{a,charcoal}$	Ash content of charcoal from proximate analysis	g
$C_{a,bm}$	Ash content of biomass from proximate analysis	g

$$Y_{liquid,DAF,Cat} = \frac{M_{liquid} - M_{biomass,wet}C_{m,bm} - M_{add,wet}(C_{m,add})}{M_{biomass,wet}(1 - C_{m,bm})(1 - C_{a,bm})} \quad \textit{Eq. 4-2}$$

Symbol	Description	Units
$Y_{liquid,DAF}$	Yield of liquid, DAF basis	g/g

Again, the gas yield has been calculated by difference, as shown in Eq. 4-3.

$$Y_{gas,DAF,Cat} = 1 - Y_{charcoal,DAF,Cat} - Y_{liquid,DAF,Cat} \quad \textit{Eq. 4-3}$$

Symbol	Description	Units
$Y_{gas,DAF,Cat}$	Total yield of gas, DAF basis for catalytic experiments	g/g

4.3 Catalytic pyrolysis screening results

This section will outline the effect of the different catalysts used on the charcoal yield. The results of catalytic pyrolysis dry ash free charcoal yield at 500 °C will be presented here, with additional results, including other pyrolysis temperatures and liquid/gas yield properties where available presented in Appendix 2.1.

The different catalyst types work to affect the pyrolysis in different ways, with expected mechanistic details explained in the literature review, section 2.4.3.

4.3.1 Sand effects

Figure 4-2 indicates that sand is inert to the pyrolysis process. This result is interesting due to some reactor systems using sand as an indirect heating medium (Brown *et al.*, 2012).

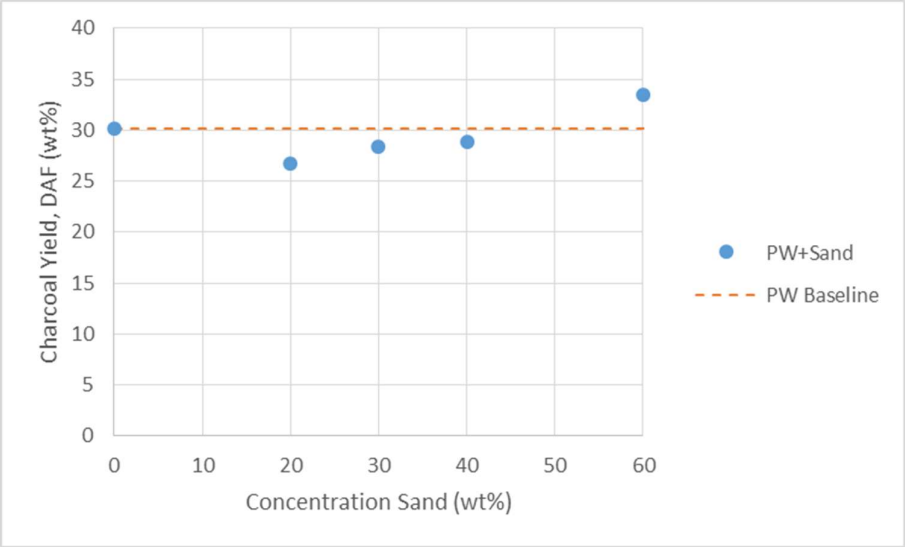


Figure 4-2 Charcoal yield effects on a dry ash free basis of increasing concentration of sand on pinewood pyrolysis at 500°C. Indicates there are no effects from sand addition

4.3.2 Cement effects

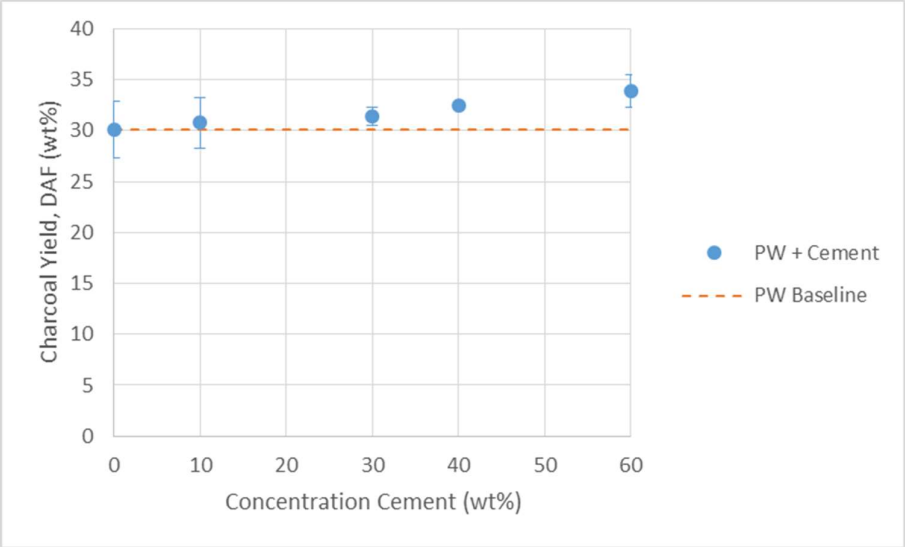


Figure 4-3 Charcoal yield effects on a dry ash free basis of increasing concentration of cement on pinewood pyrolysis at 500 °C. Indicates there are negligible effects on charcoal yield..

Figure 4-3 shows the effect of cement at 500°C, which indicates no effect on the charcoal yield. Changes are also not seen in the oil composition which indicates that no catalytic activity is occurring.

4.3.3 Bentonite clay effects

4.3.3.1 Lab grade

Lab grade bentonite clay has been shown to be useful in fast pyrolysis systems, and its low cost appeal means the results presented in Figure 4-4 are promising, as extra carbon is kept by the clay. Figure 4-5 provides more evidence that this effect is a catalytic one as when more inert material (sand) was added to the pyrolysis the amount of extra yield appears to still be proportional to the clay concentration.

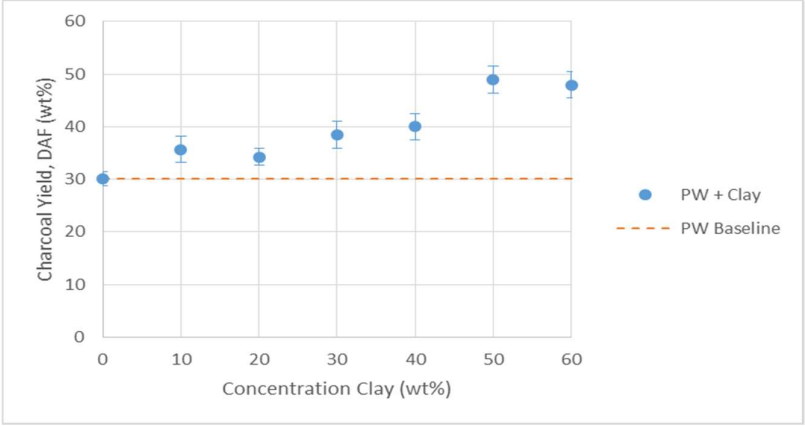


Figure 4-4. Charcoal yield effects on a dry ash free basis of increasing concentration of bentonite clay on pinewood pyrolysis at 500 °C. Indicates that there is increasing charcoal yield from adding clay to the pyrolysis

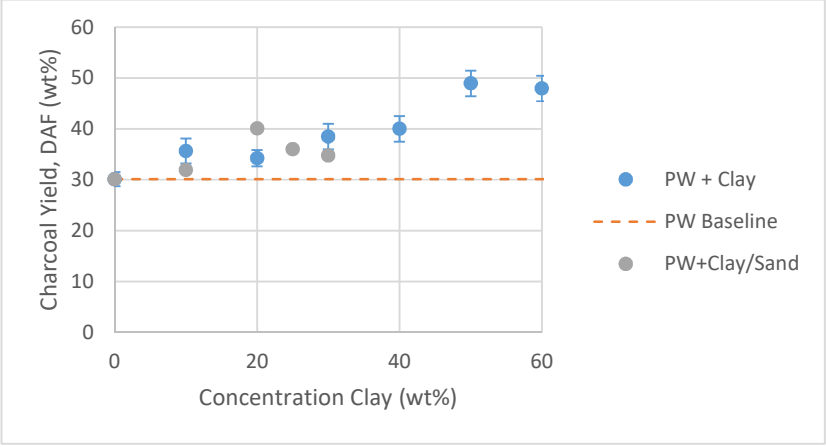


Figure 4-5 Charcoal yield effects on a dry ash free basis of increasing concentration of clay and sand addition on pinewood pyrolysis at 500°C. Indicates that that there are no dilution effects from adding sand to pinewood/clay pyrolysis.

4.3.3.2 Industrial grade

To run pilot plant studies, a new commercial scale batch of bentonite clay was required. This came as 3-4 mm granules, rather than the 100 micron powder which had been used in the lab.

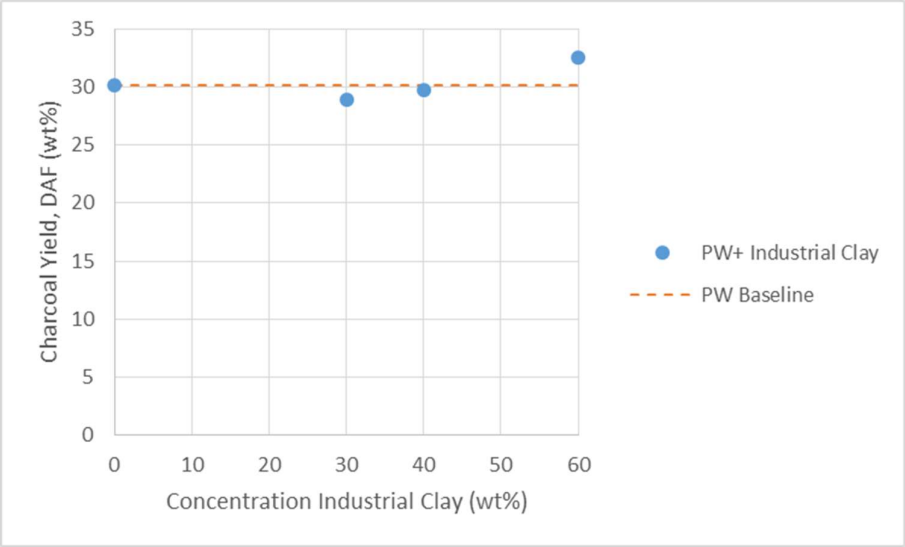


Figure 4-6 Charcoal yield effects on a dry ash free basis of granular clay on pinewood pyrolysis at 500°C. Indicates that large particles of industrial bentonite clay do not effect the pyrolysis.

As shown in Figure 4-6, no catalytic effect was observed and thought to be due to the poor contacting in the Gray King pyrolysis.

The clay granules where then milled and as seen in Figure 4-7 there is a slightly lower increase than with the lab powder. This is thought to be because the granular clay was only hand milled, and a larger particle size exists which means contacting is slightly lower.

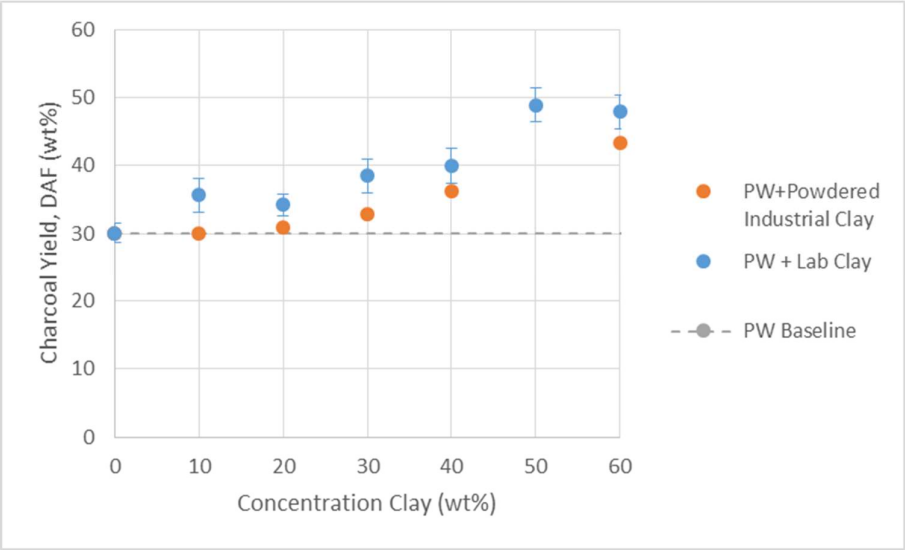


Figure 4-7 Charcoal yield effects on a dry ash free basis of powered granular clay on pinewood pyrolysis at 500°C. Shows that grinding the bentonite clay to smaller particles improves its catalytic properties.

4.3.4 Zeolite

4.3.4.1 ZSM-5

Interestingly there are two different observations about the untreated zeolite. Pinewood (Figure 4-8) observes no or slight negative change in charcoal yield, while olive cake (Figure 4-9) observes a higher yield. This could be related to the composition of two biomass types, as there is more oxygenates produced from pinewood pyrolysis than olive cake which are ignored by ZSM-5 especially in this pore sizes (Bridgewater, 2012; Uzun *et al.*, 2007; Wang *et al.*, 2016b).

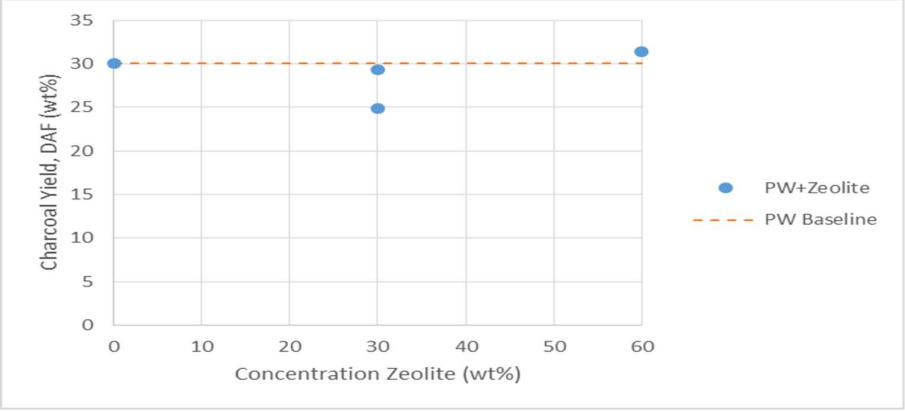


Figure 4-8. Charcoal yield effects on a dry ash free basis of ZSM-5 zeolite on charcoal yield on pinewood pyrolysis at 500°C. Shows that there is a negative to no effect on adding this to pyrolysis. Two data points at 500°C indicate potential variability in the experiment.

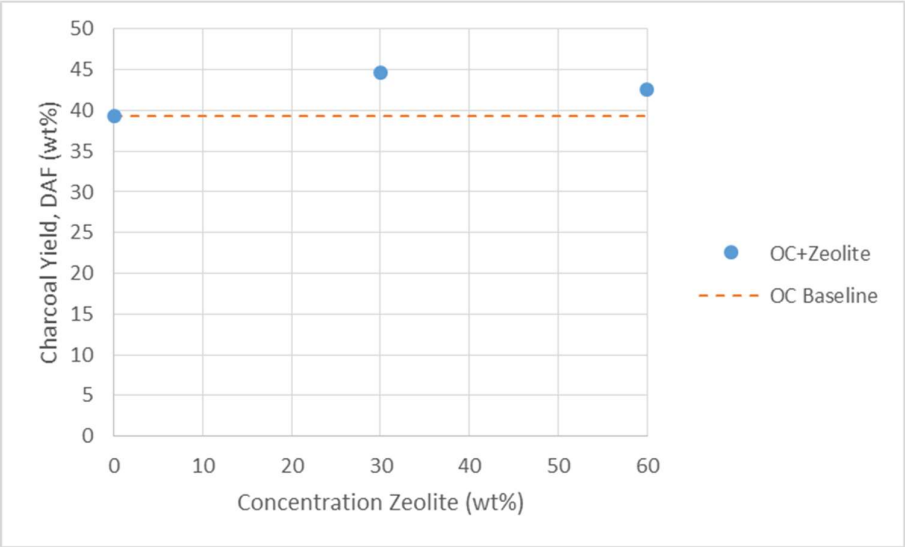


Figure 4-9. Charcoal yield effects on a dry ash free basis of ZSM-5 zeolite on the charcoal yield from olive cake at 500 °C. Indicates that there is a more positive effect on adding this to olive cake pyrolysis. Only one experiment was done at each point.

4.3.4.2 Type Y

Figure 4-10 shows the effect when larger pore size Type Y zeolite is used (Kumar *et al.*, 2017). This is a significant catalyst effect and similar to the effect observed with bentonite clay, as expected. In fast pyrolysis systems a larger catalyst effect would be expected but it is thought that the lower temperature favouring the oil to char reaction prevents this.

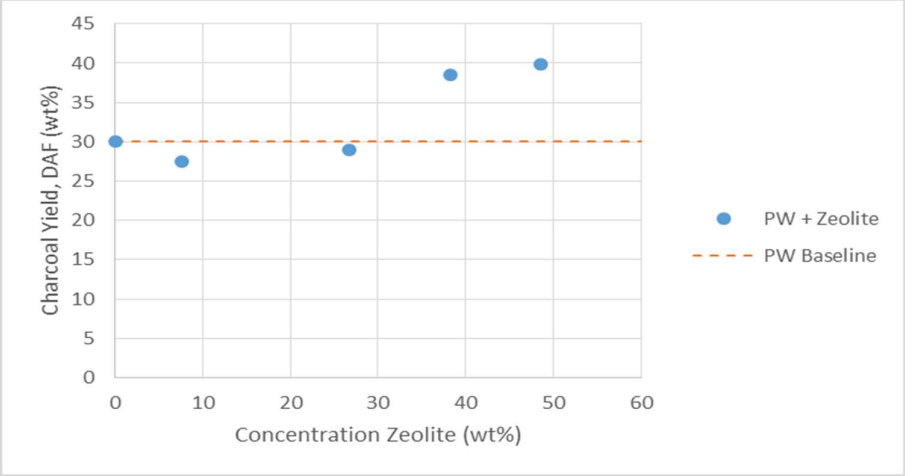


Figure 4-10 Charcoal yield effects on a dry ash free basis of Type Y zeolite on charcoal yield from pinewood at 500 °C. Shows there is likely to be a positive effect from adding larger pore size zeolite to pinewood slow pyrolysis.

4.3.5 Dolomite

Dolomite minerals, based on MgO, have been shown to heavily foul under pyrolysis conditions (Li *et al.*, 2017; Stefanidis *et al.*, 2016). Dolomite is basic compared to the solid acid zeolites or clays assessed and achieves its catalyst effect via ketonization and condensation, as opposed to the carboxylation/deoxygenation mechanism. Stefanidis *et al.* (2016) also suggest that the residue deposited on dolomite is more volatile than that on zeolite is more volatile and therefore maybe easily removed. This trial was performed after the bentonite clay was assessed, and this experiment is included to provide a basis for future work, based on a different reaction mechanism.

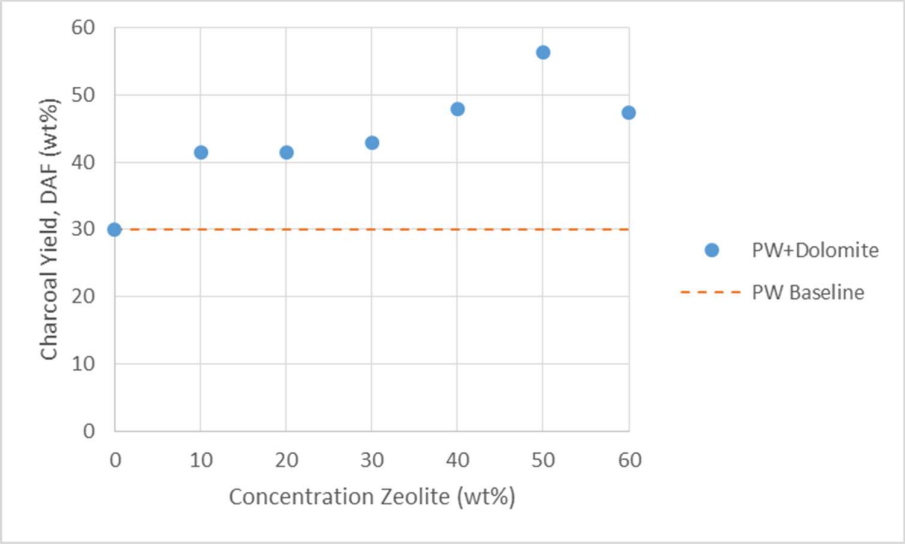


Figure 4-11 Charcoal yield effects on a dry ash free basis of dolomite on charcoal yield from pinewood pyrolysis at 500 °C. Shows there is a positive effect of adding solid base catalyst to pinewood slow pyrolysis.

4.3.6 Discussion of results from various catalysts screened

This section has indicated that there are a wide range of additives which can have a variety of different effects on the biomass breakdown during pyrolysis. As the aim of this work was to find catalytic material which were both low cost and able to increase the carbon yield as charcoal, it has been determined that solid acid catalysts are the most effective.

From these results, it has been determined that montmorillonite, dolomite, and porous acidic zeolites produce positive results. However, the cost parameter is only met by montmorillonite clay therefore, detailed characterisations will be carried out on this material.

4.4 Detailed characterisation of bentonite clay as a slow pyrolysis catalyst

This section presents detailed results from the pinewood montmorillonite experiments, as published in Russell *et al.* (2017a). Further results on the other biomass species are presented in Appendix 2.1.

Figure 4-12 and Figure 4-13 present the pyrolysis yield breakdown on a dry (relative to raw) biomass ash free, clay free basis (as clay provides mostly ash, this is referred to as dry ash free basis (DAF)). These two figures show a reduction in oil yield, which causes an increase in charcoal and gas yield, although at 700°C there is some water loss which could be due to favoured gas phase reactions utilising the water, under steam reforming pathways (Min *et al.*, 2011a). Parallels with the 1:6 weight ratio (16.7 wt%) bentonite 450°C experiment by Veses *et al.* (2015) can be seen by interpolating between the 400 and 500°C experiments in this study, indicating some agreement between the works.

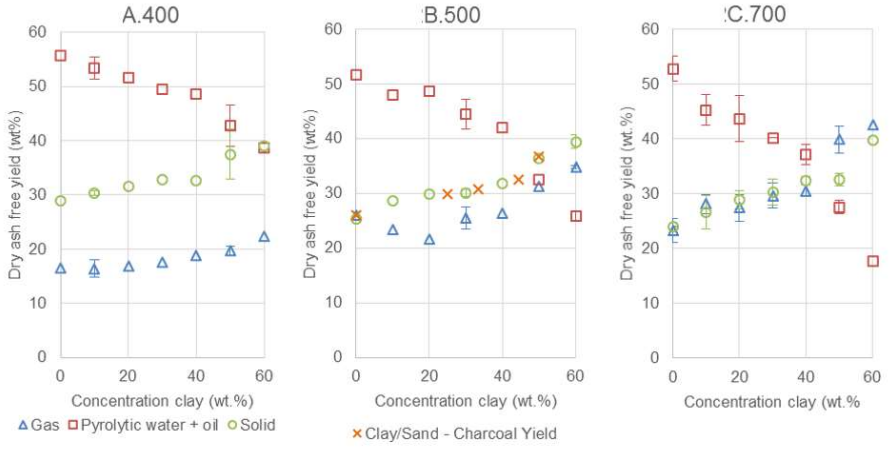


Figure 4-12. Gas, charcoal and liquid phase yields (DAF basis) of pine wood at 400°C (A), 500°C (B), 700°C (C) with 6 concentrations of clay (0, 10, 20, 30, 40, and 60 (%wt). Gas yield is calculated by difference.

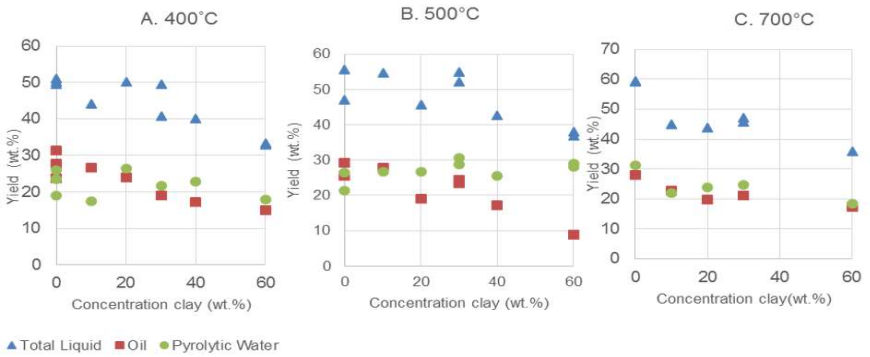


Figure 4-13. Changes in oil/pyrolytic water breakdown of liquid phase produced during pyrolysis at 400°C (A), 500°C (B) and 700°C (C).

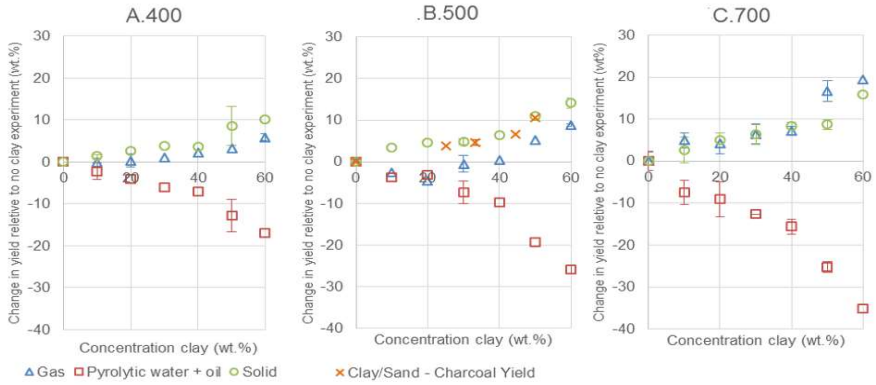


Figure 4-14. Change in product yields relative to no catalyst pyrolysis, dry ash free basis, at 400°C (A), 500°C (B) and 700°C (C).

Plotting these charts to show the difference in yield with non-catalysed pyrolysis (Figure 4-14) highlights how these changes in conversion preference are occurring and shows that the main driver for the reaction to change is temperature. Figure 4-12B and 4-14B compare the charcoal yield in a system using sand, i.e. extra inert material, as well as the clay. This shows that there is a little difference in the level of extra charcoal production when sand is added to the system, indicating secondary char formation due to pore blocking or physical oil interaction with solid particles is relatively low. This observation provides evidence that the reaction presented is an effect of the solid acid catalyst properties of the clay. The absolute extent of the oil conversion to extra charcoal may be influenced by factors not studied as part of this set of experiments aiming to determine the fundamental concept that clay catalyst can be used in context. The main factor that could affect this is volatile residence time post pyrolysis (which is relatively high in the case of Gray-King pyrolysis where

no sweep gas is used), and contact of volatiles with the clay and charcoal post volatilisation. At lower temperatures, the conversion of oil to charcoal is favoured, while at higher temperature the conversion to gas is preferred. Due to the nature of the clay mineral and findings from literature, it is speculated that these results are showing catalytic cracking of the liquid into the charcoal and gas products, which is expected to become more efficient at higher temperatures as gas phase cracking become more dominant (Min *et al.*, 2011a; Veses *et al.*, 2015). There may be some evidence in the data that low concentrations of clay experience some inactivation due to blocking of active site by charcoal condensation on the clay surface, but further experiments are required to determine the full extent of the clay's activity.

4.4.1 Effect of biomass moisture content on catalytic activity

The effect of using clay with wet biomass is presented in Figure 4-15. There are two things to observe in this plot:

- There is the same decreased charcoal yield, as observed in Section 3.3.2
- There is also a reduction in the catalytic effect, as indicated by the reduced slopes in a linear fit of the charcoal yields.

It is speculated that this reduction in yield occurs because even though there should be an increased oil yield with higher clay concentrations, in the gas phase the oil is diluted and therefore the residence time of oil in the clay bed is reduced so not as much oil can be reacted.

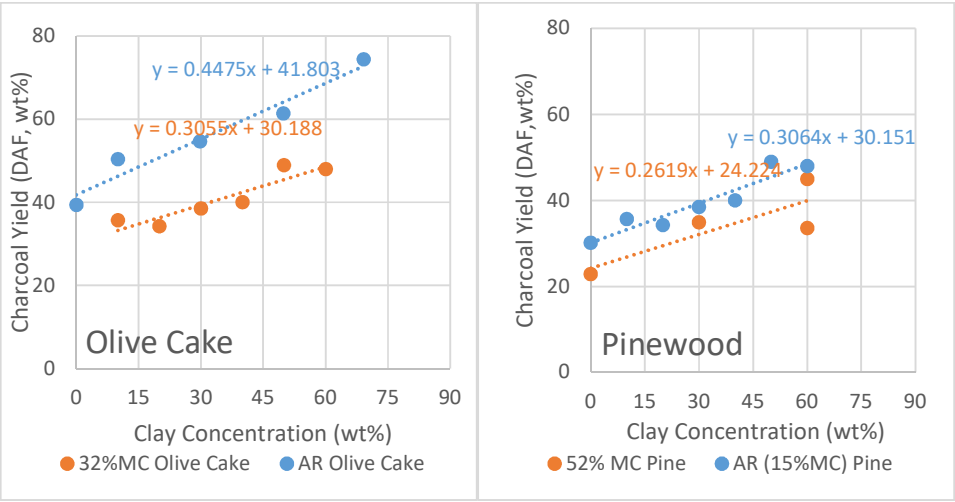


Figure 4-15. 500 °C charcoal yield using pine and olive cake with clay at various moisture content

4.4.2 Changes in product streams quality

4.4.2.1 Effect of clay addition on charcoal quality

As the clay and charcoal were not separated, the effect the clay has on the charcoal quality was estimated by determining if there were any differences between the calculated volatiles content and the content measured experimentally (Figure 4-16) by subtracting the volatiles from the clay. As can be seen, there are no adverse effects, i.e, significant change in volatiles, from the addition of clay to the experiments. Therefore it is proven that charcoal quality is not affected by clay addition.

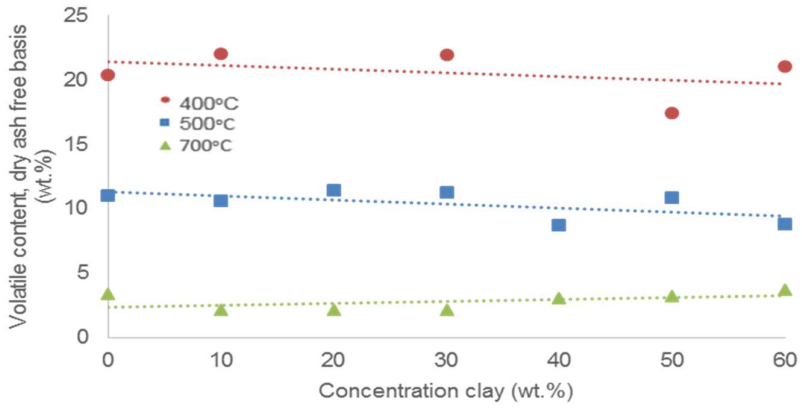


Figure 4-16. Volatile content of charcoal produced by pyrolysis of pinewood with increasing clay concentration on a dry ash free basis. Shows that there is minimal change on the volatiles content of charcoal with increasing clay concentration.

4.4.2.2 Effect of clay addition on oil composition

Figure 4-17A presents the GC-MS analysis of the liquid stream for 0, 30% and 60% clay concentration experiments at 500°C, to highlight the oil composition changes with clay concentration and Figure 4-17B shows the temperature effects from 500 – 700°C, at 60% clay concentration. Figure 4-18 breaks these streams down into heavy and light fractions, and shows that there is a significant cracking effect as light fraction increases from approximately 50% to around 80% of the total oils in the sample. From these plots, it can be seen there is considerable beneficial effect on the composition of the oil via the addition of clay, as the larger oils are cracked to smaller compounds. Figure 4-18 also indicates that there is some increase in the cracking effect by increasing temperature, as expected (Balat *et al.*, 2009; Min *et al.*, 2011b) from previous studies but in terms of the relative cracking effect, increasing temperature only increases the total amount of oil cracked.

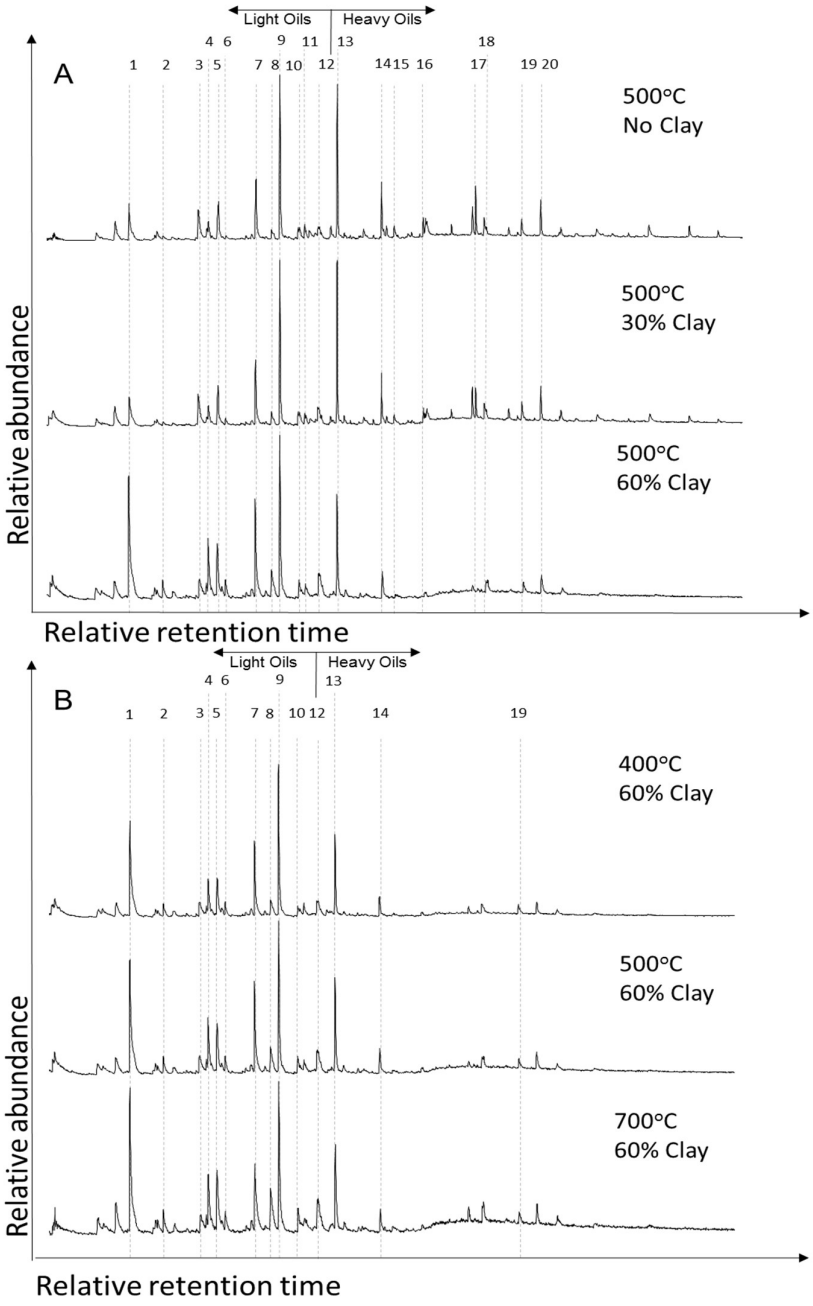


Figure 4-17 Total ion chromatograms from the GC-MS of oils from pyrolysis: Plot A. Constant temperature, 500°C increasing clay concentration, 0 -60 wt% and Plot B. Constant clay concentration, 60 wt%, and increasing temperature 500 – 700°C. Arrows above the chart are indicating heavy and light oil fractions. Peak assignments: 1. furfural 2. 2 methyl cyclopent-1-one, 3. 1,2 cyclopentadiene, 4. 5 methyl furan carboxaldehyde, 5. 2-furanone, 6. 5 methyl furanone, 7. 2 hydroxy 3 methyl 2 cyclopent-1-one, 8. phenol, 9. 2 methoxy phenol, 10. 2 methyl phenol, 11. 3 methyl phenol, 12. 4 methyl phenol, 13. 2 methoxy 4 methyl phenol, 14. 4

ethyl 2 methoxy phenol, 15. Dianhydro glucopyranose, 16. eugenol, 17. 2 methoxy 4 propenyl phenol, 18. vanillin, 19. Hydroxy methoxy phenol 2 ethanone, 20. Hydroxy methoxy phenol 2 propanone. -- Repeat these analysis on the olive cake and put in the appendix.

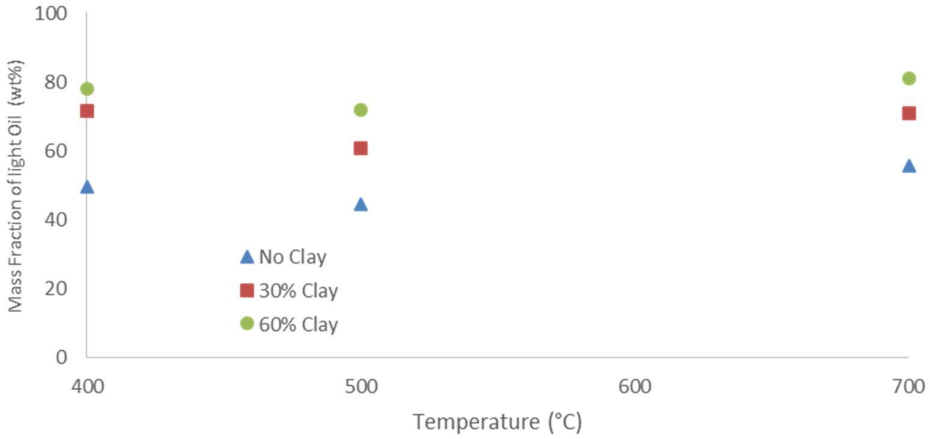


Figure 4-18. Effect of clay concentration and temperature on fraction of light oils produced by pyrolysis. Distinction between heavy and light oil based on retention time above that of 4-methyl phenol; BP of 201°C, molecular weight, 108.13g/mol.

These observations, with the loss of oil and gain in charcoal are evidence that there is a temperature and clay dependent cracking reaction occurring. This is causing the breakdown of heavy oils from the biomass pyrolysis and having the effect of improving the oil, potentially drastically lowering the cost of refining before sale or increasing heating value. More charcoal is also produced, which it is assumed could either be burnt off to regenerate the clay, or utilised as the clay/charcoal mixture in some manner.

4.4.2.3 Effect of clay on gas composition

The changes in gas composition are presented in Figure 4-19. There are two main trends to be seen from this:

- Organic gases and CO increase in concentration with both temperature and clay concentration. This is expected as more fragments from the cracking reaction are likely to be present with both of these conditions
- CO_2 levels reduce with increasing temperature and clay concentration. This is a result of the production of CO and organic gases which dilutes CO_2.

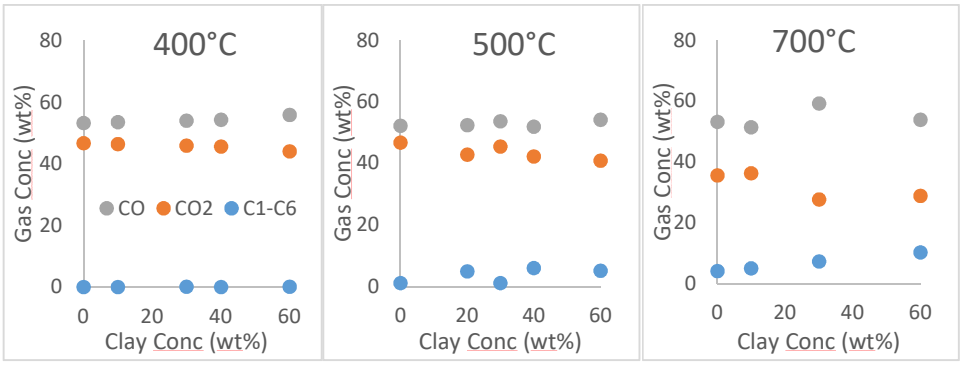


Figure 4-19. Changes in gas composition with increasing temperature and clay concentration, using pinewood at 400, 500, 700 °C

4.4.2.4 Differences in by-product quality using other biomass and catalyst

This section discusses changes observed in the liquid and gas quality when clay was contacted with olive cake, and pinewood was contacted with type y zeolite and dolomite.

Effect of olive cake and clay

As mentioned in section 4.3.4.1, olive cake produces a significantly different quality of oil compared to pinewood, as can be seen in the breakdown in oil quality changes in Figure 4-20 and GC-MS output in Appendix 2.2.1. This shows that while there is significantly less light oil produced from olive cake pyrolysis, clay addition can have a similar effect increasing the abundance of them.

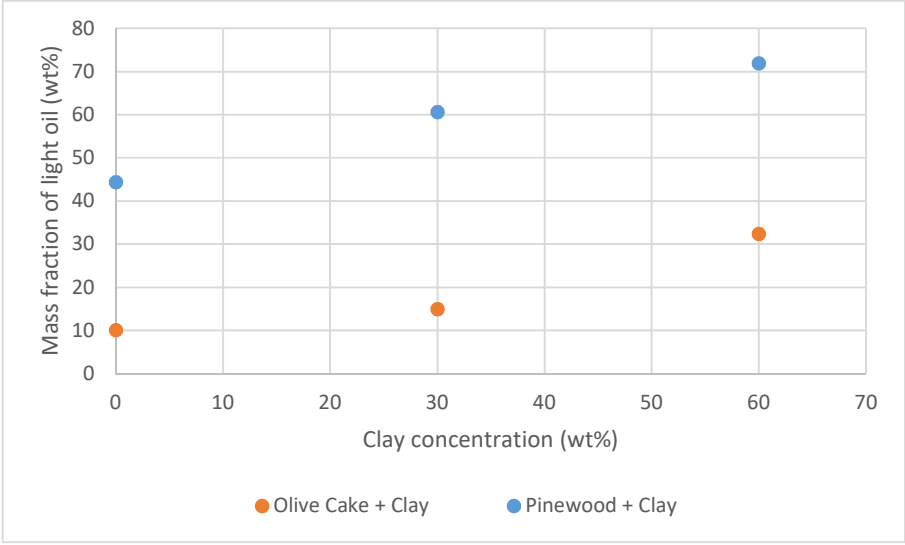


Figure 4-20. Relative mass fractions of light oil from olive cake and clay pyrolysis at 500°C. Pinewood and clay experiment at 500°C baseline shown

During these runs, characterisation of the gas streams was not possible, but as similar effect on the oil quality has been observed, it is expected that these changes occur in the gas phase here too.

Effect of Type Y Zeolite

Type Y Zeolite is a similar solid acid catalyst to the bentonite clay and therefore the changes in quality of oil in Figure 4-21 with raw GC-MS output in Appendix 2.1.1, are showing expected activity changes.

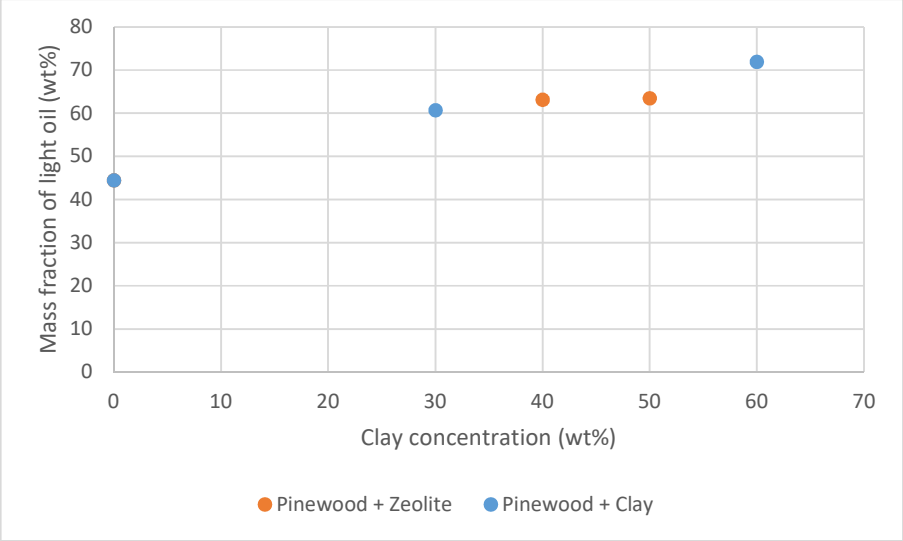


Figure 4-21. Relative mass fractions of light oil from pinewood and zeolite pyrolysis at 500°C. Pinewood and clay experiment at 500°C baseline shown. Oil analysis was not performed on other zeolite points.

Effect of Dolomite

When pinewood and dolomite were contacted, the changes in gas quality are presented in Figure 4-22, and breakdown of oil quality is presented in Figure 4-23, with raw GC-MS outputs presented in Appendix 2.1.1.

What can be seen from these plots is a more significant increase in the CO_2 levels produced in the gas phase, while similar levels of organics are present in the gas phase, which is consistent with the findings from Stefanidis *et al.* (2016). There also appears to be significant conversion to the lighter oils as seen with solid acid catalyst addition.

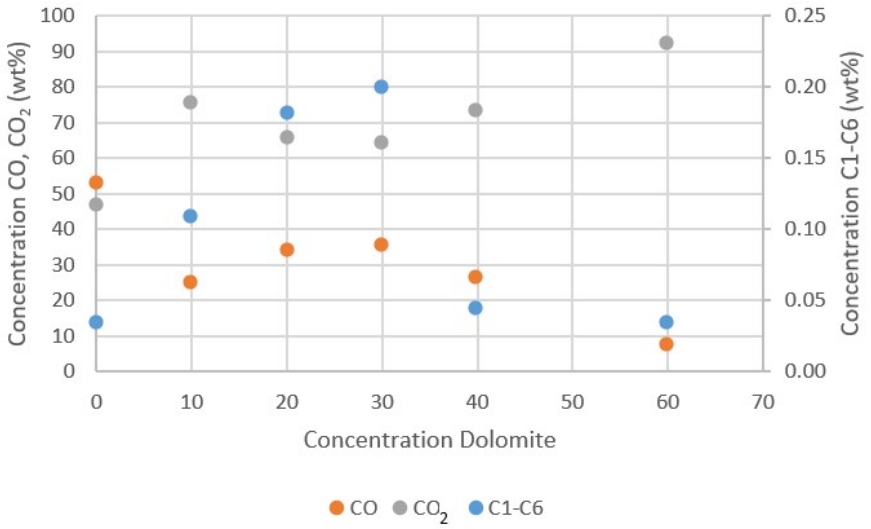


Figure 4-22. Changes in gas composition using dolomite in pinewood at 500 °C. Shows there are increasing levels of CO_2 with increasing dolomite concentration, while CO reduces. C1-C6 compounds are low concentration so experimental error could cause the trend seen here.

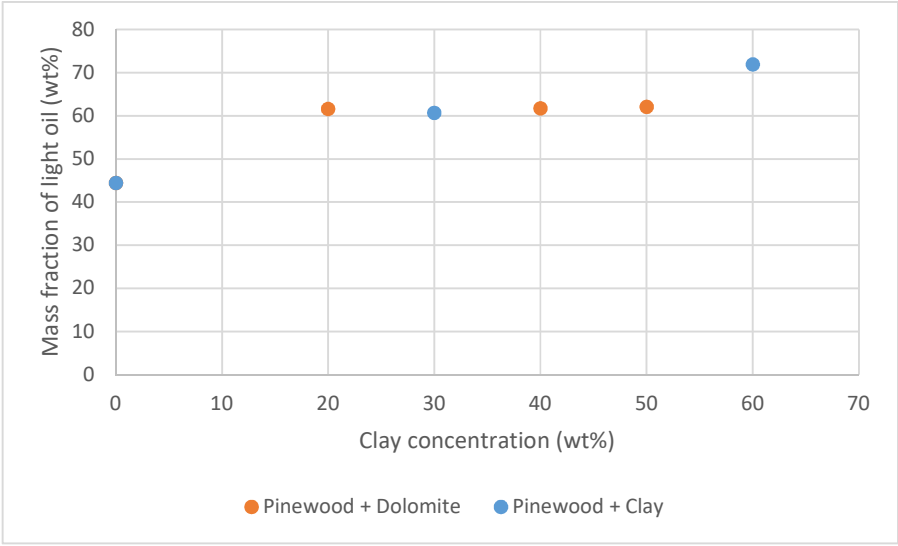


Figure 4-23 Relative mass fractions of light oil from pinewood and dolomite pyrolysis at 500°C. Pinewood and clay experiment at 500°C baseline shown.

4.5 Pilot catalytic pyrolysis

Runs have been done using pinewood and the granular clay. It is thought that the increased mixing in the pilot kiln would improve the contacting, and it was considered unfeasible to mill the quantity of granular clay required for the pilot plant

work. The yield results from this are produced in Figure 4-24, while the proximate analysis are presented in Figure 4-25.

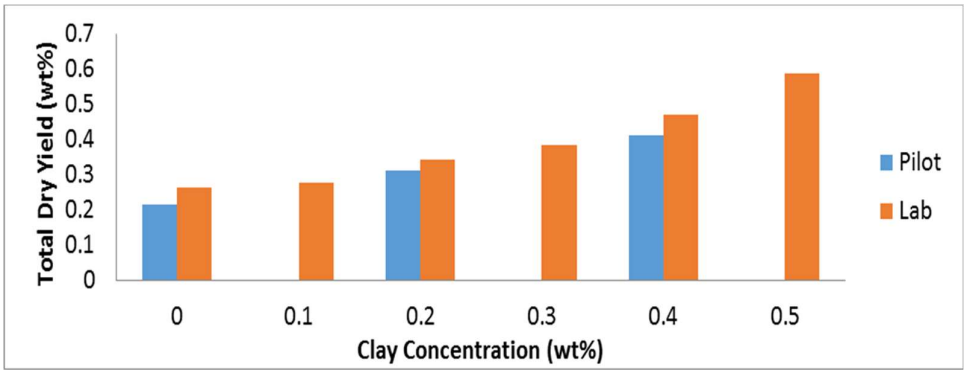


Figure 4-24 Charcoal yield on a dry ash free basis for pinewood – pilot vs lab, 550 °C. Correction has not been made for temperature as discussed in chapter 3.

The difference between the lab and pilot pyrolysis is speculated to be because of loss of biomass compared to clay, due to the lower volatiles and higher ash observed in the charcoal produced. Biomass charcoal is selectively sucked through the off gas system, while the clay is not lost.

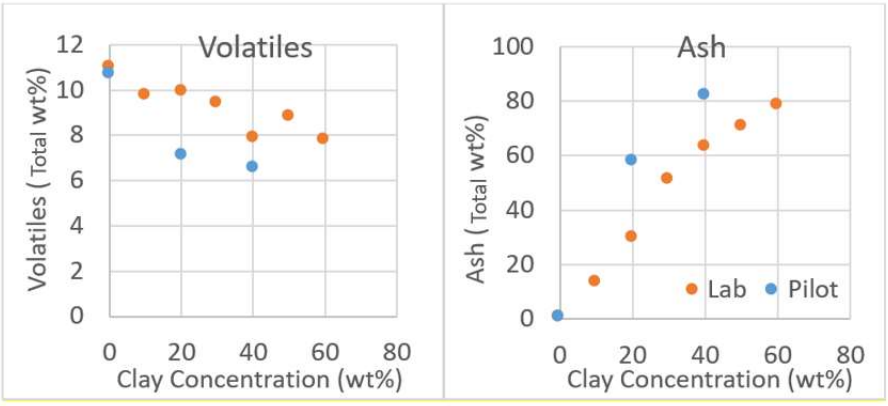


Figure 4-25 Volatiles and ash analysis of lab and pilot charcoal. Results are presented on a total basis.

4.6 Clay reaction mechanism

This section presents a set of equations relating to the reaction mechanism (Eq. 4-4).

$$\boldsymbol{Heavy\ Oil} \xrightarrow{\boldsymbol{Clay\ Mineral}} \boldsymbol{Char + Light\ Oil} \qquad \textit{Eq. 4-4}$$

This section will summarise the experimental work performed on the clay mineral and all biomass types (pine, olive cake, straw, and miscanthus) to determine how clay mass and temperature affect the distribution of product yields.

4.6.1 Catalytic activity

To make the reaction presented in Eq. 4-4 progress, oil produced by pyrolysis then reacts with clay minerals. At the three temperatures all biomass types are tested at, and extra temperature pinewood was tested at, the reaction profiles are presented in Figure 4-26 and Figure 4-27.

Figure 4-26 presents the full clay data set which provides evidence that at high clay loading (above 60% catalyst content) the reactions appear to become less efficient – this is thought to be due to high levels of clay compared to oil in the reactors, so there is not enough for the mass of clay to react with.

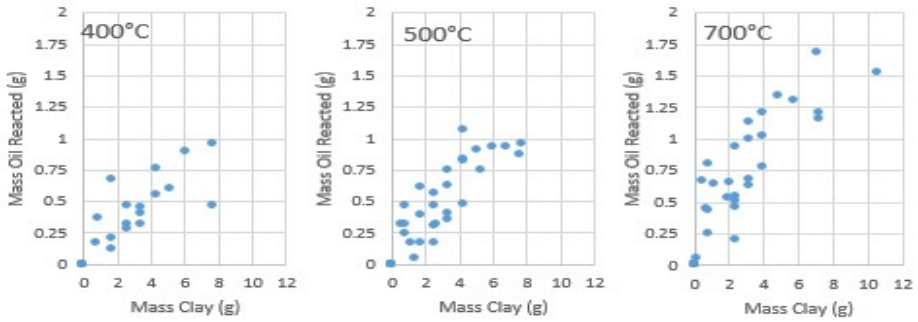


Figure 4-26. Oil reaction by mass of clay. Full data set giving indication about catalyst saturation point.

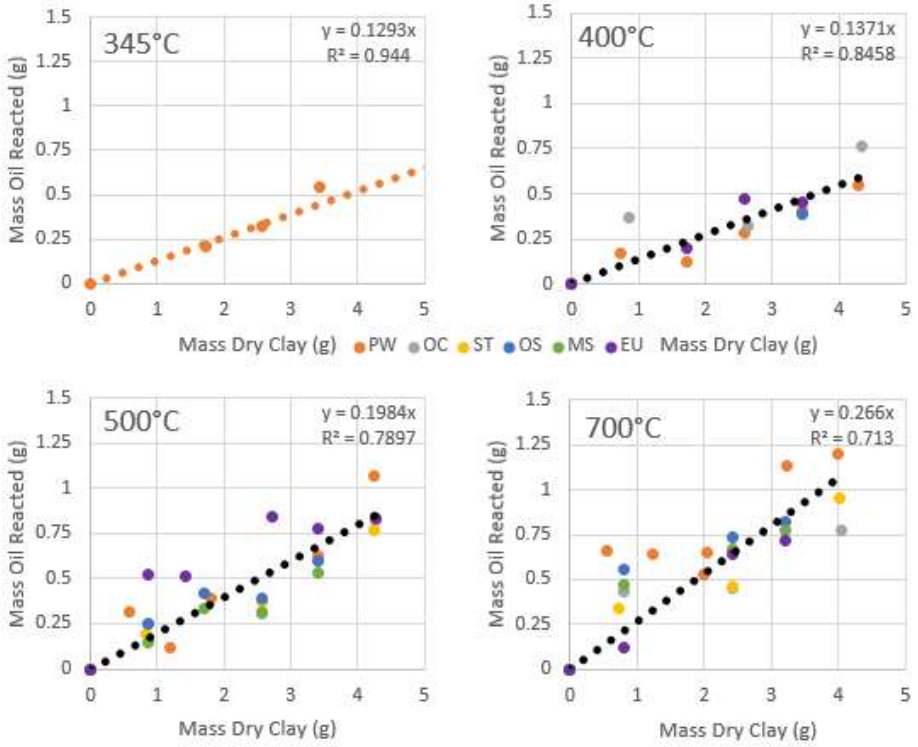


Figure 4-27. Oil reaction by mass of clay

Figure 4-27 breaks this down, by only showing the experiments with less than 60% clay in the reactors. From this there appears to be a clear trend that increasing the temperature means that the clay has a higher capacity for cracking oil. This is summarised in Figure 4-28.

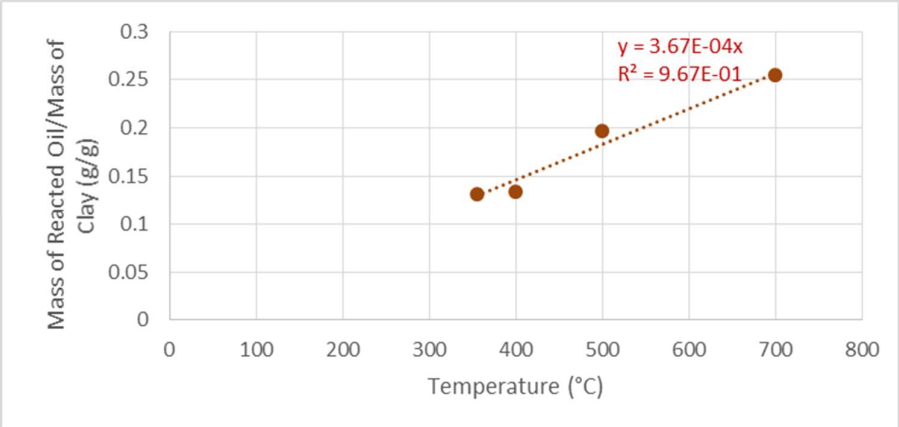


Figure 4-28. Summary of temperature dependence of clay reactions, based on all biomass.

This can then be presented as Eq. 4-5 to allow calculation of the mass of oil reacted at a given temperature and mass of clay addition.

$$\Delta M_{oil} = \left(3.67 * 10^{-4}\, T_{pyrolysis}\right) * M_{dry\ clay} \qquad \textit{Eq. 4-5}$$

Symbol	Description	Units
ΔM_{oil}	Mass of oil reacted for a given temperature and mass of clay	g (kg)
$T_{pyrolysis}$	Temperature of pyrolysis	°C
$M_{dry\ clay}$	Mass of dry clay in the reaction	g (kg)

4.6.2 Product distribution

Following the reaction, it is clear from the discussion around Figure 4-14 that the product distribution from pyrolysis changes with temperature, therefore an equation is required to predict this change. Figure 4-29 presents this in terms of increased mass of charcoal recovered from loss of oil. As it can be seen, the equations in Figure 4-29 do not provide the best fit, but give a good indication that at lower temperatures there is more charcoal recovered than at higher temperatures where it would be expected that the cracking reactions would be more complete and gas production favoured. This is summarised in Figure 4-30 and the effectiveness of this

will be assessed in Section 5.4 where the pyrolysis model, and BBQ model will be assessed together.

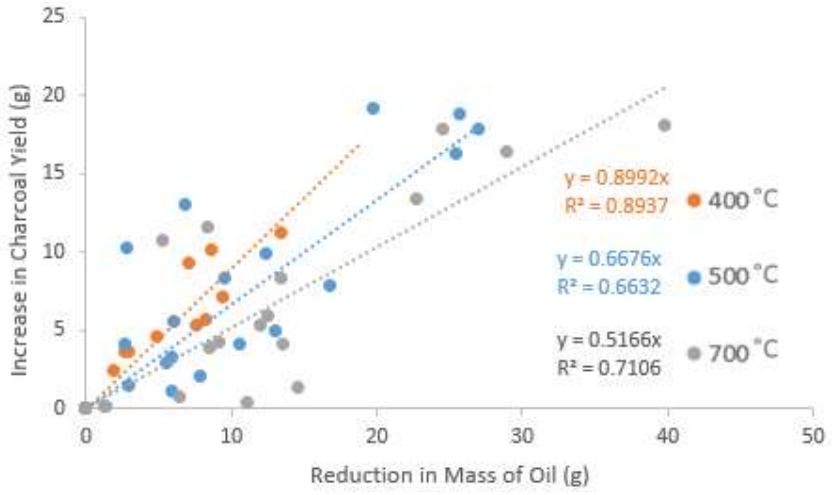


Figure 4-29. Mass of Liquid reacted into charcoal at 400 -700 °C, all biomass types. High data spread is due to the effects of all biomass types – woody to agricultural residue – which produce different oils and inherently in this different break down reactions are observed. For this study this provides an indication of the mass of oil which will be reacted from a random biomass type.

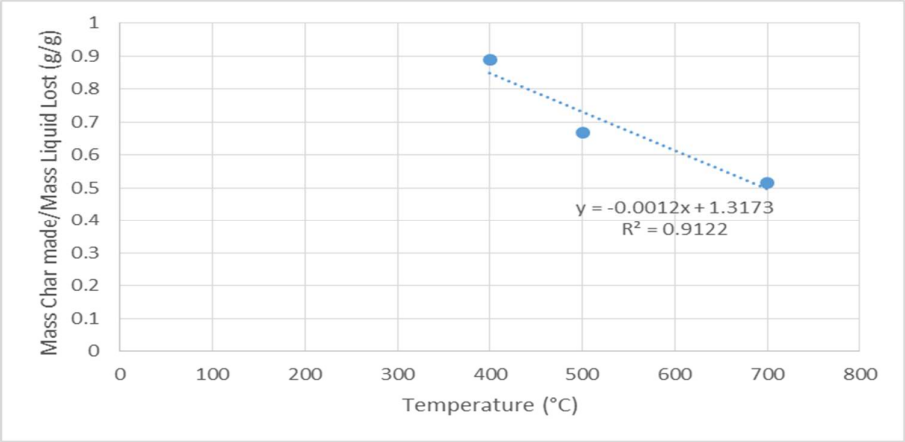
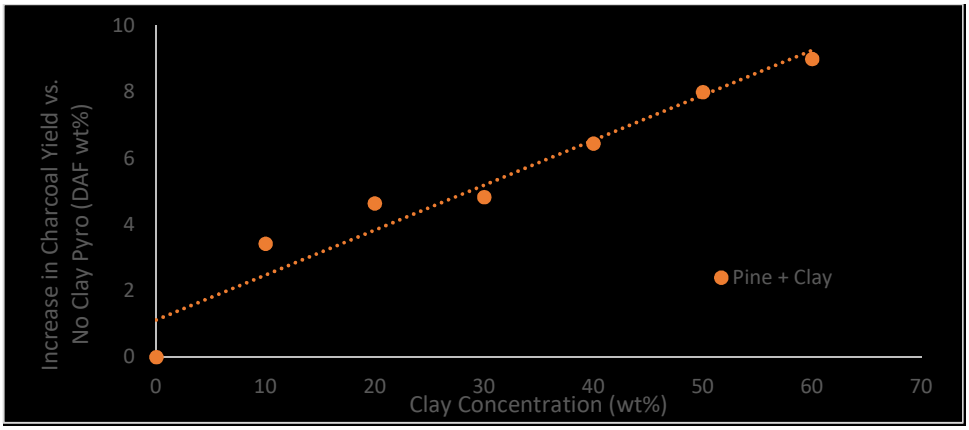


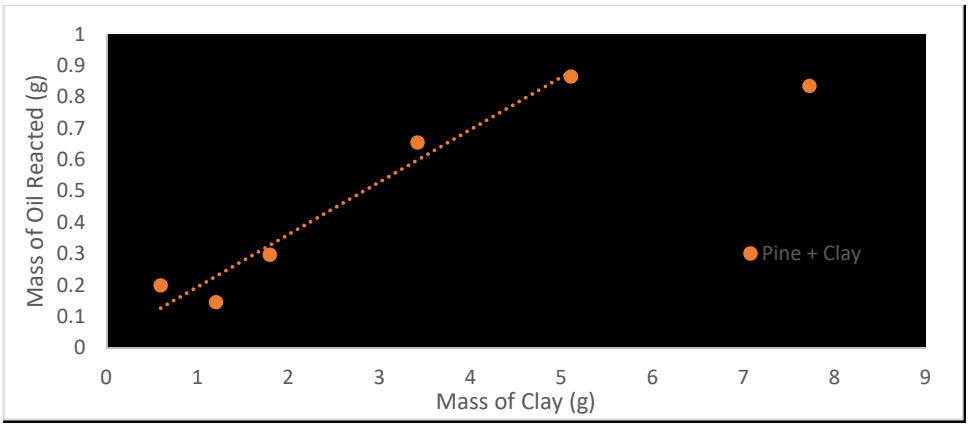
Figure 4-30. Summary of charcoal production from oil loss against temperature.

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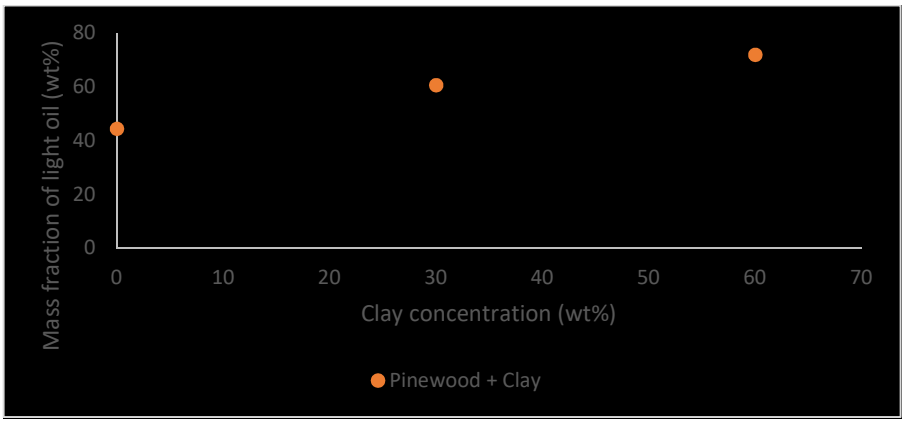
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4.7 Conclusions

This chapter has tested both inert, solid acid and solid base catalyst in slow pyrolysis to see the effect on both the charcoal yield and the liquid and gas products produced.

- Clay mineral bentonite, a solid acid catalyst addition led to the improvement of the charcoal and gas yield at the expense of heavy oils during biomass slow pyrolysis. Similar effects have been seen with type y zeolite in pinewood, while smaller pore ZSM-5 zeolite did not show any effects. However, effects with olive cake and ZSM-5 show that this is likely to be because pinewood oils are larger molecules which cannot fit in these pores.
    - Similar effects have been seen with solid base dolomite which works by a different mechanism.
    - Sand addition has been assessed and it has been confirmed that this is an inert additive to the system.
- Improvement in the remaining oils following clay addition with lighter fractions becoming more dominant, importantly producing a larger phenolic fraction which may make the oil into a valuable by product.
- Increasing pyrolysis temperature and clay mineral content lead to more solid acid reactions.
- Findings agree with and extend on other literature in the area, in which addition of catalyst to fast pyrolysis systems has been done extensively, this work shows that similar trends can be seen in the slow pyrolysis region.

Chapter 5. BBQ testing and modelling

5.1 Introduction

This chapter outlines the experimental and modelling work completed to determine the properties of charcoal which make useful BBQ briquettes. Three major areas of work will be outlined in this chapter:

- Charcoal briquetting and mixing with biomass, sand and clay to produce fuel;
- Combustion of the briquettes, and;
- Modelling work to represent the burning profiles based on the properties of the briquettes, here in referred to as the 'fire model'.

This chapter will then conclude on the properties of briquettes (types of charcoal and pyrolysis conditions, concentrations of inert and raw biomass) which can be used in BBQ charcoal production. Integration and validation of the fire model with the pyrolysis yield model presented in Chapter 3, will also be outlined.

5.2 Methods

5.2.1 Charcoal briquette production

Briquettes were produced using five material types:

- Charcoal, milled to fit through a 2 mm circular screen, from the pilot pyrolysis work (Table 5-1) (pine, mixed hardwood, straw and olive cake subject to pyrolysis at 280 – 650 °C).
- Raw biomass – in all cases this is the same as the biomass used to make the relevant charcoal, also milled to fit through a 2 mm screen;
- Kiln dried sand as described in section 4.2.2;
- Clay (also described in section 4.2.2), both from the in situ catalytic pyrolysis testing (section 4.5) and raw forms and;
- Starch (flour starch) used as a binder, with 10% water added to activate the starch.

A list of the mixtures made can be found in Appendix 3.

The bulk of the data is centred on pinewood 450 °C and olive cake 450 °C charcoals due to the volume of these charcoals available from these pilot plant runs and the expected suitability of charcoal produced in this temperature range (Lenthall, 2016).

Table 5-1. Properties of charcoal types used in experiments

Biomass type	Pyrolysis temperature (°C)	Volatiles content (wt%)	Ash content (wt%)	Fixed carbon (wt%)
Pinewood	375	25.76	0.52	73.71
Pinewood	500	10.76	0.55	88.69
Pinewood	650	4.54	3.00	92.46
Hardwood	375	17.94	1.20	80.86
Hardwood	500	10.41	1.67	87.93
Hardwood	650	3.40	4.50	92.10
Olive Cake	280	47.20	10.40	42.40
Olive Cake	450	12.50	17.00	70.50
Olive Cake	500	6.90	15.40	77.70
Straw	280	49.40	10.80	39.80
Straw	450	16.46	19.83	63.71
Straw	500	15.54	22.19	62.27

With these charcoals, mixtures were made using:

- Biomass and sand in concentrations from 0 – 40% in at most 10% concentration intervals.
- Clay which had been through pyrolysis with biomass mixtures were made from 0- 65% to capture the full range of the effect of this material. These mixtures were made by starting with the 550 °C pinewood + 20% clay pilot pyrolysis run charcoal (which had 65% clay mixed into the charcoal) and diluting with similar 550 °C pinewood charcoal produced previously
- Raw clay at concentrations of up to 40% to determine if this had a different effect on combustion compared to inert sand.
- Mixtures containing two additives (sand and raw biomass) using pinewood char 400 °C were also made at incremental concentrations to determine if these mixtures act similarly to single additive mixtures.
- Further experimental mixtures were selected with to gauge the range of the validity of the model to both charcoal type and concentration range of additive.

The method used to produce the briquettes is adapted from Lenthall (2016), and had initially been developed by CPL to screen new raw materials.

- The raw materials (approx. 2 kg) were combined in a Kenwood Major Free-standing electric mixer to ensure consistency,
- Then pressed using an EDBRO hydraulic hand press, exerting approximately 6 tonnes compression pressure into 4 cm diameter briquettes, approximately 2 cm high.
- One batch consisted of approximately 65 briquettes depending on the density and compressibility of the materials.
- The briquettes were then dried in an oven at 105°C for approximately 12 hours to allow for the starch to cure.
    - This length of time also ensured that the briquettes dried to allow for repeatability between combustion experiments due to consistent near dry moisture content when the fires were burnt.
- Once cured, a random sample of 3 briquettes was taken from each of the batches for proximate analysis.

5.2.2 Combustion testing

The material was combusted in a simulated grill (Figure 5-1) using 2 paraffin fire lighters (CPL Homefire firelighters) cut in half and placed inside the 4 corners of the grill. The location of these and charcoal briquette fill level were kept constant to ensure that the fires were lit and allowed to combust in a similar fashion. The fires were conducted in the same location under the same extraction hood to ensure that the differences observed in the fire temperature profiles were due to the properties of charcoal mixture rather than external effects potentially changing mass and heat transfer properties of the system.

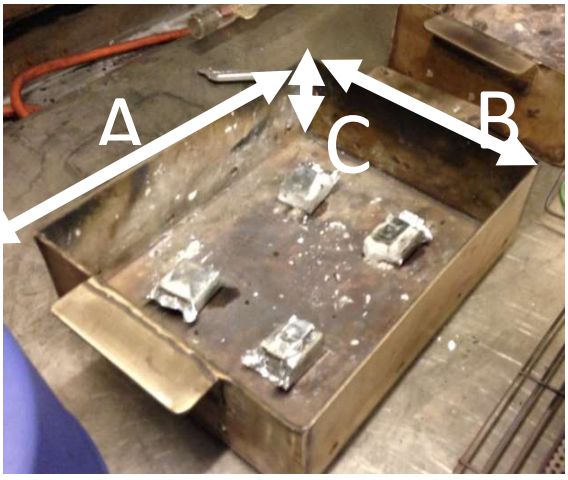


Figure 5-1. Simulated grill with location of firelighters shown. Dimensions A:270 mm; B: 210 mm; C: 80 mm.

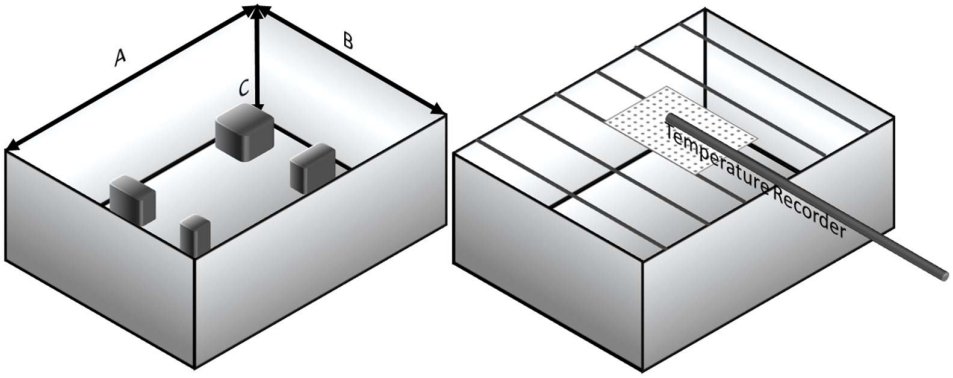


Figure 5-2. Simulated grill with grill plate and thermocouple (highlighted in black).

The temperature of the fires was recorded in the centre of a steel plate above the grill plate using a Lascar EL-USB-TC-LCD Data Logger which recorded the temperature at 10s intervals for the course of the fire. The location of the grill plate was positioned in the centre of the grill to ensure a similar heat load was available to the logger in each fire. Temperature logging was stopped after the system has cooled to room temperature.

Whilst the fires were burning observations (recorded in Appendix 3) were made about the fire, focusing on whether the fires smoked; or appear to smoulder rather than burn to embers. The fire data was then stored in a spreadsheet for analysis and modelling studies.

5.2.3 Commercial charcoal

A commercial wood charcoal briquette was sourced from a major high street supermarket, and was burnt in triplicate, presented in Figure 5-3. These four commercially available charcoal experiments were used to make an estimation on natural differences between combustion runs and to generate a baseline which fires were then compared to.

5.2.4 Analysis of fires

Initial analysis compared the mixtures with the high street charcoal, determining what fraction of the fire points fell inside the allowed error of these runs. It was determined a successful fire 70% of points should fall within 2-σ (standard deviations) from the mean (ų) of the commercial charcoal. This was determined by the following procedure, which is summarised in Figure 5-3:

- Remove the first 30 mins of all the fire data sets. This has two effects:

  - Removes the influence of the firelighters on the experimental results which had unpredictable combustion and temperature effects.
  - Removes the period of fire which charcoal manufacturers generally recommend that the fire should not be used for cooking, to minimise food contact with combustion products.
- The data after 300 mins was removed, as after this point the commercial fires are below 100 °C so is not useful for cooking.
- Determine the average of the four commercial runs, and the accepted spread of temperature based on 2-σ from ų against fire time
- Plot the fire data sets against the commercial fire.
  - A Matlab routine was then used to count the number of points inside and outside the accepted temperature spread, which was selected as 2 standard deviations from the mean of the 4 commercial charcoal runs, as shown by Figure 5-3. This was used to encompass the full variation from the commercial charcoal runs.
- Sum the total number of points, then determine the percentage that the fire in question was inside the 2 standard deviation test. This percentage is then called fire score, and compared against the specification of 70%.
  - 70% was chosen as although the fires tests by this study show a reasonably good agreement between each other, the wider variation between all commercial charcoals tested by CPL is much greater, meaning expectations for BBQ charcoal potentially are quite large. However, this is proprietary data and cannot be reproduced here.

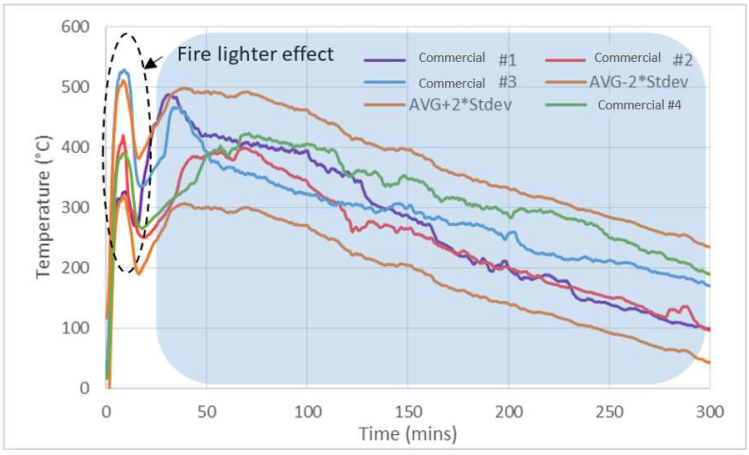


Figure 5-3. Graphical outline of the commercial charcoals and the acceptable charcoal bars. Area of interest shown in blue, +30 to 300 mins.

5.2.5 Fire modelling

The aim of this model is to produce a low input easily solvable method to allow quick screening of whether selected mixtures if charcoal, sand and/or raw biomass could meet the requirements, set out above, for BBQ charcoal.

The method chosen to model fires is based on an analogous method of modelling two first order chemical reactions in series, due to the simplicity compared to the methods reviewed in section 2.5 of the literature review.

Based on a heat balance around the block of steel where the temperature is being measured, the heat balance can be summarised by Figure 5-4. The main heat transfer modes in operation in this system are radiation from the burning briquettes to the steel plate, then to the surroundings, and convection from the briquettes to the steel plate, then losses to the air dragged over the plate by the vent. Heat also accumulates in the steel plate as the process continues. Therefore modelling this system as two first order reaction in series captures the convection terms and accumulation terms and assumes the radiative forces (which are represented a fourth order process) are not important in this system.

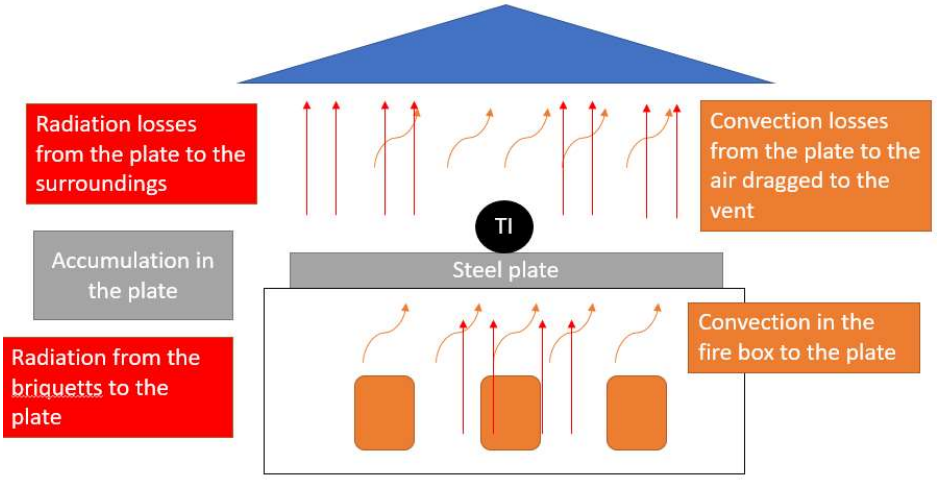


Figure 5-4. Outline of heat flows around the steel plate being represented by this equation. Can see that there are convective and radiative transfers to the plate where heat can accumulate, then losses by convection to the air dragged over the plate and radiation to the surroundings.

In a chemical setting, two first order reactions in series are outlined physically in Eq. 5-1, and is represented mathematically by Eq. 5-2 (Levenspiel, 1998). In this process, compound A changes in some way producing an intermediate, R, which is then

consumed producing S. An analogy of this chemical process with the heating and cooling curves obtained from the combustion experiments has been made by imagining temperature as a 'substance' which is created during the heating phase of the fire (i.e. A → R in Eq. 5-4) then consumed to create a new product during the cooling phase of the fire (i.e. R → S in Eq. 5-4). The theory and modifications to the equation are presented physically in Eq. 5-3 and mathematically in Eq. 5-4. A modification has been made to the mathematics of this to ensure consistency. Instead of the initial reactant concentration (C_{A0}) that is present in the chemical system, a factor Z is introduced. This becomes a function of the material properties and is the driving force for the reaction by providing information about the maximum amount of heat that can be released from the material.

$$A \overset{k_1}{\rightarrow} R \overset{k_2}{\rightarrow} S \qquad \textit{Eq. 5-1}$$

Symbol	Description	Units
A	Initial reactant	Concentration
k_1	Rate constant of reaction of A to R	s-1
R	Intermediate product	Concentration
k_2	Rate constant of reaction of R to S	s-1
S	Final product	Concentration

$$\frac{C_R}{C_{A_0}} = \frac{k_1}{k_2 - k_1}(e^{-k_1\tau} - e^{-k_2\tau}) \qquad \textit{Eq. 5-2}$$

Symbol	Description	Units
C_R	Concentration of reactant	Concentration
C_{Ao}	Concentration of A at time = 0	Concentration
τ	Time constant for the reaction	s

$$T = Ambient \overset{H_1}{\rightarrow} T = Hot \overset{H_2}{\rightarrow} T = Cold \qquad \textit{Eq. 5-3}$$

Symbol	Description	Units
T	Temperature of the fire	°C
H_1	Constant describing the heating phase of the fire, analogous to Arrhenius constant	s-1
H_2	Constant describing the cooling phase of the fire, analogous to Arrhenius constant	s-1

$$\frac{\Delta T}{Z} = \frac{k_1}{k_2 - k_1}(e^{-H_1 t} - e^{-H_2 t}) \qquad \textit{Eq. 5-4}$$

Symbol	Description	Units
ΔT	Change in temperature since the start of the fire	°C
k_1	Arrhenius constant describing the conversion of A to R	s-1
k_2	Arrhenius constant describing the conversion of R to S	s-1
Z	Material constant describing capacity for heat release	°C
t	Time since fire ignition	s

To fit Eq. 5-4 to the data, three constants are required: H_1, H_2, and Z. The significance of Z is described above. H_1 and H_2 describe the rates of heating and cooling in the system and were thought to either be properties of the material, or properties of the environment.

To determine Z, H_1 and H_2, the following methodology was applied to each of the fires:

- As with the analysis in Section 5.2.4, the temperatures before 30 mins and after 300 mins was cut off
- The data sets were split into a model training and validation set where 80% of the trials were used for model building
- The model (Eq. 5-4) was applied to the BBQ fires
    - Using the Solver function and least squares regression in Microsoft Excel, best fit values of H_1, H_2 and Z were found.
- These were then correlated against the proximate analysis (either volatiles, ash or fixed carbon content) to determine the form of the equations required to predict them i.e. $\boldsymbol{Z = f(x, y)}$.
- These equations for H_1, H_2 and Z were applied to the model, to find constants which best fit the range of data.
- A global optimisation routine in Matlab was used to find the constants in the functions for Z, H_1 and H_2 to maximise the average r^2 value of the building data set.
- This new model was then applied to the validation data set, and a second average r^2 value was found.

- The model was then compared against the commercial charcoal standard as defined in section 5.2.4, then compared with the corresponding raw data set to see if the same decision regarding fire acceptability would be made.

Proximate analysis was the only parameter used for this model building (rather than concentration of clay, sand or biomass) as the model aims to be usable for analysing the burning performance of unknown fuels even though this development has not been done in this project.

5.3 Results

Due to the large volume of data collected for this section, the fire charts and proximate analysis are presented in Appendix 3.2, where the fires are presented in the two sets defining the model building set and validation set. These sets were chosen randomly, with 80% of the data used in building the model and 20% for validation.

5.3.1 Fire repeatability

Due to the large number of mixtures made, a full replicated experiment was not considered feasible, therefore only a selection of fires was repeated with a selection of these fires included here as evidence that the fires are similar.

5.3.2 Comparison of the fires with standard commercial charcoal

The fires are compared to the standard commercial charcoals in Figure 5-6 to Figure 5-9. This analysis has compared two characteristics:

- The additive free combustion tests to the pyrolysis conditions (temperature and biomass used, Figure 5-6 and Figure 5-7)
- The effect of adding sand and raw biomass into the combustion tests (Figure 5-8 and Figure 5-9).

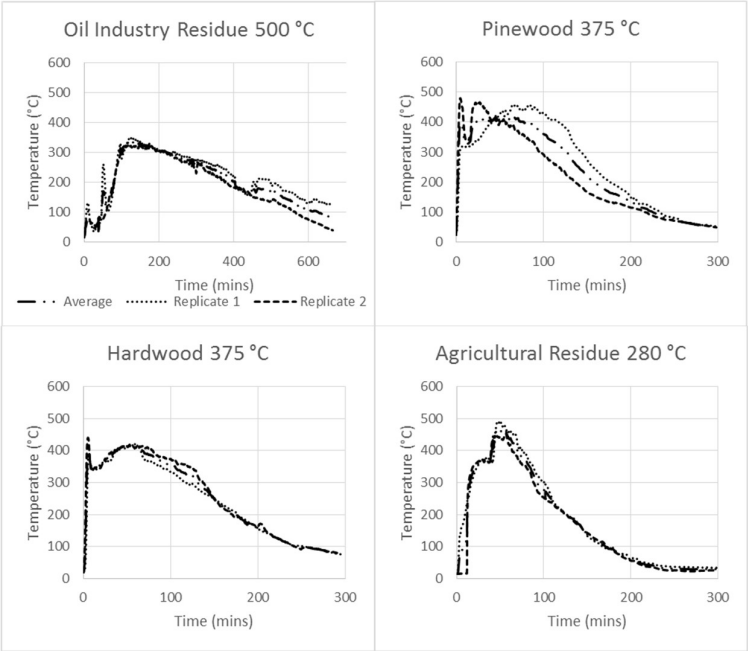


Figure 5-5. Selection of fire repeability charts

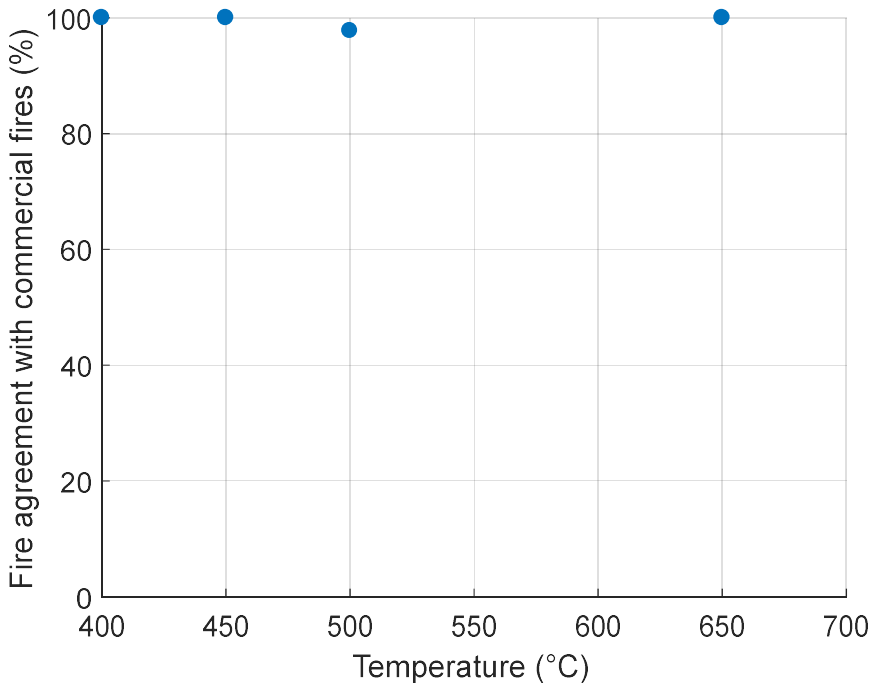


Figure 5-6. Average fire agreement (defined as points inside 2 standard deviations of the mean of commercial runs) of all biomass runs with charcoal produced at the various temperatures. 400°C is average of 8 runs, 450°C = 15 runs, 500°C = 28 runs, 650 °C = 2 runs.

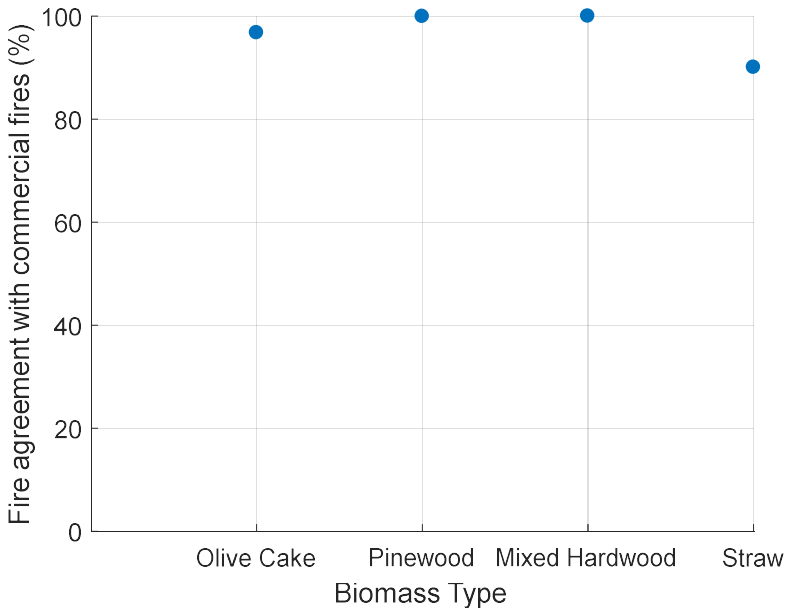


Figure 5-7 Average fire agreement (defined as points inside 2 standard deviations of the mean of commercial runs) broken down by biomass type. 15 runs used olive cake, 25 runs used pinewood and 9 runs used straw over all temperatures and briquette compositions.

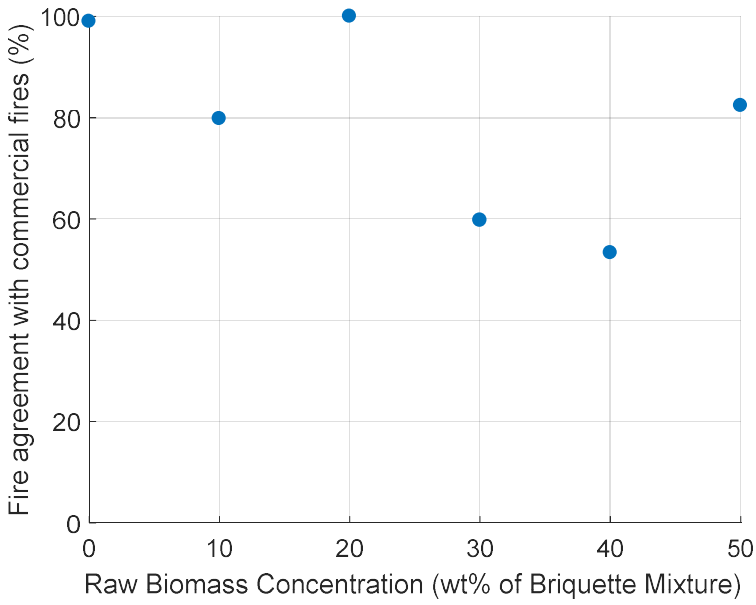


Figure 5-8. Average fire agreement (defined as points inside 2 standard deviations of the mean of commercial runs) broken down by raw biomass concentration. 0% value indicates there was no biomass added to the charcoal briquette.

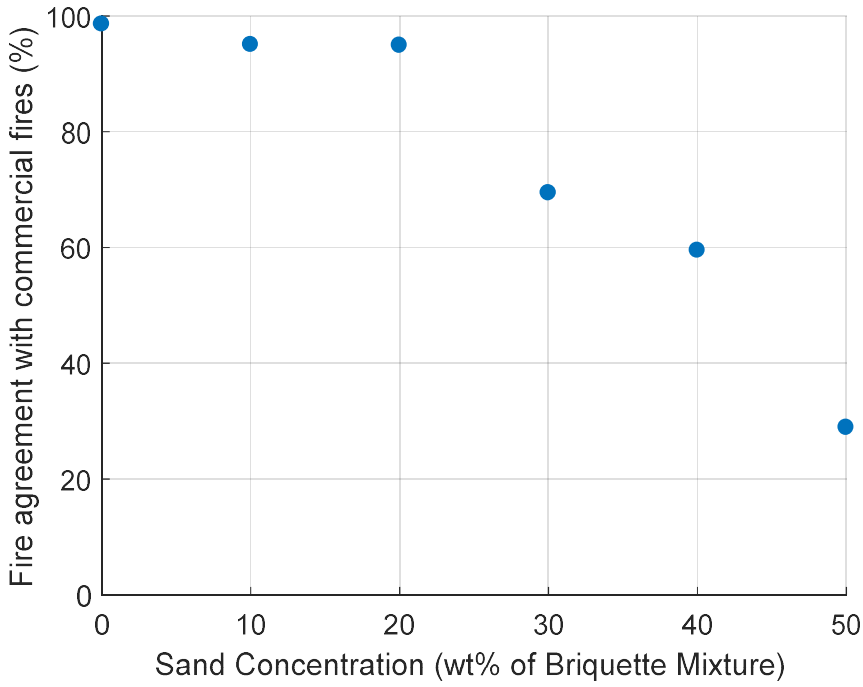


Figure 5-9. Average fire agreement (defined as points inside 2 standard deviations of the mean of commercial runs) broken down by sand concentration. 0% value indicates there was no sand added to the charcoal briquette.

As can be seen from Figure 5-6 and Figure 5-7, the temperature and biomass used do not appear to influence the charcoal suitability. However, it was observed that at lower temperatures there was a problem with fires smoking during large periods of the fire, and at higher temperatures the charcoal did not burn as well due to smouldering for long periods of time before full ignition, as shown by Figure 5-10. Ideally these characteristics should be have passed in the start-up phase of the fire.

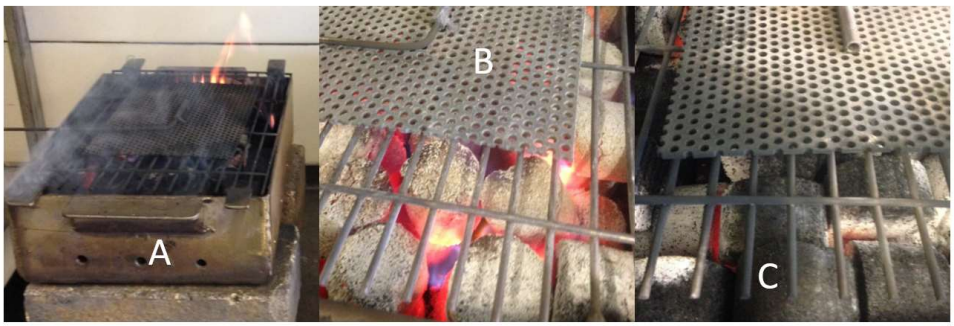


Figure 5-10. Photos of various states present in the fire systems. A = Smoking fire, B = good well burning fire, C = smouldering fire – not as fast combustion leading to slow burn out compared to B.

The effect of sand and biomass addition to the fires has some effect on the system however.

Biomass addition (Figure 5-8) has a more varied effect. From this analysis it can be seen that above 20% biomass concentration, the fire can fail but above 50% biomass, the single run done at this point passed, indicating the influence of biomass may not be as negative as these results suggest.

Increasing sand (Figure 5-9) has the effect of making the fires perform poorly against the standard, with approximately 30% sand addition being the maximum level sustainable for a successful fire. Analysis presented in Figure 5-11 has also shown that addition of clay (whether or not it has been through pyrolysis) or sand has a similar effect on the fire, therefore it has been assumed that the ideas presented here about sand apply to clay.

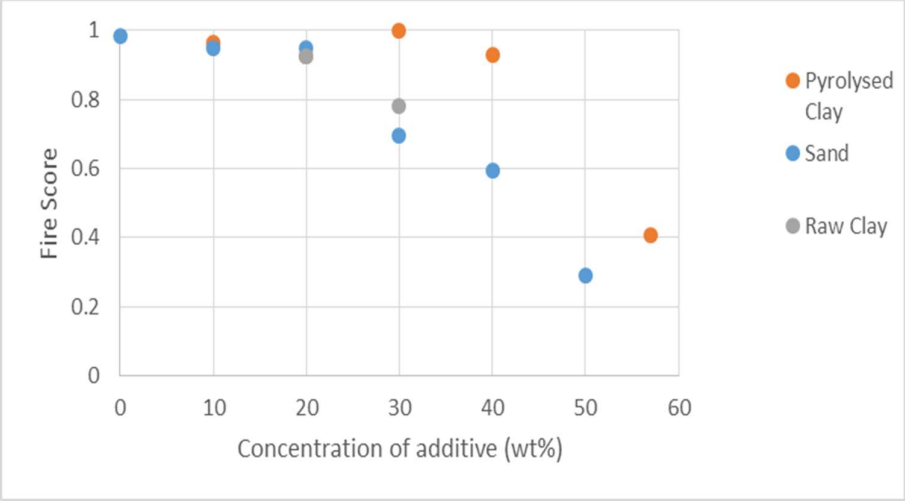


Figure 5-11. Comparison of the effects of Sand and Clay on the BBQ fire, as defined by the fire score which is the percentage points inside 2 standard deviations of the mean of commercial runs

What can be read from this is that there should be a maximum level put on the total allowable additive which is assumed to be around 30%, but potentially as high as 40%. This is backed up by the biomass + sand additive runs, the scores for which are presented in Figure 5-12.

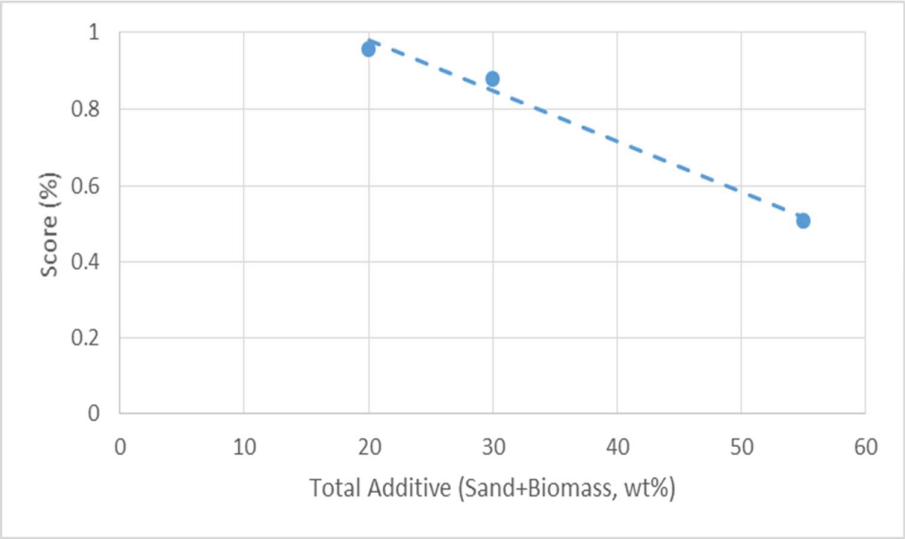


Figure 5-12. Acceptability score of two additive runs vs the total concentration of additive used; base material is 450 °C pinewood charcoal. Score defined by the fire score which is the percentage points inside 2 standard deviations of the mean of commercial runs

5.3.3 Development of fire model

To be useful, the fire model requires values or correlations to determine the constants H_1, H_2 and Z as specified in Eq. 5-3 and Eq. 5-4. H_1 and H_2, which define the heat transfer rate to and from the steel plate, can either be constants due to mass transfer effects inherent in the system as controlled by the ventilation airflow used, or variables based on the rates of combustion of charcoal, which may be able to be explained by the proximate analysis. Also from this analysis, Z is based on the volatiles and fixed carbon concentrations of the charcoal briquettes. Short descriptions of various methods chosen for calculating each of the constants are described in sections 5.3.3.1 and 5.3.3.2, with Table 5-2 providing an overview of the various errors from each model build.

Table 5-2. Correlations of fire model constants against the model fit from Matlab routine

	Model trial 1	Model trial 2
Z correlation	$Z = f(C_{fc}, C_v)$	$Z = f(C_{fc}, C_v)$
H_1 correlation	$H_1 = f(C_v)$	H_1=constant
H_2 correlation	$H_2 = f(Z)$	H_2=constant
r^2 model building set	-1.43	0.78
r^2 model validation set	-2.05	0.74

5.3.3.1 Model 1 development – H_1 and H_2 variable; Z related to volatiles and fixed carbon

In this iteration of model development, H_1 is related to the initial rate of heating (higher value giving a higher initial heating rate), which was assumed to be a function of the load of combustible material in the system, which in this case can be represented by the volatile content of the charcoal. The resulting correlation is presented in Figure 5-13.

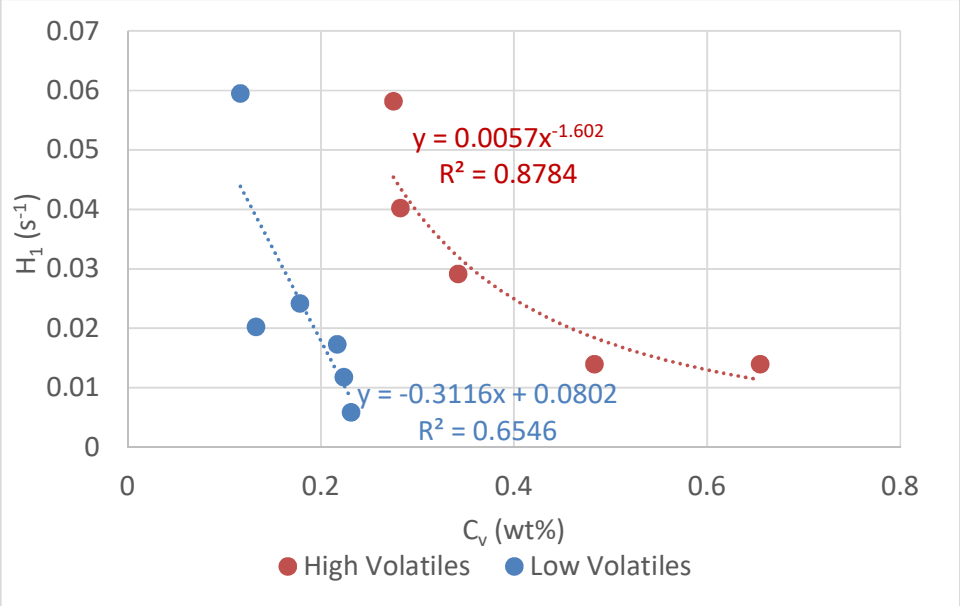


Figure 5-13 Variation of H_1 with the concentration of volatiles in the briquette. Indicates that there is a trend where the level of volatiles in the system speeds up the rate of combustion of the charcoal, meaning that H_1 which controls how the steel plate heats up, is higher with increasing volatiles level.

Z (Figure 5-14) is related to the peak temperature the fire reaches (higher value giving a higher initial heating rate), which is a function of the volatile matter in the system, which burns quickly, and fixed carbon which maintains the fire over time.

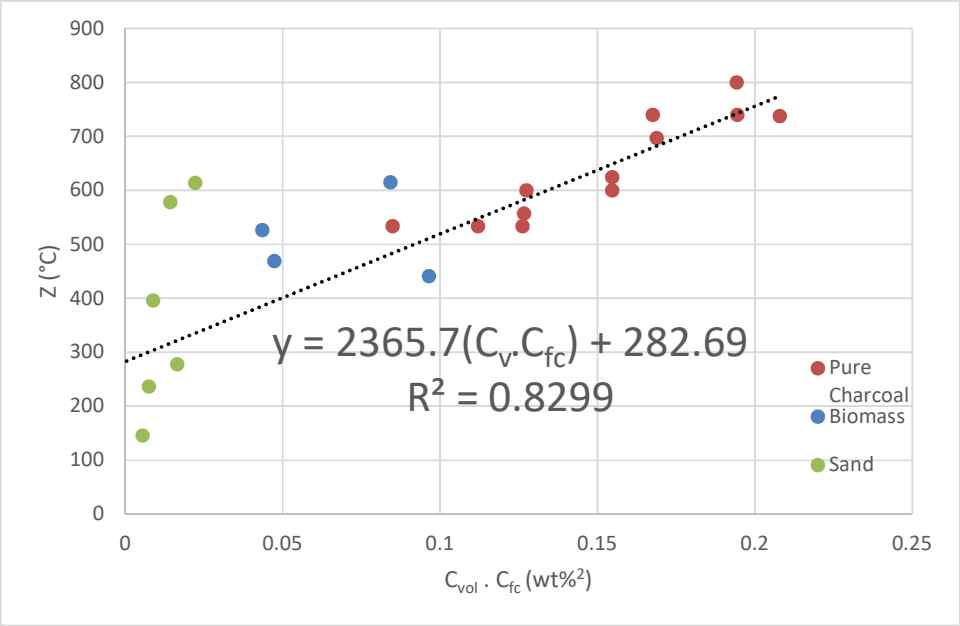


Figure 5-14 Correlation of Z against the product of C_v and C_{fc}. This indicates that increasing volatiles and fixed carbon cause the steel plate to have a higher peak temperature. There are some other effects with sand, which could indicate that the heat retention in higher sand runs prolongs the heating.

H_2 is related to the rate of cooling, (a higher value meaning that the system would cool faster), and initially the only correlation which was statistically significant was the relationship with the Z parameter. Physically, this makes some sense as the hotter the system gets it is assumed the fuel is burnt out more rapidly so there is less material present to prolong the fire life. This correlation is presented in Figure 5-15.

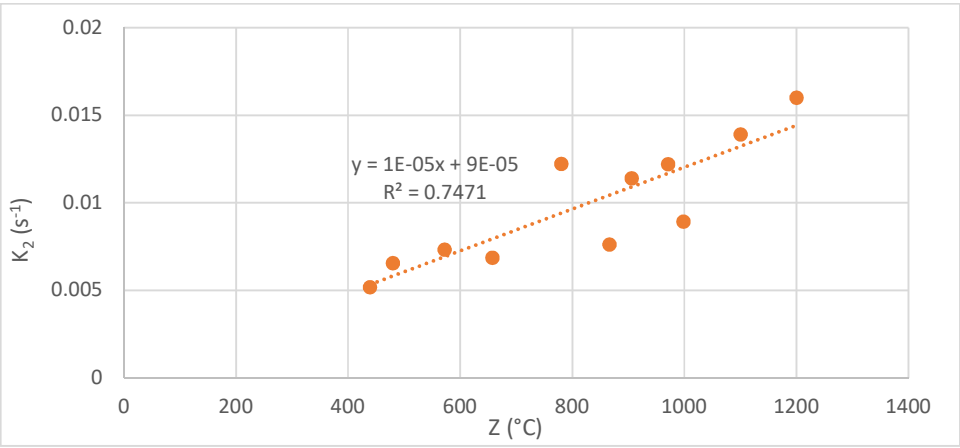


Figure 5-15 Correlation of H_2 against Z for model version 1. Indicates that the rate of cooling is influenced by the peak temperature the fire reaches, which is consistent with the system being convention dominated.

Following the global optimisation of the model using these forms of correlation for the H_1, H_2 and Z parameters, the model is presented in Eq. 5-5. However, as shown in Table 5-2 this form of the model has a poor fit over the data set.

$$Z = (-917.34 * (C_{FC}) + 1414.2) \qquad \textit{Eq. 5-5}$$

$$H_1 = \begin{cases} -0.2318 * C_{Vol} + 0.0645, & V \leq 0.25 \\ 0.05 * {C_{Vol}}^{-1.765}, & V > 0.25 \end{cases}$$

$$H_2 = 1x10^{-5} * Z - 0.003$$

5.3.3.2 Model 2 Development – H_1 and H_2 constant; Z related to volatiles and fixed Carbon

Because of the observations that correlations for H_1 and H_2 did not work well, the second iteration of the model attempted to treat these as properties of the system was developed. The basis for this development is shown in Figure 5-16 where the fires are reaching a peak temperature at approximately the same point in time, then cooling at a similar rate.

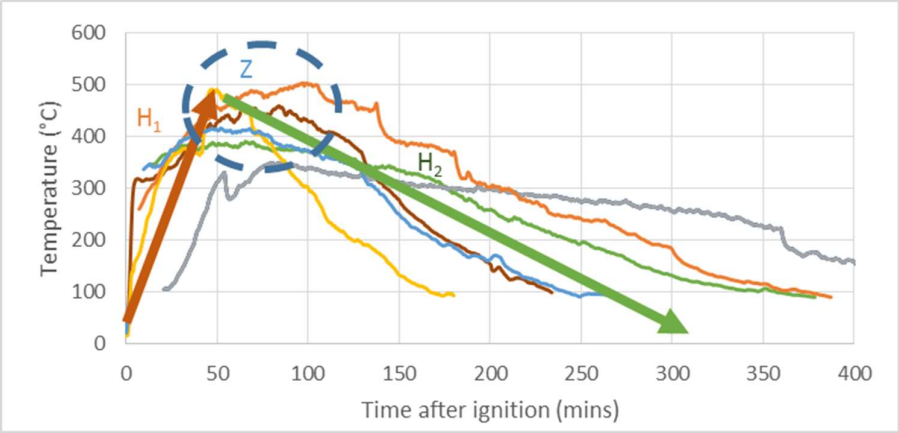


Figure 5-16 Plot of several fire curves, with characteristics overlaid. This is a visualisation that the rates of heating (H_1 and H_2) can be considered similar for each of the fires.

This model was optimised by keeping the Z correlation found in Eq. 5-5, and using a least squares regression to minimise the r^2 for all fire fits by changing the values for H_1 and H_2, so global values of these for the system could be found.

The final form of this model after optimisation is shown in Eq. 5-6, and as shown in Table 5-2, this method has been shown to work well in terms of overall model fit. While r^2 above 0.7 is not generally considered acceptable, there is strong agreement between the fire score when compared to the raw charcoal produced by this model

and the raw data. In cases where there is a lack of agreement, the agreement is generally on the side of caution, i.e. the model fails while the experiment passes, so for use as a charcoal screening tool. Therefore for the purpose of screening biomass types and pyrolysis conditions for producing BBQ charcoal, the model in its current form is considered acceptable..

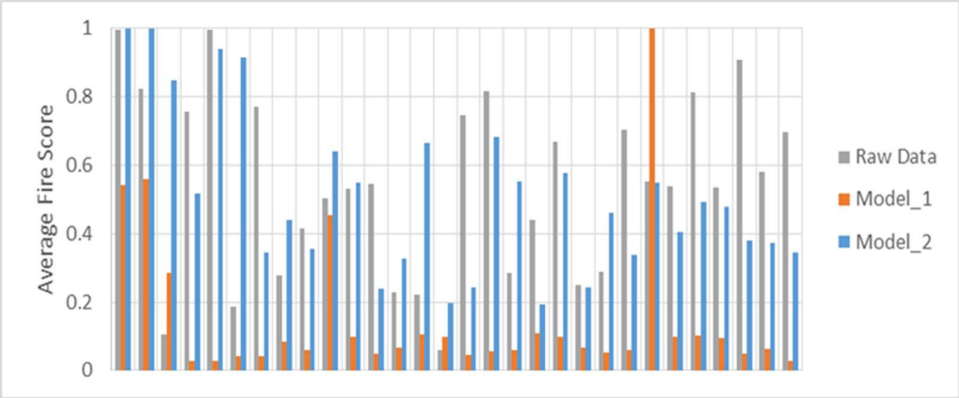


Figure 5-17 Comparison of fire score from the raw data with models 1 and 2

A selection of fire fits for each model are presented in Figure 5-18-Figure 5-21.

As can be seen from these charts (Figure 5-18 to Figure 5-21), a wide range of biomass subject to a varying array of conditions can be simulated to a certain degree with this new method. Future steps accounting for more simple information, such as ranges of ash or volatile content and simple mass transfer parameters such as airflow during the fire, could improve these results.

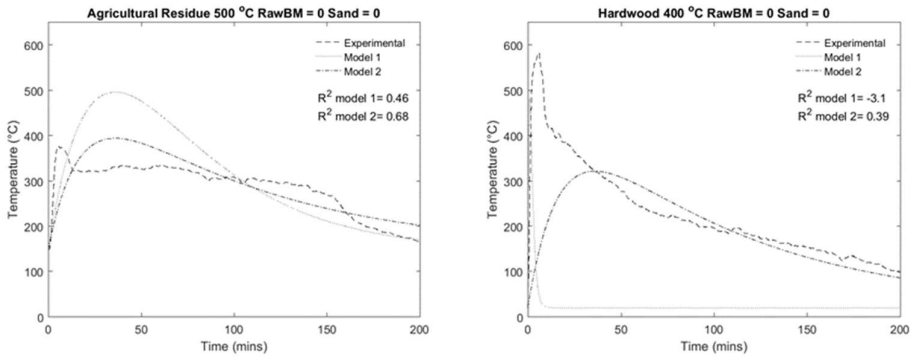


Figure 5-18. Fire fits for the charcoal briquettes with no additive

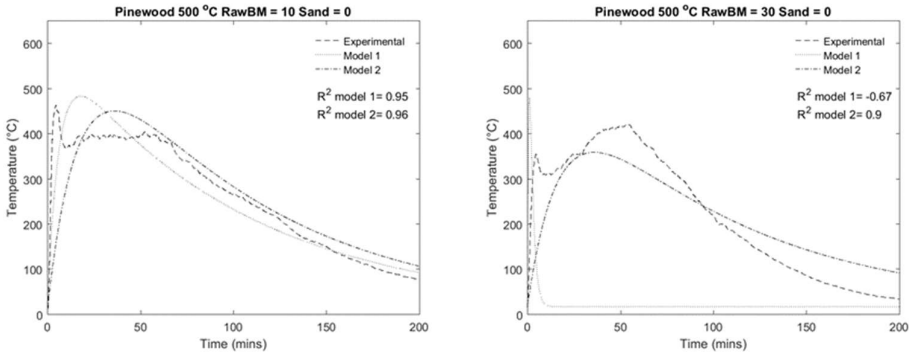


Figure 5-19. Fire fits for the charcoal briquettes with biomass mixed in

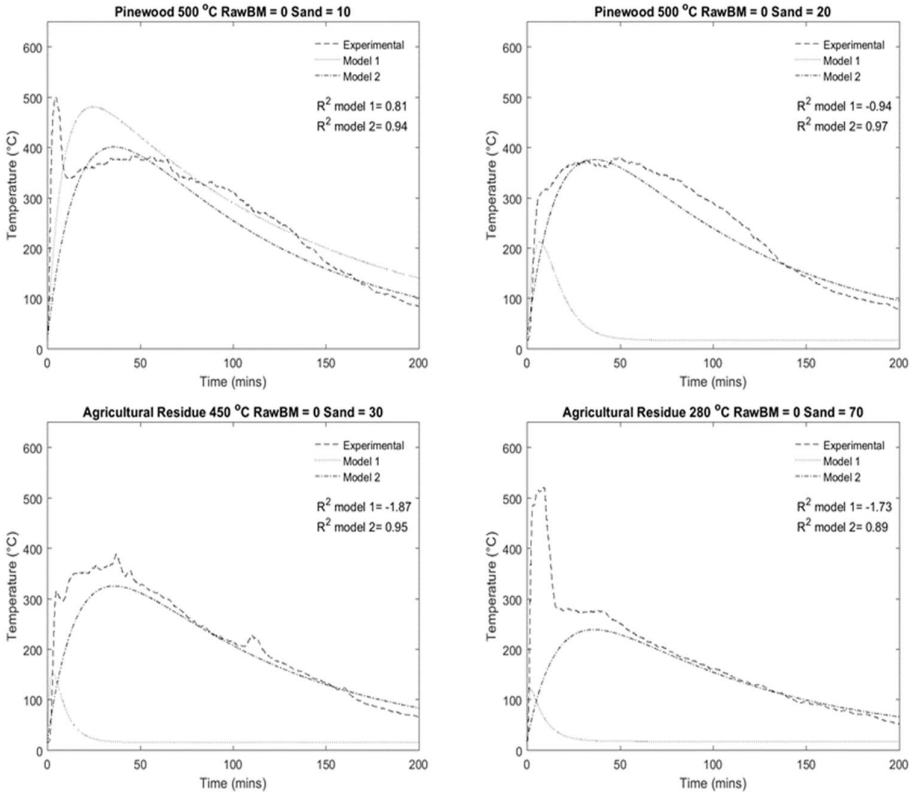


Figure 5-20. Fire fits for the charcoal briquettes with sand mixed in

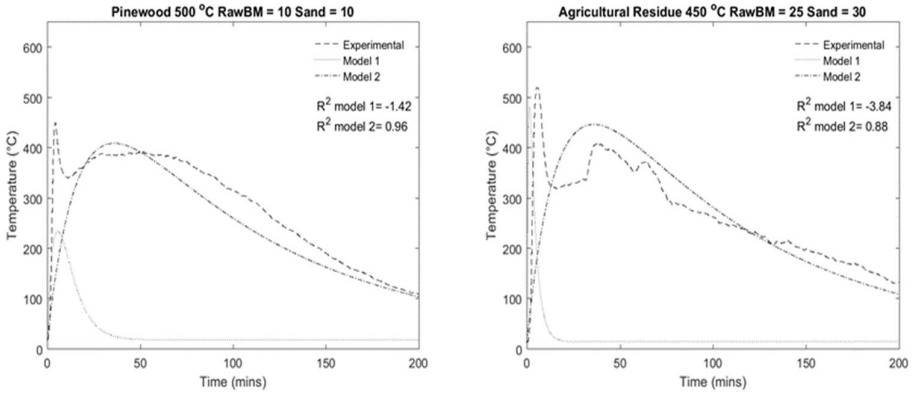


Figure 5-21. Fire fits for the charcoal briquettes with biomass and sand mixed in

$$For\ X_{sand} < 0.35 \qquad T = T_{initial} + Z\left(\left(\frac{H_1}{H_2 - H_1}\right)(exp(-H_1 t) - exp(-H_2 t)\right) \qquad \text{Eq. 5-6}$$

$$Z = 2635.7\left(C_{v,charcoal} \cdot C_{FC}\right) + 282.69$$

$$H_1 = 0.0288$$

$$H_2 = 0.0095$$

5.3.3.3 Validation of Fire Model Acceptability

As the concentration of additive to the fire has been identified as an important characteristic for the fires, further examination of the acceptability of the model has been conducted, as shown in Figure 5-22.

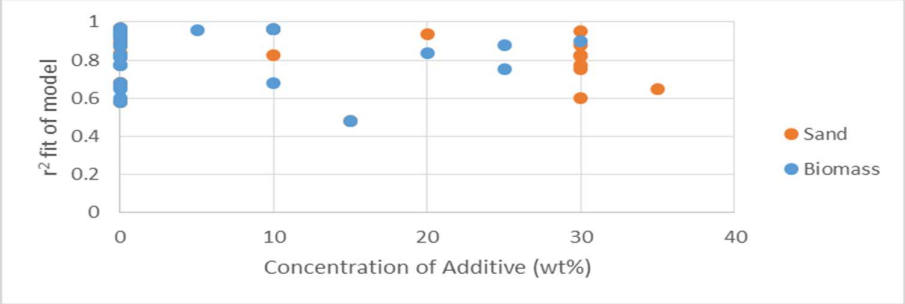


Figure 5-22 Effect of sand and biomass on the r^2 fit of the model. This shows that while there is some variation, particularly with 15% biomass addition, overall there is an r^2>0.7 which suggests that it performs well enough for the purpose of screening material combinations.

This chart shows that there is no systematic failure of the model to deal with the increasing concentration of additive, therefore it is expected that the model can be used to predict the effect of additive concentrations up to 30%wt as determined acceptable by the comparison with the commercial charcoal.

5.4 Development and testing of an integrated pyrolysis & fire model

For the pyrolysis model presented in section 3.4 and 4.6 to be useful, the results need to be able to be used by the fire model to predict the fire test result, as indicated by Figure 5-23.

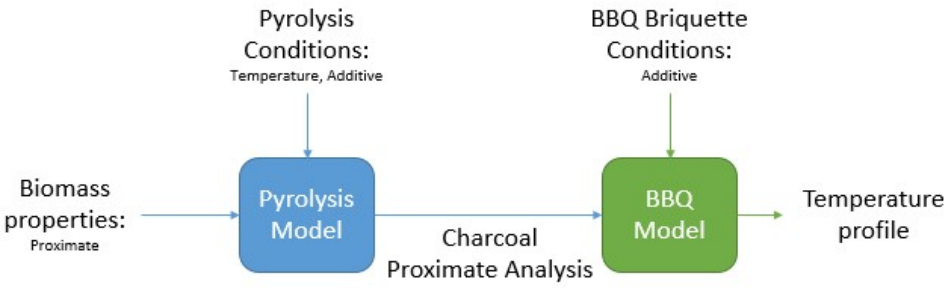


Figure 5-23. Flow scheme of integrated pyrolysis and BBQ model. Biomass properties are fed into the pyrolysis model with operating conditions. The outputs of this are then used to run the BBQ model to develop the expected BBQ temperature profile.

Some example fits have been included Figure 5-24, with further fits in Appendix 3.6. These indicate that if the model acceptability conditions are met in both cases then the combination of the two models fits.

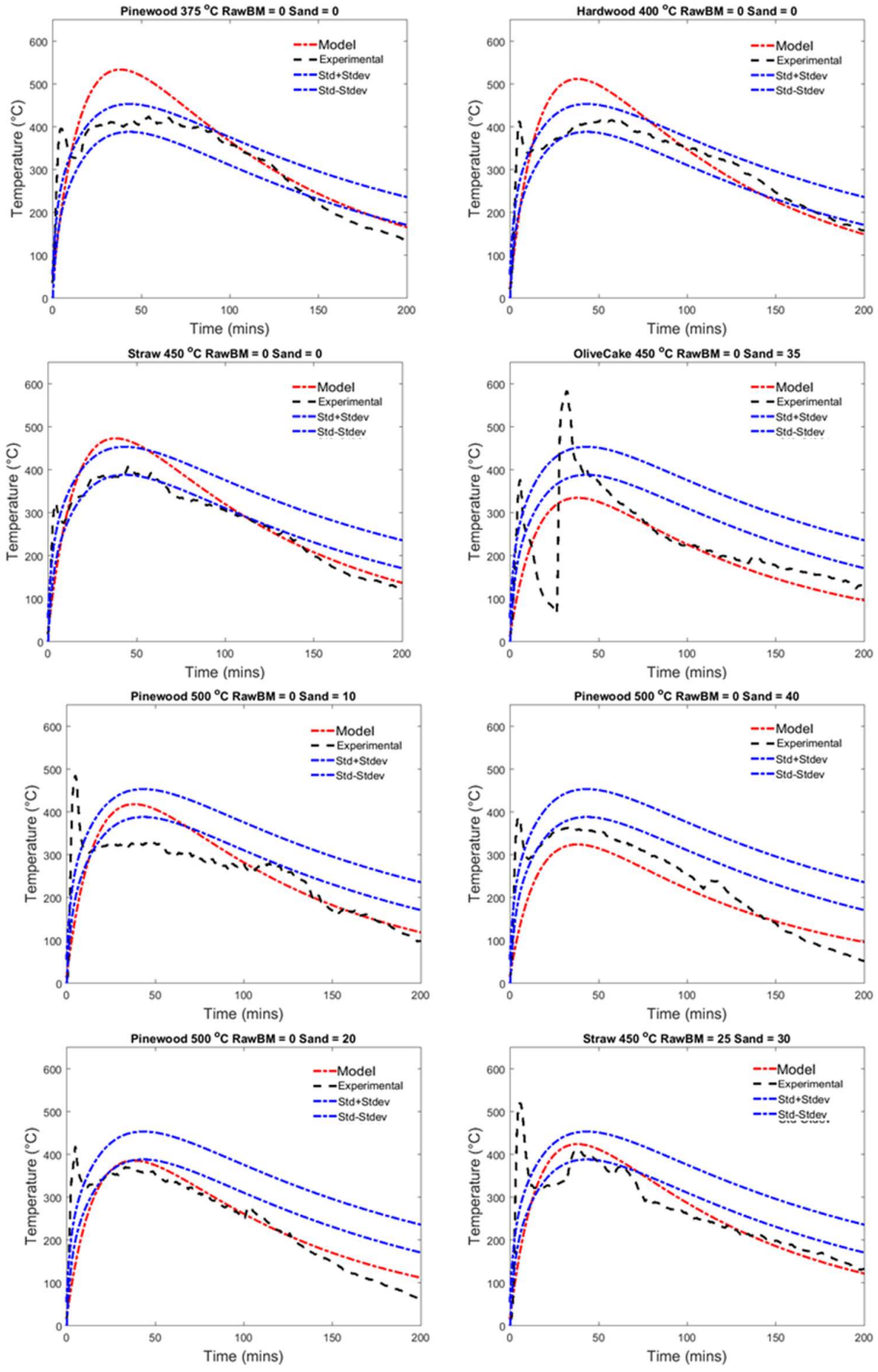


Figure 5-24. Model fits when the pyrolysis and combustion model are used in series against experimental dat

5.5 Conclusions

This section has concluded the following:

- Commercial charcoals produced by this process can safely contain up to 30% additive mixed between inert material and raw biomass.
- Clay and sand have the same effect on charcoal combustion
- A model has been developed which is likely to predict the combustion curve of a BBQ fire in a mass transfer controlled setting, where the simple proximate analysis is all that is required, which have a correlation coefficient greater than 0.7 which is suitable for using the model to screen charcoal mixtures for BBQ use.
- The model has applied the analogy of a two first order chemical reactions in series to the heating and cooling process of the fire system, and shown it can be a method of investigating the overall effect of combusting materials.

Future work could look at expanding the model into the following areas:

- Investigating the effect of shape of the charcoal on the fire
- Method to make fire modelling more general and applicable to a wider range of fire systems (e.g. are the factors suggested able to predict to the level required for regulatory screening of home fire fuels to aid mixture development for fuel alternatives)

Chapter 6. Techno-economic model development

6.1 Introduction

To begin developing design tools for selection of future slow pyrolysis charcoal systems, choices need to be made about the process unit operations used. This work has developed a Techno-economic assessment (TEA) which is used to make these decisions.

This chapter will focus on assessing by product oil and gas usage. This can represent up to 85% of the input biomass (Chapter 3), which provides potential for production of side products along with the charcoal: heat, electricity and chemicals.

Some decisions about the core pyrolysis process and supply chain also need to be made however this will be discussed in relation to the optimal by-product use process flows in Chapter 7.

6.2 Techno-economic model and process selection screen outline

This section will outline the three major parts of this model: process, economic and carbon balances. A decision-making model used to screen the relevant process outcomes will also be presented.

There have been several stages to this model development process (Figure 6-1) which screened a range of process options and at each step increased the level of complexity of the plant process flows, economic analysis and carbon flows. Process flow diagrams (PFD) for the 17 core options and 3 variations are outlined in Appendix 4.1.

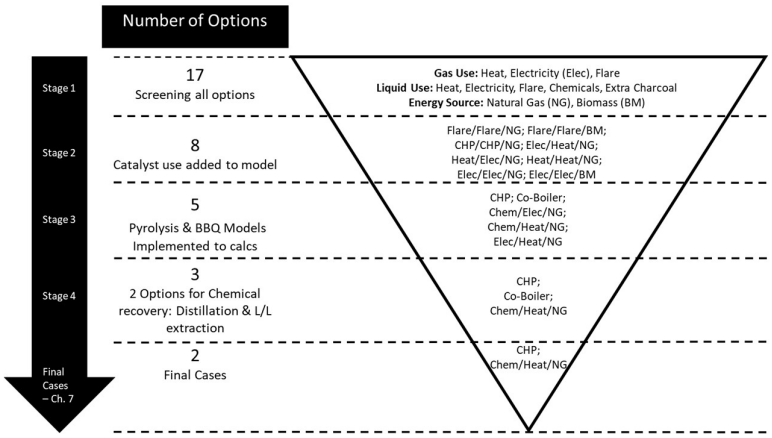


Figure 6-1. Process followed in screening experiment. Started with 17 options in the first stage of the screen, in the different stages of the selection process added results from experimental work and increased the complexity of the process modelled

6.2.1 Process mass and energy balance

There are several unit operations common to each model (the core process model), and some which change (by-product processing options). The core process model will now be defined, with an overview of the by-product processing options in section 6.2.1.2. Further detail about the mass and energy balances used to describe the specific cases in the four process screening rounds is presented in sections 6.4.2-0.

6.2.1.1 Core process model

The core process model used in all model cases is presented in Figure 6-2. A detailed calculation outline is presented in Appendix 4.2, and required process inputs are outlined in Table 6-1.

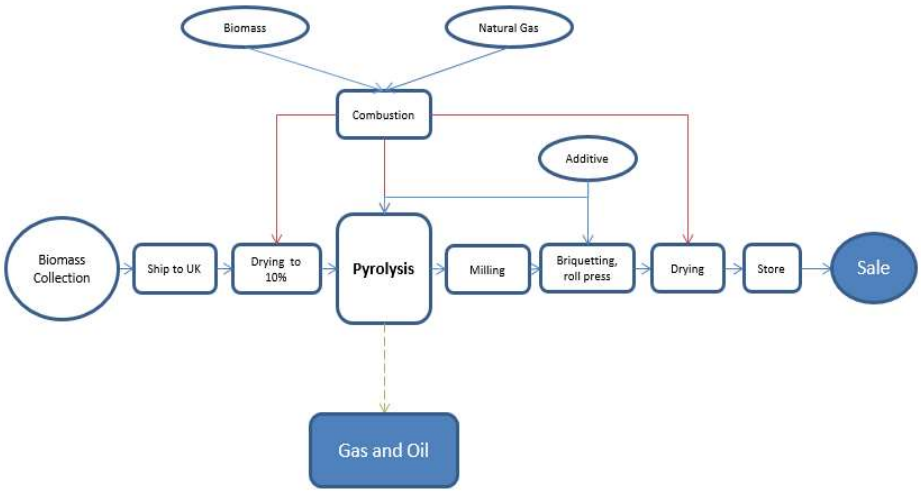


Figure 6-2. Process flow diagram of the core charcoal producing process. This shows the unit operations required for producing charcoal from biomass.

In this system:

- Biomass is transported to site,
- Then dried in a rotary drier to 10% moisture content. This is chosen as literature (Antal *et al.*, 2003) suggest this is the optimal content for charcoal production and this also in the range of the biomass moisture level for the bulk of the pyrolysis experimental work (Table 3-1).
- Biomass is then subject to pyrolysis which is heated from combustion of either natural gas or biomass. In some process configurations heat from combustion of oil and gas. Additive and catalyst if used can be added in at this stage.
- Charcoal is then milled to a powder before briquetting in a roll press briquette with a starch/water binder system,

- This then requires curing before the charcoal can be sold.

Table 6-1. Summary of inputs required for the process model

Symbol	Description	Units
M_{briq}	Mass of briquettes produced per year	ton/year
t_{op}	Operating hours per year	h
$C_{briq_{sand}}$	Concentration of sand in briquettes	g/g
$C_{briq_{bm}}$	Concentration of raw biomass added in briquettes	g/g
$C_{briq_{clay}}$	Concentration of clay in briquettes	g/g
$C_{briq_{starch}}$	Concentration of starch in briquettes	g/g
T_{peak}	Temperature of pyrolysis	°C
BM_{type}	Type of biomass – defines proximate analysis	(-)
$C_{bm_{MC\ Raw}}$	Raw biomass moisture content	g/g
$C_{MC_{bm-Dry}}$	Dried biomass moisture content – assumed to be 10%	g/g
Fire Test	PASS	

6.2.1.2 Side unit process models

These models develop in complexity with each stage of model development, due to the reduction in time required to fully develop each one, as for example in the first round of the process screen one there are 18 cases, while in screen four there are 4 cases Figure 6-3 indicates the process under taken for each process option and these are briefly described in Table 6-2. There are two main routes that these processes can take – liquid and gas can be separated or used mixed.

The actual combinations used in each round will be discussed in section 6.4 to 0.

Table 6-2. Description of by-product processing options. These options are being assessed in this option screening process.

Unit/Parameter	Mass balance
Mixed use	
Flare	All gas/liquid products are immediately sent to after burner/flare system
CHP boiler	All gas/liquid products are burnt in a boiler system with a recovery generator on the steam. Produces heat and electricity
Boiler for heat	All gas/liquid products are burnt in a boiler system. Steam produced to make heat
Separate use	
Gas to heat	Post separation gas used to provide direct process heat to the pyrolysis
Gas to electricity	Gas is sent to an energy recovery engine
Liquid to chemicals	Liquid is taken and purified for specialty chemicals. Processes used differ by option
Liquid to recycle	Placeholder used before catalytic pyrolysis was considered. Assumes recovered liquid could be sent back to pyrolysis for greater char recovery
Liquid to heat	Liquid is burnt in a conventional heavy oil burner and heat recovered
Liquid to electricity	Liquid is burnt in a conventional heavy oil burner and steam recovered and used for electricity generation

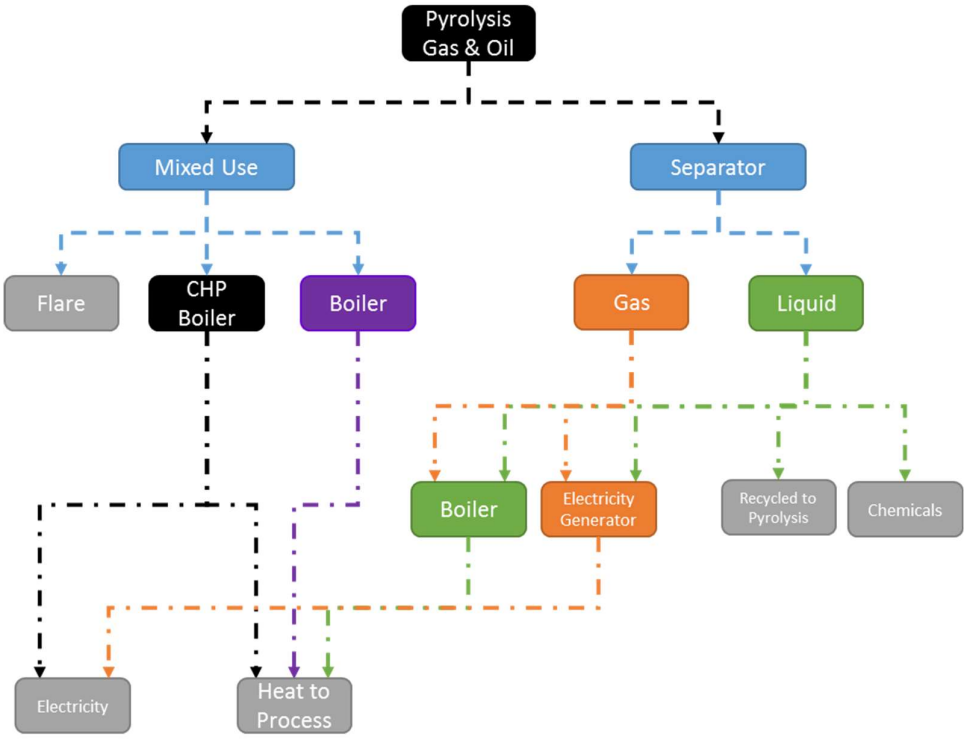


Figure 6-3. Flow diagram showing potential flow schemes for the use of by-product gas and liquid produced from the pyrolysis. The combinations of these options form the basis of the options being screened.

6.2.2 Financial model

The financial model used at each step was largely similar, depending on the components used at each stage in the process. There are three main parts to the financial model:

Capital cost, operating cost and revenue and, a Net Present Value used as a measure of project profitability.

Several inputs are required for the financial model, as indicated by Table 6-3.

Table 6-3. Outline of inputs required for economic model.

Symbol	Description	Units
c_{elec}	Electricity cost	£
c_{gas}	Gas cost	£
$C_{briq_{sell}}$	Briquette selling price	£
c_{bm}	Biomass cost	£
L_{plant}	Plant life	Years
i	Interest rate for NPV	%

The overall basis for the capital and operating cost balance sheets were taken from Sinnott *et al.* (2005), and are summarised in Table 6-4 and Table 6-5.
Unless state Sinnott *et al.* (2005) is the line item source. The Cost Method 'Aspen Model' was only used for the final model development, in previous rounds either the assumption (for values assumed negligible) or source correlation was used.

6.2.2.1 Capital cost calculation

Several assumptions have been made to produce this balance:

- Biomass and product storage and other costs are negligible on the process and accounted for in the design factors used
- Solid and liquid conveyance costs are included in the design factors used
- Several components were modelled in Aspen Plus to develop cost models in the final round of modelling. These models will be described in Appendix 4.
- The Retort Kiln estimates were converted to cost curves by applying the six-tenths rule (Sinnott *et al.*, 2005) to the costs for retort kilns presented in Shackley *et al.* (2011) and those published by the FAO (2008).
- Plant costs have been estimated for 2016. Costs from other years have been updated using the cost escalation method presented in (Sinnott *et al.*, 2005). Chemical engineering price index information was sourced from *Chemical Engineering Journal.*

Table 6-4. Capital cost calculation summary. The basis of this scheme comes from Sinnott and Towler, 2005)

Cost Area	Line Item	Cost Method	Reference
ISBL			
Pyrolysis			
	Rotary Dryer	Aspen Model or Source	(Sinnott & Towler, 2005)
	Retort Kiln	Source	(FAO, 2008; Shackley et al., 2011)
Briquetting			
	Hammer Mill	Aspen Model or Source	(Sinnott & Towler, 2005)
	Briquetting Plant	Source	(FAO, 1990)
	Tray Dryer	Aspen Model or Source	(Sinnott & Towler, 2005)
Heat Production			
	Natural Gas burner	Lang Factor	(Sinnott & Towler, 2005)
	Pyrolysis Gas Boiler	Lang Factor	(Sinnott & Towler, 2005)
	Pyrolysis Liquid Boiler	Lang Factor	(Sinnott & Towler, 2005)
	CHP Engine	Source	(EPA, 2012)
Other Products			
	Air Cooler	Aspen Model or Source	Appendix 1
	Water Cooler	Aspen Model Assumption	No Source - £200,000/20,000 ton/year
	Distillation	Aspen Model Assumption	No Source-£800,000/20,000 ton/year
	Bio-Oil Storage	Source	(Sarkar & Kumar, 2010)
	Phenol Recovery	Source	Ref
	Purchased Capital Equip.	=PCE	
OSBL		0.25*ISBL Costs	
Other Costs			
	Equipment erection	0.5*PCE	
	Piping	0.45*PCE	
	Instrumentation	0.15*PCE	
	Electrical	0.1*PCE	
	Process Buildings	0.1*PCE	
	Site Development	0.05*PCE	
	Physical Plant Cost (PPC)	=PPC	
Design Costs			
	Design and Engineering	0.25*PPC	
	Contractors Fee	0.05*PPC	
	Contingency	0.1*PPC	
	Design Costs	=Design	
Fixed Capital		=PPC+ Design Costs	

6.2.2.2 Operating costs and revenue calculation

The operating position statement used is presented in Table 6-5. Fewer assumptions are required for this statement but:

- Labour requirements have been assumed to cover 5 shift teams of 3 people
- Biomass costs are subject to those found in the literature review

More discussion on the by-product chemical selling process will be established in section 6.4, where the compounds produced where selected.

Table 6-5. Operating position summary calculation. Basis for this calculation comes from Sinnott and Towler (2005).

Cost area	Line item	Cost method	reference
Variable			
Raw Materials			
	Biomass	c_{bm}	
	Clay	c_{clay}= 120	CPL quote
	Sand	c_{sand}=100	CPL quote
	Starch	c_{sand}=100	CPL advice
Utilities-Main			
	Electricity	c_{elec}	
	Natural Gas	c_{gas}	
Utilities-Side			
	Electricity	c_{elec}	
	Natural Gas	c_{gas}	
Total Variable Operating Cost			
Revenue			
Charcoal			
	Charcoal Briquettes	$c_{briq_{sell}}$	
Side Process			
	Electricity	c_{elec}	
	Chemicals	See discussion in relevant sections	
Total Revenue		Rev	
Other Operating			
Fixed Op Costs			
	Labour – Manager	1 @ £30,000	Assumed
	Labour – Shift	18 @ £25,000	Assumed
	Labour – Maintenance	1@ £25,000	Assumed
Other Overhead			
	Maintenance	%5 ISBL Capital	
	Insurance	1% of Fixed	
	Other Costs	1% Total	
Total Other Costs			
Operating	=Revenue-Variable cost-Other costs		

6.2.3 Net present value

The capital and operating positons were then used to determine the net present value of the project as discussed in the literature review, section 2.6.2.1.

6.3 Carbon model

The carbon model used was developed to allow the determination of operating carbon emissions for the process, rather than develop a full Life Cycle Analysis (LCA) for the system, however, the process outlined in the literature review section 2.6.1 was followed.

This was due to complexity of the modelling process and time constraints of the project, and what is presented here will give an adequate estimate of the structural differences between the processes. Only two further inputs are required in this model, as outlined in Table 6-6.

Table 6-6. Inputs to carbon model

Symbol	Description	Units
MD_{ship}	Biomass shipping method	(-)
D_{ship}	Biomass shipping distance	km

The outline of carbon balance and calculations involved is presented in Table 6-7.

Table 6-7. Outline of carbon model calculation.

Step	Line item	Calculation
Biomass		
	Biomass	See Note 1
	Shipping of	See Table 6-8
Energy Supply		
	Natural Gas	Net kWh*0.4120 kgCO_2-
	Electricity	Net kWh*0.204 kgCO_2-
By-Product Use		
	By-Product	Note 2
	Chemical	Note 3
Charcoal End use		
	Shopping of	See Table 6-8
	Combustion of	-3.741 kgCO_2/kg Charcoal
Net Carbon		

Note 1: Sequestration of carbon by biomass growth is calculated as follows: Trees generally have a C content of 43% (Lugt, 2013) which compares with the C-content of biomass This is converted to $CO_{2\text{-eq}}$ by 0.43*12/44 This is then multiplied by the total mass of biomass used.
Note 2: Emissions from combustion processes found by using assumed factors for $CO_{2\text{-eq}}$ content of syngas and bio-oil, which were then used as constants Gas combustion was taken at 60% of total mass; oil 50% of total mass. Limitation for the analysis but this puts a tax on 'free energy' and represents reality that utilisation as alternate chemicals or conversion to charcoal is more environmentally favourable.
Note 3: Chemical production off sets are taken as the $CO_{2\text{-eq}}$ of carbon weight of compound, as used in Note 1. This assumes this process would be replacing compounds which come from fossil sources.

Table 6-8. Carbon emissions by transport method sourced from World Shipping Council (2017)

Shipping method	g CO_2/ton BM/km
Ship	-10
Rail	-21
Truck	-59
Air	-470

6.3.1 Outline of option decision making model used to assess option screen

Four main outcomes from each option have been selected to determine if the case suitability, show in Table 6-9. These have been weighted for inclusion in a simple multicomponent decision analysis (MCDA) (Chong, 2011) to analyse the effects of all the criteria.

MCDA determines a score for each of the criteria based on its rank out of all the options in a study.

- The options are ranked from best = high score to worst = low score – i.e. NPV high is good, CAPEX low is good.
- The rank is multiplied by the weighting giving a weighted score

- Then these 4 weighted scores are summed to give an overall score for the option

Options are highly weighted towards NPV as projects which are not profitable or have low profitability will be ignored in the long run. Because of this, the case NPV will be presented alongside the weighted score. A higher score indicates a better option.

Table 6-9. Criteria used for option decision making.

Parameter	Unit	Description	Weight for MCDA
Net present value (NPV)	£	Measure of project profitability	0.4
Carbon Balance	$kgCO_{2\text{-}eq}$/Ton Char	Measure of plant suitability	0.2
Internal Energy	%	Measure of plant suitability & biomass utilisation	0.2
Capital cost (CAPEX)	£	Indicator of investment likelihood	0.2

6.4 Side unit process options screening

6.4.1 Model inputs

To ensure the models compare similar cases, this analysis has been performed using the general inputs outlined in Table 6-10. Briquette composition was kept at 15% biomass and 15% inert material, which refers to clay or sand addition. These levels are selected based on the BBQ combustion work presented in Chapter 5 as at these levels of input charcoal will still burn acceptably. Biomass and sand are required to be added as they are cheaper than charcoal costing £60 and £100/ton respectively where was charcoal at 30% yield costs using £60/ton charcoal is at minimum £120/ton without considering energy costs, labour and other plant running costs. Further thermodynamic inputs can be found in Appendix 4.2.

6.4.2 Process option screen round 1

The initial screen experiment covered the options presented in Table 6-11. The process flows assessed by this case can be summarised in Figure 6-4, while Appendix 4.1 contains the individual PFD used for each model case.

These 17 cases cover the range of project options. Because of this, only simple models have been constructed for the mass balance of each case, as highlighted in Table 6-12.

Table 6-10 TEA model input constants throughout screen experiment.

Symbol	Value	Units
Process model inputs		
M_{briq}	20000	ton/year
t_{op}	8000	h
$C_{briq_{sand}}$	15	g/g
$C_{briq_{bm}}$	15	g/g
$C_{briq_{clay}}$	15	g/g
$C_{briq_{starch}}$	5	g/g
T_{peak}	500	°C
BM_{type}	Pine wood	(-)
$C_{bm_{MC\ Raw}}$	20	g/g
$C_{MC_{bm-Dry}}$	10	g/g
Fire Test	PASS	
Cost model inputs		
c_{elec}	0.06	£/kWh
c_{gas}	0.04	£/kWh
$C_{briq_{sell}}$	350	£
c_{bm}	60	£
L_{plant}	15	Years
i	8	%
Carbon model inputs		
MD_{ship}	Road	(-)
D_{ship}	350	km

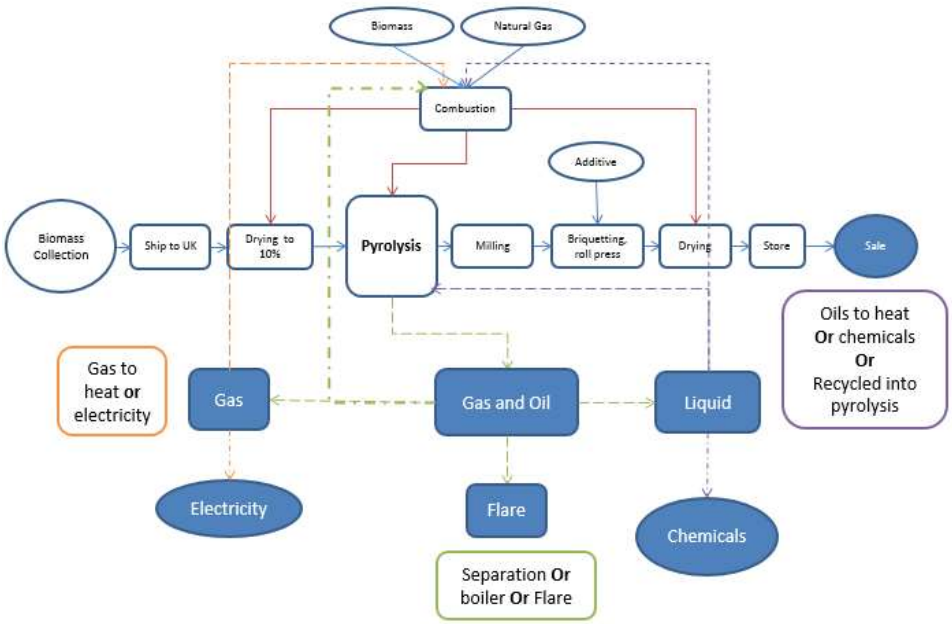


Figure 6-4 Graphical outline of the cases assessed in the screen experiment. This encompasses all the 17 options covered by this study. Appendix 4.1 contains the individual PFD for each of the options.

Table 6-11. Outline of cases used in initial screen experiment. These codes are used throughout this chapter to track the 17 cases through the screening process outlined in Figure 6-1. The Process flow diagrams for each of these 17 options are presented in Appendix 4.1

Case ID		Liquid By-Product Use				
		Heat	Electricity	Chemicals	Pyrolysis	Flare
Natural Gas heating + Syn Gas Use	Heat	**2**	**3**	**4**	**5**	
	Electricity	**6**	**7**	**8**	**9**	
	Flare					**1** Note 1
Biomass heating + Syn Gas Use	Heat		**10**	**11**	**12**	
	Electricity	**13**	**14**	**15**	**16**	
	Flare					**17**

Note 1: Flare not used in conjunction with other unit operations due to increased CAPEX due to high cost of liquid and gas separation. Biomass heating with heat production from liquid and gas is not included either due to excess heat production from gas/liquid products in case 2

Table 6-12. Model equations for by-product processes used in screen round one

Unit	Mass Balance	Energy Balance
Flare	N/A – See assumptions in Carbon model	N/A. Even though natural gas would be used, considered outside scope of case. Penalty for not utilising biomass fully seen as financially more significant
Boiler	N/A – See assumptions in Carbon model	Heat = 60% Loss = 40%
Separator	Full separation of liquid and gas products	Assumed air cooling from peak temperature to 100 °C then water cooling to final temperature of 20 °C. Cooling efficiency of water assumed to be 60% and electricity required to produce this. Simple heat balance -Aspen Model NOT used.
Electricity Generation	N/A – See assumptions in Carbon model	Combustion assumed to produce 40% recoverable energy from either liquid or gas streams
Pyrolysis	Oil could be returned to pyrolysis, where 5% was converted to charcoal	Extra water/oil added to pyrolysis heat demand calculation.
Chemicals	Assume that input liquid fraction is separated into a water/oil/distillate solid stream (Zhang *et al.*, 2013) which is recycled to	Assume distillation of oil stream with a reflux ratio of 3 and energy efficiency of 60%. Natural gas required for re-boiler and electricity required for condenser cooling water. Simple heat balance – Aspen Model Not Used

The outputs from the simulation of this experiment are presented in Figure 6-5 and Figure 6-6.

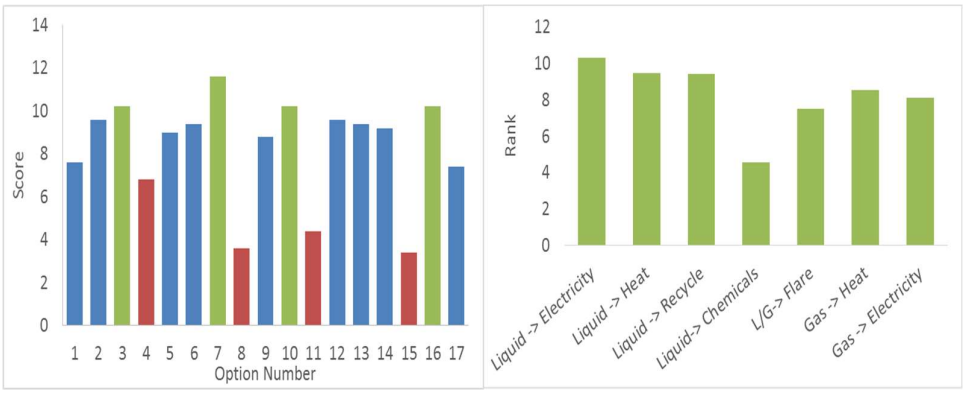


Figure 6-5. Average score – all options.

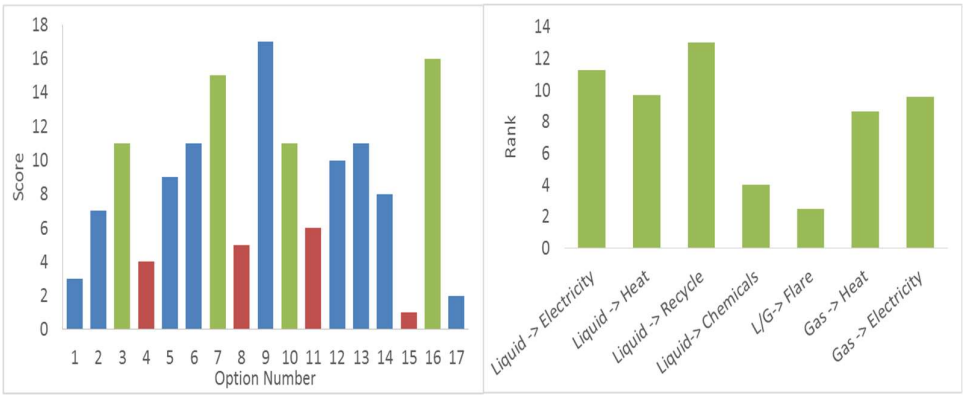


Figure 6-6. Average score – all options – NPV rank only

Table 6-13. Screen 1 MCDA Experiment scores visualised. Green = Good – Red = Bad

Screen Experiment 1 MCDA Score		Liquid By-Product Use				
		Heat	Electricity	Chemicals	Pyrolysis	Flare
Natural Gas heating + Syn Gas Use	Heat	11	5.6	12	8.6	
	Electricity	10.6	8.6	9.8	6.2	
	Flare					12.6
Biomass heating + Syn Gas Use	Heat		9.8	6.2	10.6	
	Electricity	7.6	7.2	7.8	7.6	
	Flare					9.4

The main findings from this initial study are as follows:

- Options producing chemicals with current assumptions perform poorly. This due to the high cost of distillation system.
- Using biomass to generate heat for the system instead of natural gas appears to be economically un-favourable, however option 14 (which produced electricity from all by-products) will be kept for the next round of analysis to see if model improvements mean this option, which has the highest revenue, improves.
- Options which contain the flare system have varied performance, with the high cost of the biomass powered system against the natural gas system (option 17 vs 1) but overall, flare options perform poorly. This is due to the inefficiency with this system, as most of the raw materials are vented.
- Options where liquid and gas both are assigned to produce heat also perform poorly, as there is inefficiency as too much heat is produced.
- Heat from the gas stream produced is not as valuable as that from liquid, as more heat is generated by liquid
- Gas for electrical production appears more efficient.
- An interesting finding from this analysis is that the simulated recycle of oils performs well, given the low yield that is simulated. This finding further emphasises that charcoal is the most valuable product in this framework.
    - With this point in mind, it should be noted that these results could be subject to bias: the selection parameters chosen largely lean to financial outcomes. This is because this process development has been done with the aim of providing CPL insight to which processes they should investigate investing in, and to meet their company goals financial parameters are the most important criteria to meet as positive indications in these areas are required for investment.

With this discussion in mind, the remaining options for analysis are presented in Table 6-14 and Figure 6-7. The flare and boiler options have been kept at this stage for baseline testing.

Table 6-14. Summary of options remaining from screen round 1

Case ID		Liquid By-Product Use				
		Heat	Electricity	Chemicals	Pyrolysis	Flare
Natural Gas heating + Syn Gas Use	Heat	2	3		5	
	Electricity	6	7		9	
	Flare					1[Note 1]
Biomass heating + Syn Gas Use	Heat					
	Electricity		14			
	Flare					17

6.4.3 Process option screen round 2

This round of modelling aimed to further test out the effect of the oils returning to pyrolysis, the concept was changed to include the addition of clay to the pyrolysis with the aim of cracking heavy oils and retaining some of this as charcoal.

Finer comparisons were also made between the options, which are summarised in Table 6-15, and the process flows are the same as used in Figure 6-7.

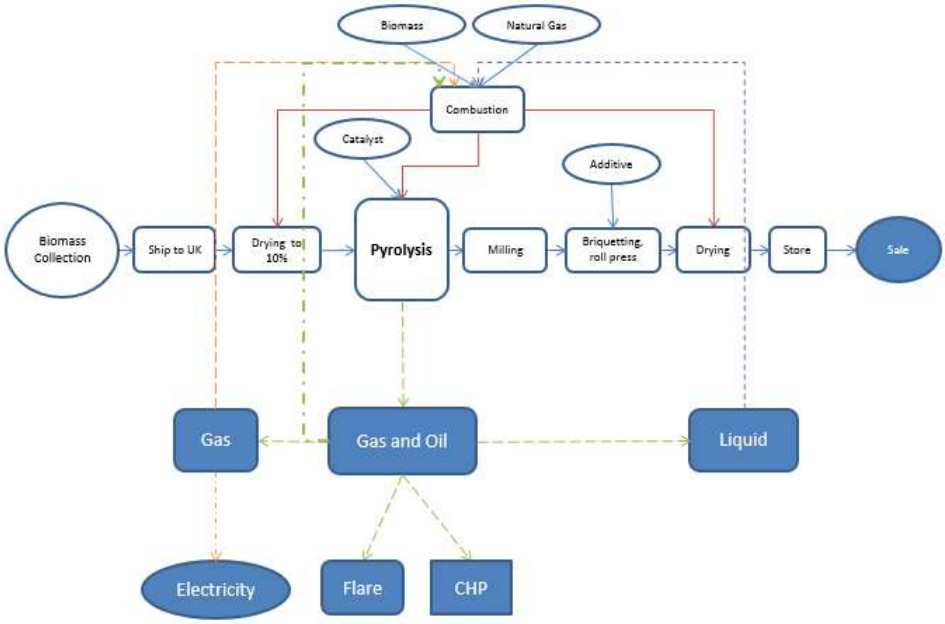


Figure 6-7. Summary of process flows remaining after screen round 1

Table 6-15. Description of options used in screen round 2.

Option Number	Description
1	By products go to flare and system heated by natural gas
2	By products go to heat and make up heat by natural gas
2A	By products go to CHP system and make up heat by natural gas
3	Gas goes to heat, Liquid goes to electricity production. Make up heat by natural gas
6	Gas go to electricity, Liquid go to heat production. Make up heat by natural gas
7	By products go to electricity and make up heat by natural gas
14	By products go to electricity and make up heat by biomass
17	By products go to flare and system heated by raw biomass

To consider the excess heat identified from the case where all by-products, a sub-option 2A has been introduced which assumes this boiler is part of an electricity recovering CHP system.

The mass and energy balances used for the side processing options are presented in Table 6-16. The model was run twice, once with catalyst and once without to see the effect of this.

The results from this simulation are presented in Figure 6-8. From the overall score, there appears to be minimal difference between the options with or without the catalyst present and in some cases the catalyst causes the sore to become worse. However, on analysis of the results this comes from the lower amount of biomass required to produce the briquettes with catalyst present, and in a financial sense, this catalyst addition greatly improves the finances of all of the cases.

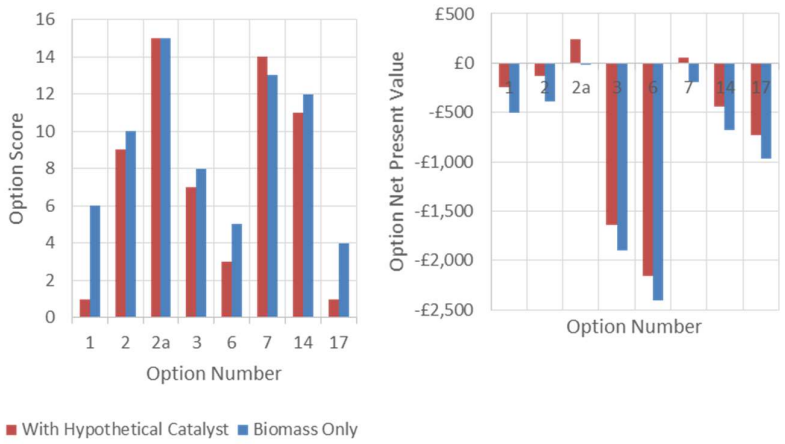


Figure 6-8. Output from screen round 2 simulations. From this it can be seen that option 2a performs the best both in terms of score and project NPV. It can also be seen that catalyst addition makes projects financially more positive.

Table 6-16. Model equations for by-product processes used in for screen round 2

Unit	Mass Balance	Energy Balance
Flare	N/A – See assumptions in Carbon model	N/A. Even though natural gas would be used, considered outside scope of case. Penalty for not utilising biomass fully seen as financially more significant
Boiler	N/A – See assumptions in Carbon model	Heat = 60% Loss = 40%
CHP Boiler	N/A – See assumptions in Carbon model	Basic breakdown was assumed: Electricity = 30% Heat = 30% Loss = 40%
Separator	Full separation of liquid and gas products	Assumed air cooling from peak temperature to 100 °C then water cooling to final temperature of 20 °C. Cooling efficiency of

		water assumed to be 60% and electricity required to produce this. Simple heat balance
Electricity Generation	N/A – See assumptions in Carbon model	Combustion assumed to produce 40% recoverable energy from either liquid or gas streams
Catalyst	Model Assumes that 5% extra charcoal is produced at the expense of oil	Heating of a sand like catalyst added to pyrolysis (15% weight charcoal) is added to heat balance.

Table 6-17 Remaining options from screen experiment 2

Case ID		Liquid By-Product Use				
		Heat	Electricity	Chemicals	Pyrolysis	Flare
Natural Gas heating + Syn Gas Use	Heat	2/2A	3			
	Electricity	6	7			
	Flare					

Based on these results, two major directions were taken (

Table 6-17):

- Drop the flare from the analysis, but keep the boiler case as a baseline
- Drop biomass powered options, as they have consistently score worse and perform worse economically than other options.

This work has suggested that the catalyst addition could have a significant effect on the process and became the basis for the catalytic pyrolysis work presented in Chapter 4. This also opens up other process configurations as the catalyst effect can be to generate higher concentrations of lighter compounds and increase the relative value of the pyrolysis oils, than that suggested in the first screen experiment.

6.4.4 Process option screen round 3 – Integration experimental work

Between screen 2 and this work (screen 3) there was a large amount of work done producing the charcoal combustion model (Chapter 5), catalytic pyrolysis (Chapter 4) and pyrolysis yield model (Chapter 3). This has meant several things for the modelling systems used:

- A true/false test for BBQ acceptability has been added in based on the work from Chapter 3. As the conditions assumed for this analysis pass this test, this addition will become relevant in next chapter when the inputs to the model are optimised.
- Pyrolysis yields calculated based on input conditions (temperature, biomass proximate analysis and catalyst effects)
- And further understanding was gained about the effects of catalysis and the actual value of the chemicals produced from the system, so this was brought back in to consideration.

For this round of model then, the options that were considered were listed in Table 6-18.

The largest effect on these results was as expected from variable net present value. While the chemical option NPV is negative, there are many assumptions made around this simulation which suggest that for future cases where more time is spend developing accurate systems it will be kept in. The other options which require separations are being excluded at this stage because of poor performance, which means even though electricity generation has been a good performer up until now it is being dropped.

The results from this model are presented in Figure 6-9 and the options being kept on for the final round of modelling are presented in Table 6-20.

Table 6-18. Model options for screen round 3

Option	Description
2	By products go to boiler system, make up heating by natural gas
2A	By products go to CHP system, make up heating by natural gas
4	Gas to boiler oils to chemicals
5	Gas to electricity oil to boiler
8	Gas to electricity oils to chemicals

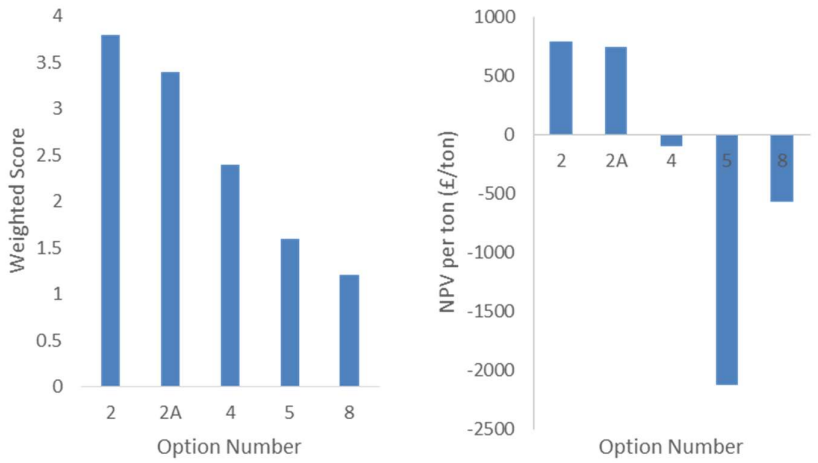


Figure 6-9. Output from screen round 3

Table 6-19. Model equations for by-product processes used in screen round three

Unit	Mass Balance	Energy Balance
Flare	N/A – See assumptions in Carbon model	N/A. Even though natural gas would be used, considered outside scope of case. Penalty for not utilising biomass fully seen as financially more significant
Boiler	N/A – See assumptions in Carbon model	60% efficiency
CHP Boiler	N/A – See assumptions in Carbon model	32% Loss 40% Heat 25% Electricity (EPA, 2012)
Separator	Full separation of liquid and gas products	Assumed air cooling from peak temperature to 100 °C then water cooling to final temperature of 20 °C. Cooling efficiency of water assumed to be 60% with a coefficient of

		performance of 3. Electricity required to produce this. Simple heat balance -Aspen Model NOT used.
Electricity Generation	N/A – See assumptions in Carbon model	30% Efficiency
Chemicals	Assumes that only 5% of the total oil stream can be recovered and sold. Sold for £10/ton as hypothetical chemical.	Low recovery efficiency and selling price assumed to account for no energy demand

6.4.5 Screen Round 4

For this final round of modelling more detail was added to several steps of the by-products processing by production of Aspen models (presented in Appendix 4.3), and production of specific chemicals was added. As with the other models the options used have been described in Table 6-20, and the unit operations used have been summarised in

Table 6-21.

Table 6-20. Outline of options used in screen round 4

Option No.	Description
2A	By products go to CHP system, make up heating by natural gas
2	By products go to boiler system, make up heating by natural gas
4A	Gas to boiler oils to chemicals – production of furfural
4B	Gas to boiler oils to chemicals – production of phenol

Table 6-21. Mass and energy balances for by-product processes used in screen round 4

Unit	Mass Balance	Energy Balance
Boiler – Mixed Case	N/A – See assumptions in Carbon model	30% Efficiency
Boiler – Gas Only	See Gas Combustion model in Appendix 4.3	
CHP Boiler	N/A – See assumptions in Carbon model	32% Loss 40% Heat 25% Electricity (EPA, 2012)
Separator	See Separator model in Appendix 4.3	
Chemicals –(Chong, 2011)	Phenol production – See Aspen Distillation Model Phenol recovered this way is assumed to sell for £750/ton	
	Furfural Production – By a 2 stage decanting system followed by a simple distillation model, based on that presented for phenol. Stage 1 of the decanting process requires 1 kg fresh water to every input kg Stage 2 requries 2.5 kg NaOH to 1 kg Oil	N/A – see Hysys distillation equation Appendix 4.3.

	Overall recovery of oil as product is assumed to be 15% Selling price is assumed to be £650/ton	

6.4.5.1 Output from round 4 screen experiment

The output from this model case is presented in Figure 6-10.

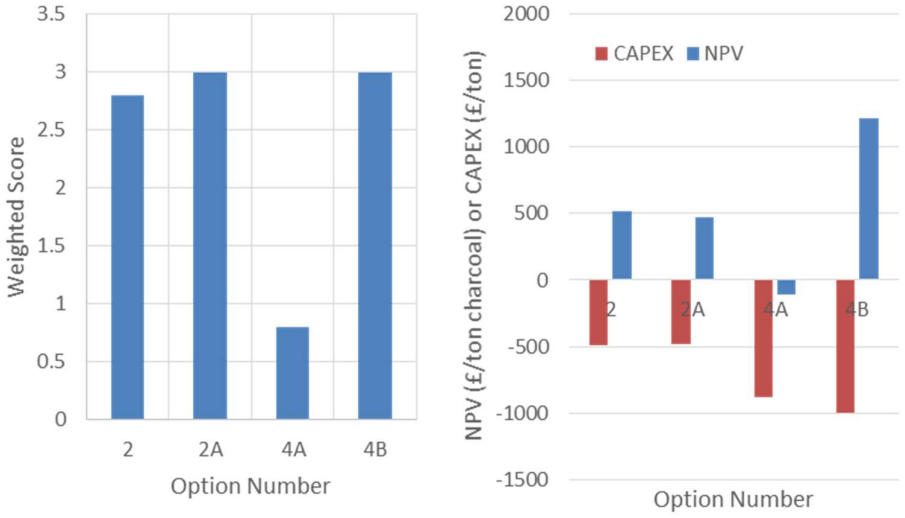


Figure 6-10. Outputs from screen round 4

Three things are clear from process option screen round four:

- The low recovery of the more expensive furfural alcohols in option 4A means this option is not being used further.
- Option 2A and 4B appear close, with the straight boiler case (Option 2) appearing more favourable due to the greater NPV of this case compared to the CHP engine.
    - However, as the CHP case outperforms the boiler case on process and biomass efficiency this case will be kept on. This is being done for two reasons:
        - Option 2B would outperform Option 2 if carbon emissions were taxed, as may occur in various forms in the future

- Option 2B produces more internal energy than Option 2 so is more stable compared to changing energy prices.

6.5 Conclusions

This chapter has determined several important characteristics required for optimal production of charcoal under the framework used here.

- Options producing chemicals with current assumptions perform poorly, unless specific chemicals with a high value can be produced from the process. The addition of clay can aid this.
- Using biomass to generate heat for the system instead of natural gas appears to be economically un-favourable, due to the lower cost of energy over wood chips.
- Options which contain the flare system have overall poor performance. This analysis has suggested that a system using a boiler to process off gas makes a better baseline case as this option is likely to be the cheapest financially viable case.
- Options where liquid and gas both are assigned to produce heat also perform poorly, as there is inefficiency as too much heat is produced.
- An interesting finding from this analysis is that production from electricity from by-product gas and liquid is un-economic and scores poorly. This is due to the high cost of the equipment required for this conversion.
- Finally it should be noted that some bias has been added into these results as options which score higher in financial stability measures are favoured.

Option 4B and Option 2A have been chosen as the best case options, and will be assessed further in chapter 7.

The reasons for this are:

- Options 2A and 2B perform well in both the financial and process acceptability factors
- They highlight two extremes of the potential project financial outcomes:

    - Option 4B is double the capital expenditure of Option 2A, which may impact investment decisions in the future by funding bodies
    - Option 4B generates a much greater level of revenue than Option 2A due to the products being sold.
- The product mix also presents two extremes for potential process conditions:
    - Option 2A gains all revenue from charcoal so optimal conditions could be different to option 4B which gains a significant amount of revenue from chemical sales.

Chapter 7. Model application and studies

This chapter aims to apply the two process flow cases generated from the screening experiment presented in Chapter 6, and suggest optimal conditions for producing BBQ charcoal from these plants. These case are:

- Option 2A: by-products sent to a boiler and energy is used to produce low grade process heat and electricity (Figure 7-1)
- Option 4B: where gas is used for process heat and .oil is collected and distilled leaving residual char and chemicals (Figure 7-2)

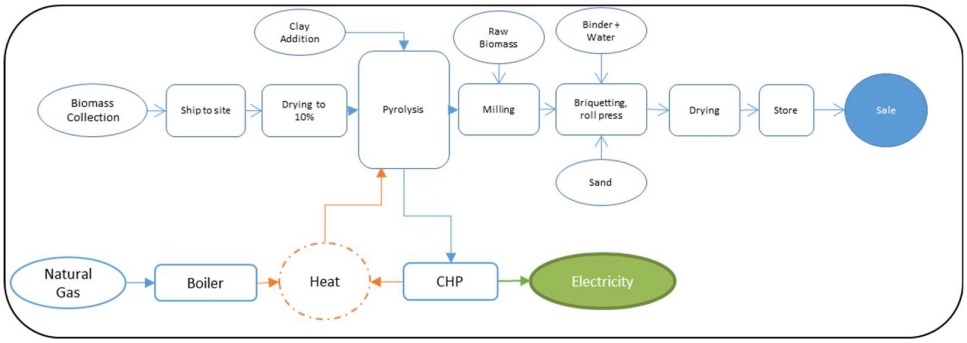


Figure 7-1. Option 2A process flows: gas & oils to CHP

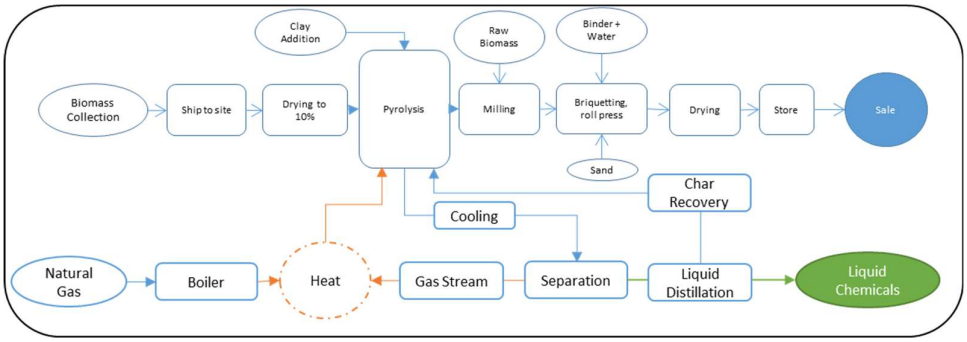


Figure 7-2. Option 4B process flows: gas to heat and liquid to chemicals

The sensitivity of key process variables and their effect on the optimal outcomes for each of these cases will then be presented.

Following this, process alterations affecting the core part of the process, due to the absence of experimental data, have been tested:

- The effect of biomass drying as part of the process
- Using clay in a post catalyst bed (instead of in situ) to react all oil to extinction

Finally a study looking at the effect of producing charcoal in different European countries or shipping various biomass types to the UK for processing will be presented.

7.1 Optimal case

7.1.1 Method

The model presented in Chapter 6 was set up with the following inputs and constraints on optimisable variables, outlined in Table 7-1.

Table 7-1. Inputs to optimisation study. For definitions refer to Table 6-1. As discussed in Section 6.4.1, $C_{briq,bm}$, $C_{briq,clay}$ and $C_{briq,sand}$ refer to biomass, clay and sand which are mixed with the charcoal into the final briquette.

Symbol	Value	Units
Process model inputs		
M_{briq}	10-20,000	ton/year
t_{op}	8000	h/year
$C_{briq_{sand}}$	0-15[Note 1]	g/g
$C_{briq_{bm}}$	0-15[Note 1]	g/g
$C_{briq_{clay}}$	0-15[Note 1]	g/g
$C_{briq_{starch}}$	5	g/g
T_{peak}	450-700	°C
BM_{type}	Pine wood, Olive cake, Straw, Mixed Hardwood	(-)
$C_{bm_{MC\ Raw}}$	20[Note 2]	g/g
$C_{MC_{bm-Dry}}$	10	g/g
$Fire\ Test$	PASS	(-)
Cost model inputs		
c_{elec}	0.06	£/kWh
c_{gas}	0.04	£/kWh
$C_{briq_{sell}}$	350	£/ton
c_{bm}	60	£/ton
L_{plant}	15	Years
i	8	%
Carbon model inputs		
MD_{ship}	Road	(-)
D_{ship}	2500	km

Note 1: maximum concentrations of briquette additives are based on the results of fire testing, see Chapter 5

Note 2: Moisture constant has been kept constant at 20% for simplicity

Biomass Types considered are outlined in Table 7-2. Cost of biomass was kept constant at £60/ton for this analysis so the process operation effects can be observed. Section 7.4 will present a study based on specific biomass source cases which will examine the impact of the transport associated with these locations.

Table 7-2. Properties of biomass used in optimisation study (see Table 3-1).

Biomass type	Moisture (wt%)	Volatiles, dry basis (wt%)	Ash,, dry basis (wt%)
Hardwood	20	85	0.4
Pinewood	20	81.9	0.6
Olive Cake	20	66.3	6.7
Straw	20	75.1	6.8

The optimal system was then found by using the evolutionary solver in Microsoft Excel 2013, due to the ability it has to converge on a solution from multiple model start points, and run through categorical optimisations as required by the biomass selection parameter. This ensures that the global optimal solution is found. The system NPV was used as the objective to maximise in the process, as this has been considered the most important characteristic up until this point.

Carbon emissions based on these effects are presented to give an indication how the changing process variables effect the sustainability of the process.

7.1.2 Results

The optimal conditions in both models are outlined in Table 7-3.

Table 7-3. Optimal conditions for production BBQ charcoal from options 2A and 4B

Symbol	Value	Units
M_{briq}	20,000	ton/year
$C_{briq_{sand}}$	0– Option 2A 15 – Option 4B	g/g
$C_{briq_{bm}}$	15	g/g
$C_{briq_{clay}}$	15– Option 2A 0 – Option 4B	g/g
T_{peak}	450	°C
BM_{type}	Pine wood, Olive cake, Straw, Mixed Hardwood	(-)

Table 7-3, shows these parameters are similar for both process options, with differences between the biomass types and clay or sand addition which will now be discussed.

- The economic effects due to biomass type, are shown in Figure 7-3, which shows the class of biomass favoured in each case is different. Option 2A, which gains all its revenue from charcoal production, benefits from olive cake/straw biomass types which have high ash contents; while Option 4B, which gains a significant revenue stream from oil distillation, favours low ash woody biomass with high volatiles. Further analysis on this topic will be presented in Section 7.1.3.1.
- Figure 7-3 shows the reverse of this trend applied to the carbon emissions for each of these options. For Option 2A option this is because higher charcoal yields mean that there is more external energy required in the pyrolysis phase, while for Option 4B higher volatiles yields mean more emissions are made heating the process.

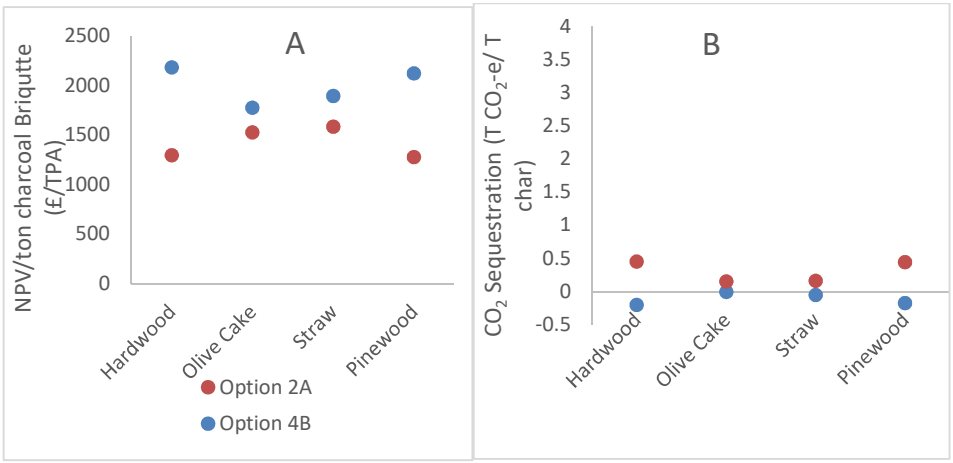


Figure 7-3. Option 2A (using clay) and 4B (using sand) against the four biomass types used in this study. A) effect on project profitability; B) Effect on CO_2 emissions (scale for this large to allow for comparison with Figure 7-5)

- Clay is favoured by Option 2A and sand is favoured by Option 4B. Analysis of this presented in Figure 7-4 which shows the difference in economics when sand or clay are used in each case.
    - Option 2A benefits from the clay addition due to the increased charcoal yield from the catalytic effect, which has the overall economic effect of requiring lower investment in biomass which improves the economics.

- However, with Option 4B the clay utilises the oil produced by the process which both reduces the amount of income from oil and lowers the amount of atmospheric distillate returned to the process.

What has not been reflected in this analysis is the potential economic effect of oil-upgrading, presented in section 4.4.2.2. This is because the changing value of mixed pyrolysis oils does not exist in open literature. Therefore, as Figure 7-4 suggests there is not a significant difference between the addition of clay or sand for Option 4B NPV (both are within the 30% accuracy expected by a preliminary cost study of this type (Sinnott *et al.*, 2005)) this study would still recommend that Option 4B utilises clay. Future modelling work is presented with this in mind.

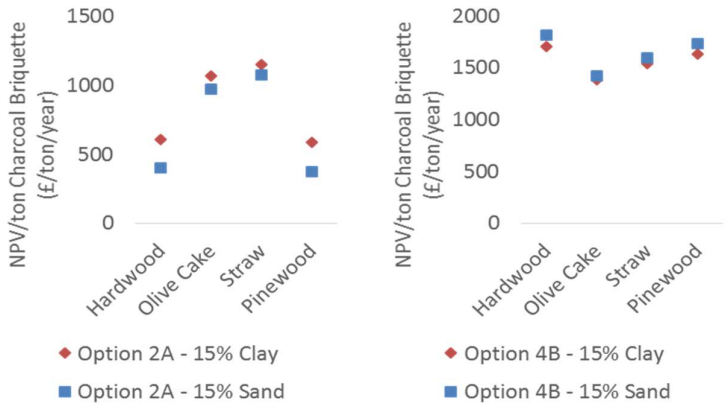


Figure 7-4. Options 2A and 4 comparing the effect of adding clay and sand

7.1.3 Sensitivity study

This section will now examine these results, discussing the sensitivity and effects of changing process parameters.

7.1.3.1 Effect of biomass composition

The effect of changing biomass composition over a wide range of biomass was investigated. This was done by using 36 simulated biomass types with the concentration of ash content at 1, 2, 3 and 6%wt, dry basis and volatiles concentration at 10-90% wt, dry basis at 10% concentration intervals. The results from this analysis are presented in Figure 7-6.

This analysis highlights the largest difference between the two options.

- Option 2A is more positively influenced by increasing ash than Option 4B. This is because Option 2A is only influenced by charcoal yield, and increasing ash content means that whether the fate of the volatiles the charcoal yield will always be higher.

- Option 4B gains a significant portion of revenue from volatile component recovery as oils. Because of this, charcoal into the process with increased ash means that there will be less volatile fractions for the treatment unit operations.

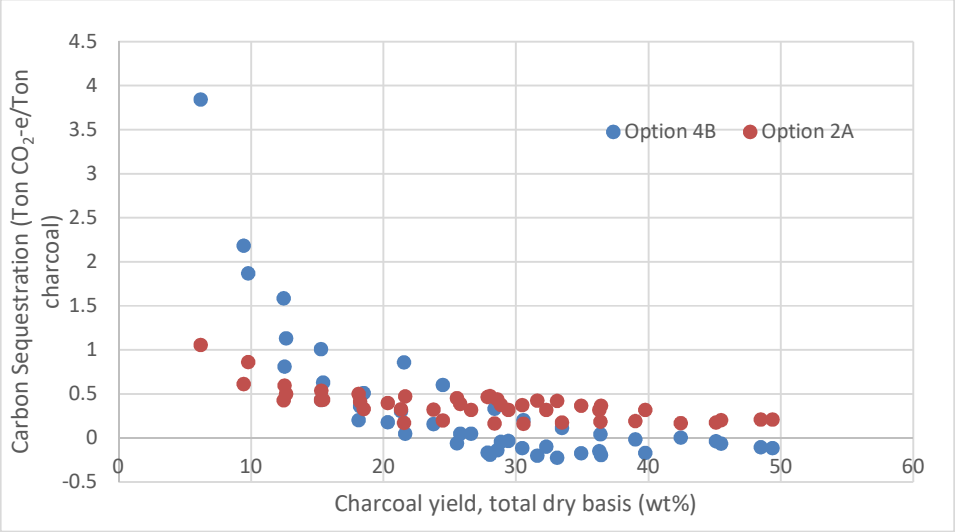


Figure 7-5. Carbon emissions relationship with charcoal yield.

Figure 7-5 shows the relationship between the charcoal yield and carbon emissions.

- As expected Option 2A indicates that there are lower emissions with increasing charcoal yield as there are lower amounts of biomass required. The variation shown in Figure 7-5 agrees with the trend presented in Figure 7-4. Figure 7-4 is for a specific portion of this graph where the overall mass of biomass do not change greatly but as mentioned the product distribution causes the trend seen. This distribution change means there is high variation in Figure 7-5 for this reason.
- Option 4B shows the same effect. The emissions for this option become worse than for Option 2A when the amount of energy required for distillation of oils becomes significant, which is above 20% charcoal yield (i.e. 80 oil/gas yield).

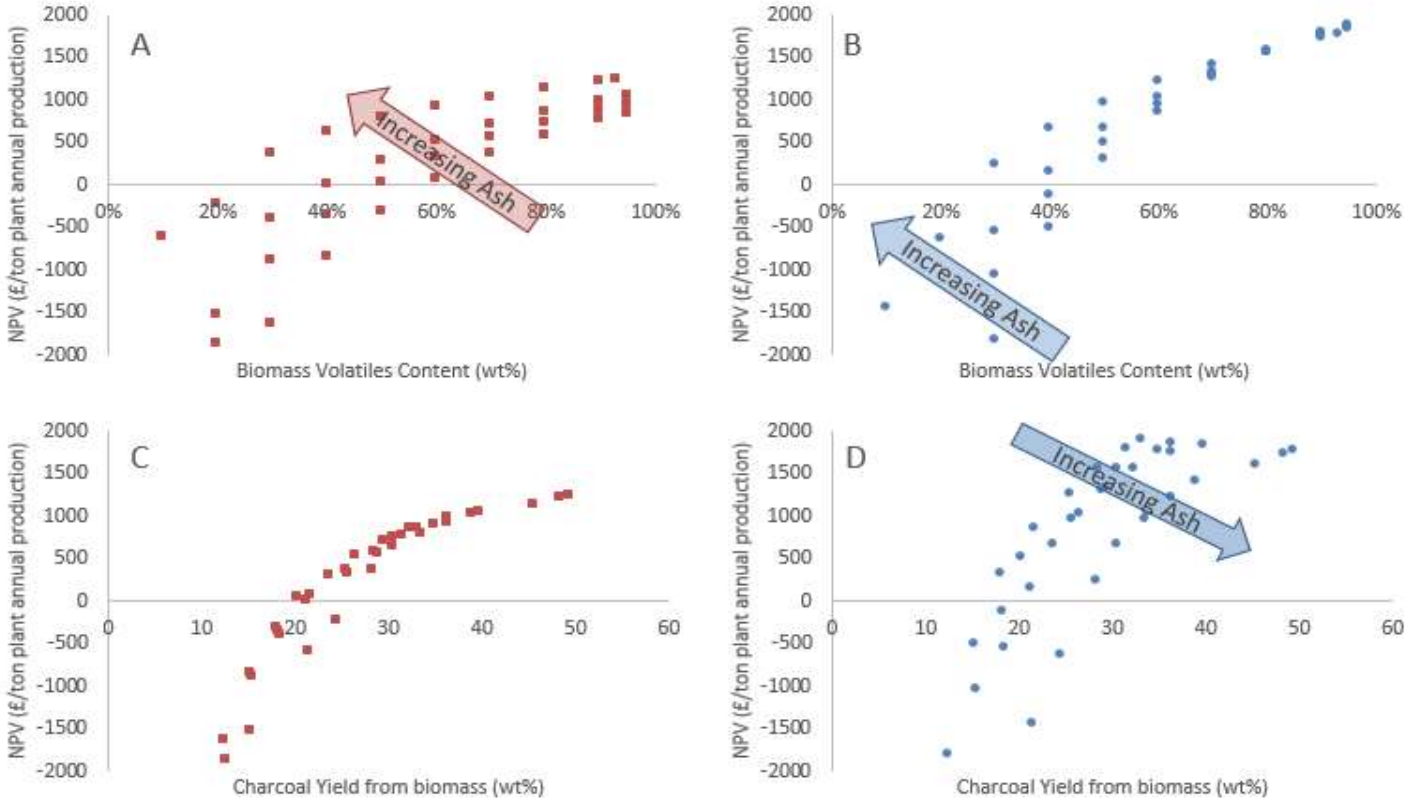


Figure 7-6. Outputs from biomass composition study. A – Option 2A NPV vs Volatiles Content; B - Option 4B NPV vs Volatiles Content; C - Option 2A NPV vs charcoal yield; D - Option 4B NPV vs charcoal yield

7.1.3.2 Effect of Temperature

Figure 7-6 and Figure 7-7 show the effect of producing charcoal over the range of 200 – 700 °C using pinewood. While Chapter 5 highlighted that charcoal could only be produced between the ranges 400-600 °C, and both options have lower returns at higher temperatures, but Option 2A is more severely affected than Option 4B.

- Increasing temperature produces more oil in the pyrolysis process therefore Option 4B generates more revenue and more char is recovered from the distillation step. This balances the amount of biomass required by the process (Figure 7-8), which makes for more stable economics compared to Option 2A.

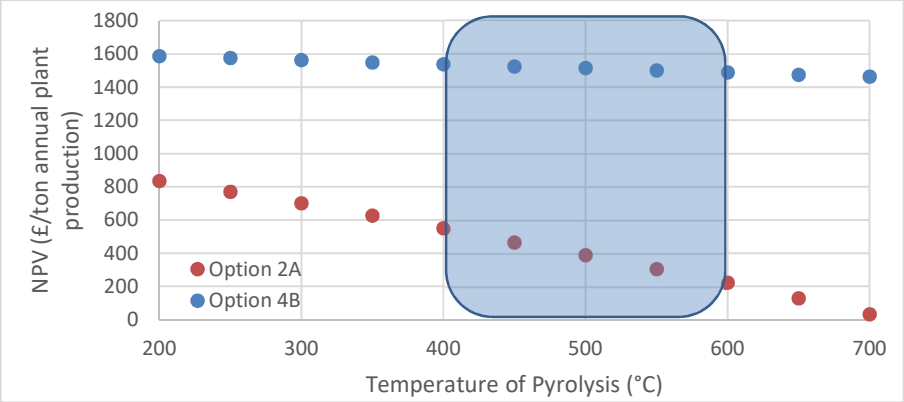


Figure 7-7. NPV of Options 2A and 4B vs temperature of pyrolysis using pinewood. Acceptable temperature region for BBQ charcoal shown in box

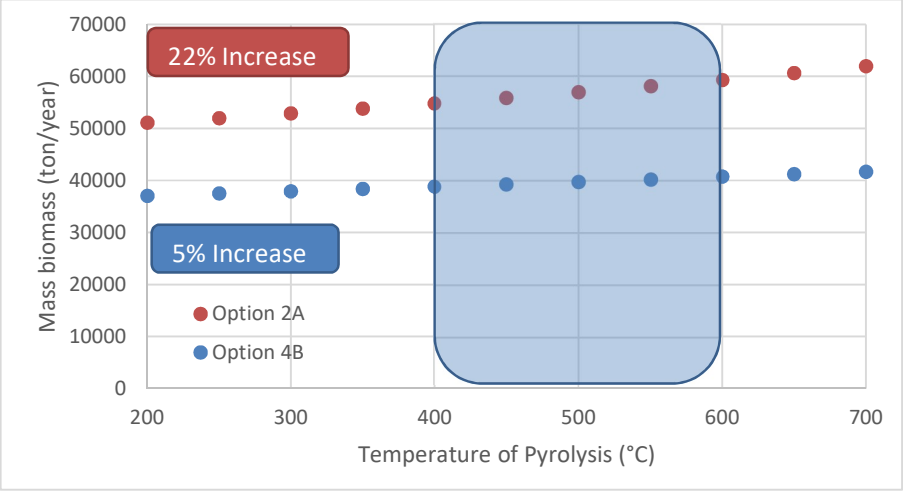


Figure 7-8. Change in biomass demand with temperature for Options 2A and 4B. Acceptable temperature region for BBQ charcoal shown in box

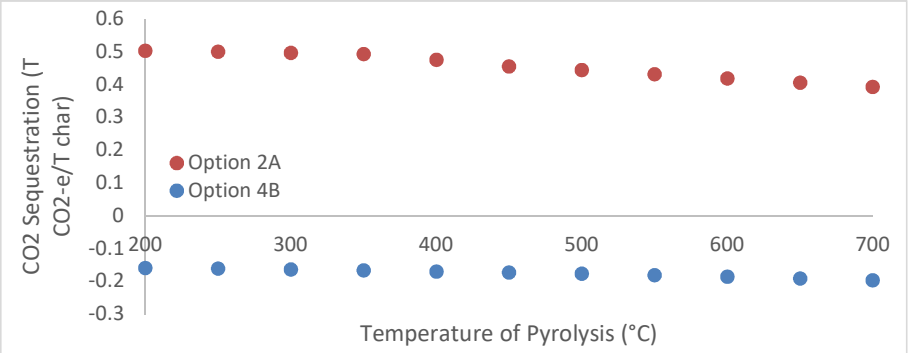


Figure 7-9. Carbon sequestration for Option 2A and 4B variation with temperature

Figure 7-9 shows that the carbon emissions for each of the options are relatively stable but they reduce with increasing temperature; while Option 2A is more affected by this than Option 4B. The increase is due to the higher energy demand to pyrolysis accounting for both the higher temperature and mass of biomass in. Option 4B is buffered by higher energy recovery and the lower change in biomass demand.

7.1.3.3 Effect of plant scale

Figure 7-10 shows the influence of plant scale on the NPV of the project assuming pinewood is used, at 450 °C with briquette composition of 15% clay and 15% raw biomass.

As can be seen from this, the minimum scale of production for Option 2A is 4600-6700 t/year and for Option 4B 3900- 4320 ton/year. There are three main observations from this plot:

- Option 2A and 4B requires larger scale due to the increased profit obtained from the sale of chemicals and decreased biomass demand from distillation residue recovery in Option 4B.
- The trend previously observed between Option 2A preferring high ash biomass types and Option 4A preferring high volatile biomass types is continued in this analysis.
- After approximately 10,000 tons production per year the marginal returns do not increase by a large amount, highlighting that plants above this scale are not done for marginal return, but total return.
- CO_2 emissions effect on these cases is not shown on a per ton basis this is not affected. In reality if a full cradle to grave accounting was being used there may be economies of scale when emissions relating to the equipment construction is considered.

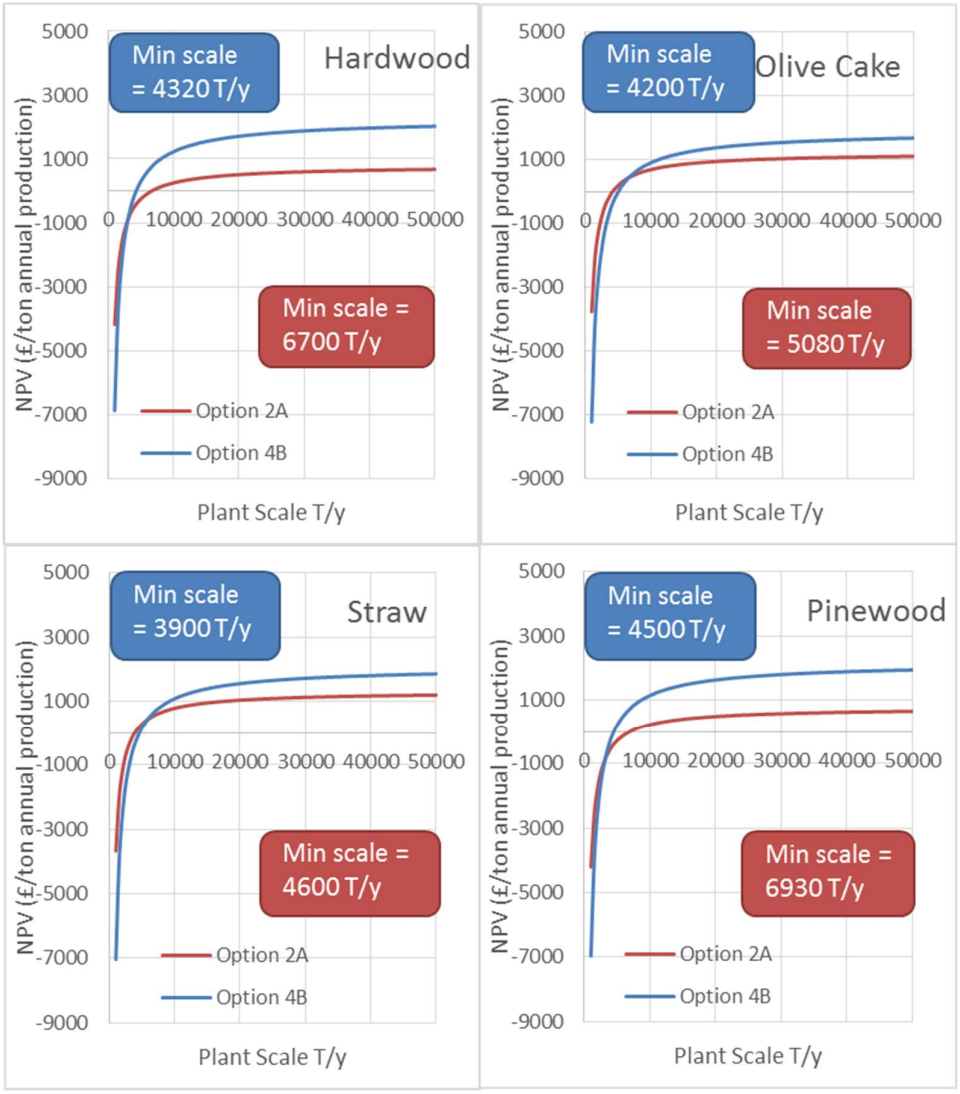


Figure 7-10. Effect of scale on plant options using pinewood, olive cake, straw and hardwood.

7.1.3.4 Effect of briquette composition

The effect of varying the concentration of the different additives in a pinewood charcoal briquette has been tested. This has been done in two ways:

- Testing the effect of increasing the concentration of each of the additives (sand, clay and raw biomass) independently from 0-30%.
- Setting the total concentration of additives at 30%, then varying the mixture between sand-biomass and clay-biomass blends.
    - These levels of additives were chosen to highlight the effect of being able to add more than the 15% of each additive constrained due to the findings from Chapter 5, while still maintaining the 30% total additive requirement.

Other conditions were kept the same as in the optimal case (temperature, scale, and costs) while the pinewood composition is used as the biomass type. The results of this analysis have been presented in Figure 7-11-Figure 7-13. Figure 7-11 and Figure 7-13 present the NPV changes with additive mixtures and levels while Figure 7-12 shows the carbon balance changes with individual additive level.

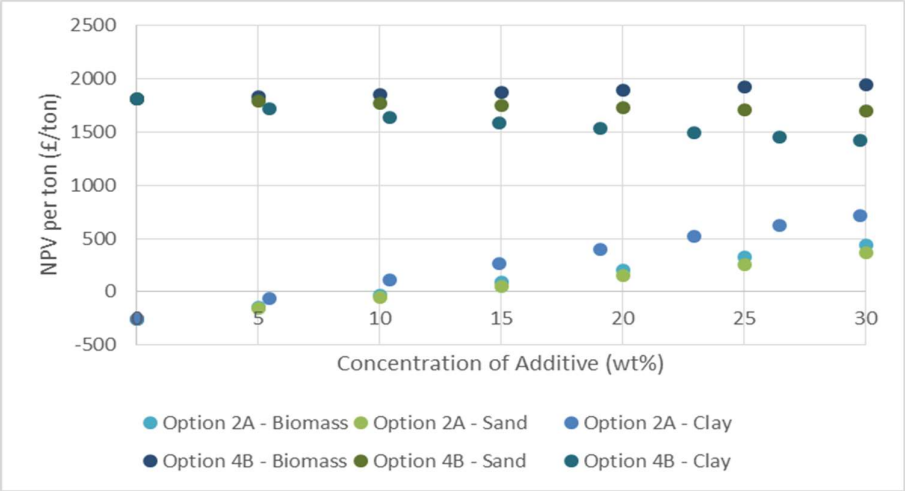


Figure 7-11. Effect of changing biomass, sand and clay concentration between 0-30% on NPV of process

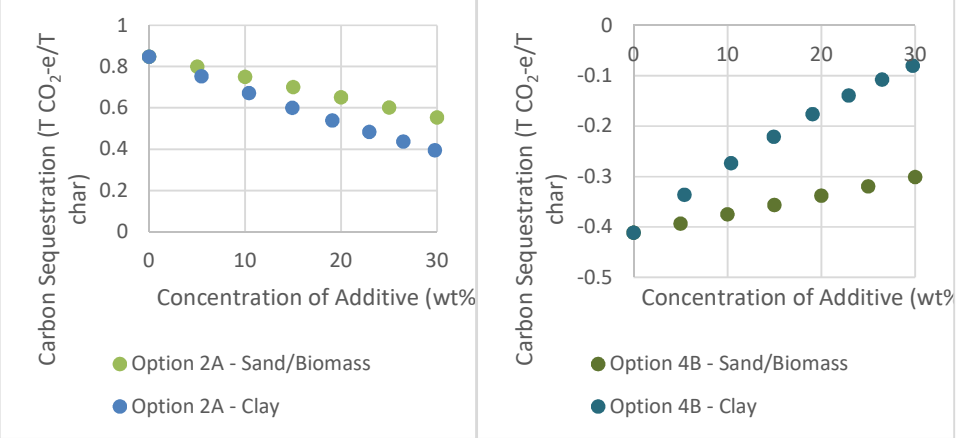


Figure 7-12. Carbon emssions changes with increasing concentation of additive

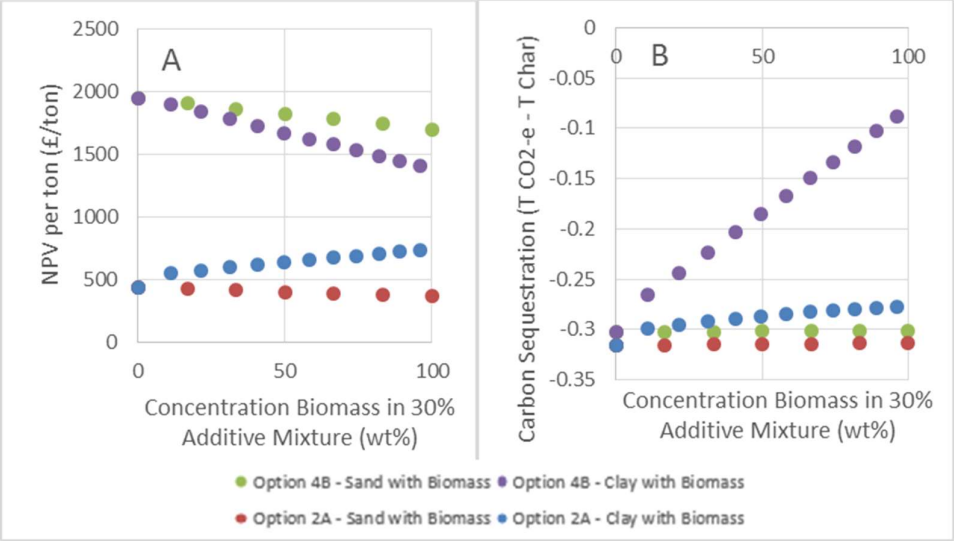


Figure 7-13. Effect of changing ratio of sand or clay in a 30% additive mixture with biomass on process A) on NPV and B) on carbon sequestration.

The two options both follow similar trends as with previous cases.

- Option 2A favours clay over other additives at increasing concentration as this increases the pyrolysis yield over the other two additives so benefits from this increase. Biomass is more favoured than sand addition due to the lower cost (£60 per ton) of biomass compared to sand (£100 per ton).
- Option 4B favours biomass addition over sand, due to the cost difference mentioned above. Clay has a lower effect again due to the increased cost (£120 per ton) compared sand (£100 per ton) and the utilisation of volatiles. A discussed previously the value for oil in high clay cases is potentially being under estimated due to the cracking effects.

Figure 7-12 and Figure 7-13 B shows the carbon emissions effects from these cases.

- Option 4B benefits from additive addition to the process; but benefits more greatly when clay is used. This is because clay addition reduces the amount of oils produced due to the cracking effect meaning more energy is recovered via gas combustion and less demand for distillation energy is required.
- Option 2A becomes more emitting with increasing additive, which is exacerbated by clay addition. This is potentially an artefact from the incomplete nature of the carbon balance, as increasing additive means less biomass is required by the process which represents a lower level of sequestration by the process. Combustion emissions are then fixed based on

the total mass of briquette burnt when they will be reduced with the increased level of inert additive into the process.

- In both cases, the carbon model assumes biomass and sand are similar because biomass not carbonised is assumed to have equal input/output emissions when used in combustion. As discussed in Chapter 5, these levels of clay, sand and raw biomass can be added to charcoal with limited effect on the combustion properties and is required due to the lower cost of clay biomass and sand compared to charcoal as discussed in section 6.4.1.

In the optimisation study, it was determined that with the constraints provided a 30% additive mixture should contain 15% biomass and 15% clay. What this analysis suggests is that in reality higher levels of each of the additives may benefit some of the cases, but this would need to be physically tested in combustion testing as it is nearing the limited presented in the BBQ modelling (Chapter 5).

7.1.3.5 Effect of Cost Model Sensitivity

Analysis of the stability of the options to fluctuations in cost has been performed. A worst case was developed assuming that costs are 50% under estimated and revenues are 50% over estimated and a best case assumed the reverse. Intermediate cases have also been used to view overall trends as presented in Table 7-4.

Table 7-4. Cases used to determine model sensitivity to changes in estimates of financial parameters: capital cost, utilities, material and biomass/chemical revenue.

Case	Parameter	Factor
Best Case (+50%)	Capital Cost	-50%
	Utilities Cost	-50%
	Material Cost	-50%
	Product Revenue	+50%
Intermediate (+25%)	Capital Cost	-25%
	Utilities Cost	-25%
	Material Cost	-25%
	Product Revenue	+25%
Base Case (0%)	Capital Cost	0%
	Utilities Cost	0%
	Material Cost	0%
	Product Revenue	0%
Intermediate (-25%)	Capital Cost	+25%
	Utilities Cost	+25%
	Material Cost	+25%
	Product Revenue	-25%
	Capital Cost	+50%
	Utilities Cost	+50%

Worst Case (-50%)	Material Cost	+50%
	Product Revenue	-50%

The results from this analysis are presented in Figure 7-14, with 30% error bars indicating the expected range of acceptability for a preliminary cost analysis of 30% error (Sinnott *et al.*, 2005).

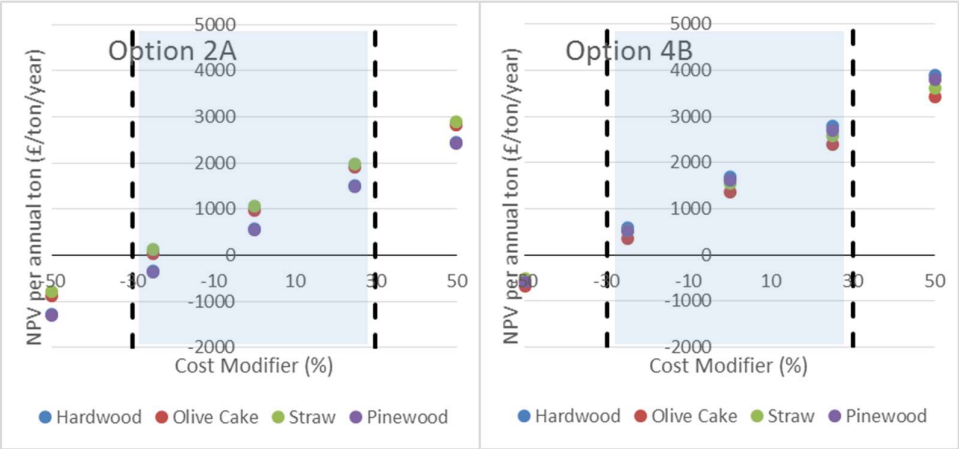


Figure 7-14. Results comparing the effect of sensitivity of financial parameters. This is based on the cases presented in Table 7.4. What can be seen from this is that within the +/-30% error Option 4B remains positive, while Option 2A with high error comes negative.

From Figure 7-14 when assuming 30% error, Option 4B is still expecting similar profitability as the base case for Option 2A. This is due to the increased revenue per ton biomass generated because of the chemical sale.

Option 2A is more complex, as profitability is more dependent on the composition of the raw biomass into the process. With 30% error, high ash non-woody biomass sources are still marginally profitable while woody biomasses with low ash are not.

7.1.3.6 Summary of Optimised Results

- Option 2A favours high ash non-woody biomass types due to higher retention of raw biomass as charcoal
- Option 4B favours high volatile biomass types due to higher oil yield; which in turn means there is more revenue generated from oil sales and char recovered from atmospheric distillation
- Lower temperature is favoured by both processes due to the higher retention of biomass as charcoal, which lowers the main cost to the process

- The minimum economic scale of production for both options is between 4000 – 7000 Ton/year with no increase in marginal return over approximately 10,000 ton/year.
- Option 2A favours clay addition due to the increase in charcoal yield, while Option 4B economically favours sand addition due to clay utilising oil for this extra charcoal yield. However, it is expected that clay addition is likely to increase the value of the bulk oil so this addition remains recommended by this process.
- Option 4B is still profitable when accounting for 30% error in the cost analysis; while Option 2A is marginal.

7.2 Drying trade off

This scenario tested the effect of using wetter cheaper biomass (pinewood) and the potential effect that not pre-drying the biomass before pyrolysis could have on each of the options.

This analysis has been done, using optimal conditions for the other variables for both cases discussed in section 7.1.2. The flow schemes used are presented in Figure 7-15.

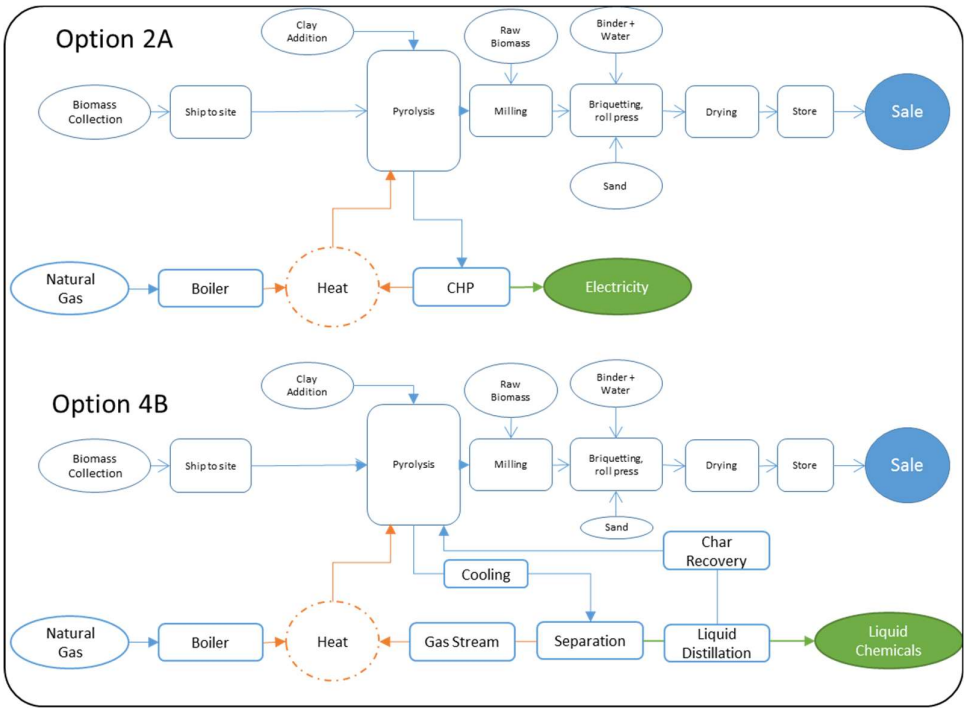


Figure 7-15. Alterations to flow schemes for drying study

There were two stages to this analysis:

- Running the models with the same pyrolysis inputs – just changing the drying stage and biomass cost model.

- Running the models with the pyrolysis model for wet biomass, based on the results presented in section 4.4.1, which have been summarised in Table 7-5 and indicate an increased oil recovery at the expense of charcoal.

Table 7-5. Comparison of yield breakdown – base case vs high moisture case

Unit/Parameter	Total Yield at 15% Moisture in Pyrolysis (wt%)	Total Yield at higher Moisture Content in Pyrolysis (wt%)
$Y_{charcoal}$	29	11
Y_{oil}	25	25
Y_{water}	35	54
Y_{gas}	10	10

The results from this study have been presented in Figure 7-16.

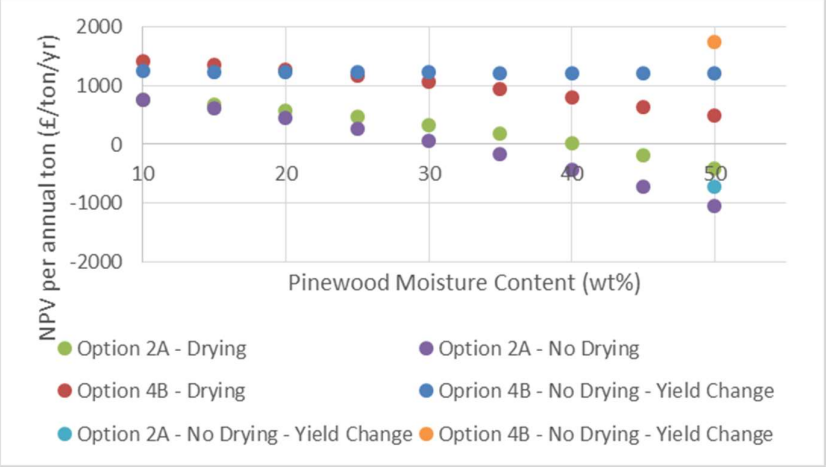


Figure 7-16. Comparison of drying vs no drying options

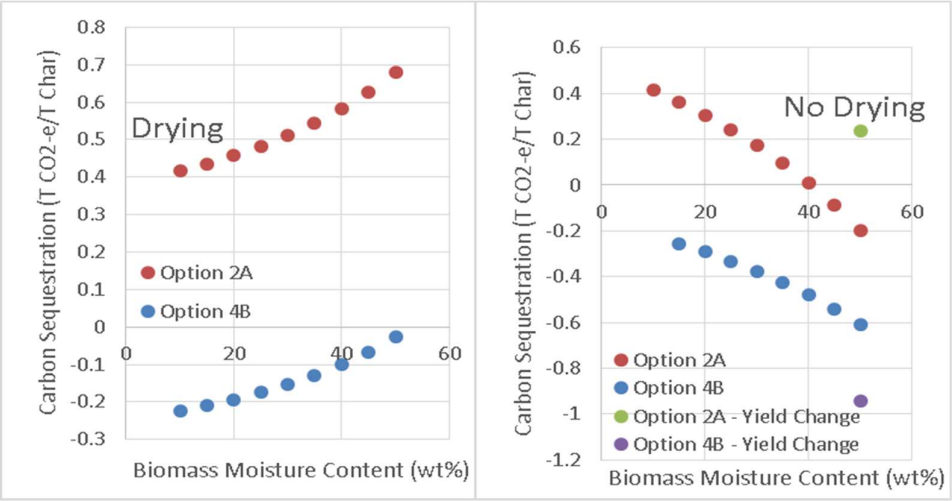


Figure 7-17. Carbon emissions from drying vs no drying with wet biomass test

What can be seen from Figure 7-16 is that:

- Option 2A when wet biomass is use performs poorly due to increased energy cost as the model requires that the extra water into pyrolysis is required to be heated to the peak temperature.
    - However, when the potential yield change is considered, there is more gas and oil produced by the option which off sets some of this extra expense.
- A similar effect is observed in Option 4B when the yield is not changed, although as with the temperature study, the effect is not as pronounced.
    - When the yield change is considered, this becomes more efficient as the higher yield of liquid and gas mean is more heat produced and extra revenue is made from the increased oil production.

In both Option 2A and 4B the level of water present could be high enough to mean that the boiler system (Option 2A) or distillation system (Option 4B) may not work.

- Plant logistics for Option 4B may also incur extra cost in waste treatment of the distillation aqueous phase which has not been assessed in this study.

Figure 7-17 shows the effect of carbon emissions when using the wet biomass in these systems. It can be seen from this that pre-drying biomass is more efficient. This is due to the greater energy demand to heat the wet biomass to the peak pyrolysis temperatures than the drying temperature. The drying case appears more efficient as the carbon model assumes that the wet biomass purchased has these effect of increasing carbon sequestration, which may or may not be accurate as discussed with the flaws in this balance.

[redacted]

7.4 Effect of biomass source on project economics and carbon emissions

Until this point process modelling work has aimed to understanding how the biomass properties, process conditions and catalyst effects can affect the overall pyrolysis process outcomes in terms of financial stability of pyrolysis processes. The effect of location of available biomass on the specific cost and shipping effects has not been considered due to the level of complexity this would have added to the previous analysis. This section aims to provide an insight into how these logistics effects may play into optimal process selection.

7.4.1 Biomass sources and locations

12 biomass sources have been identified from the information identified in section 2.3 of this thesis, and outlined in Table 7-6.

These biomass types have been selected to reflect the range of biomass types that have been identified by the literature search, and locations have been selected to reflect the distribution of biomass around the world. This is not a comprehensive list of available types and sources, but aims to give an overview of the effects of agricultural vs woody biomass sourced from domestic and EU sources and effect of sourcing cheaper woody biomass from far away sources, from those identified as important to CPL and in the Literature Review.

Table 7-6. Summary of biomass sources for location modelling. Full table of model inputs is presented in Appendix 5.

Location	BM Type	BM Cost	Shipping Method	Distance (km)	Shipping Method	Distance (km)
UK	Hardwood	150	Truck	90		
UK	Miscanthus	60	Truck	90		
UK	Straw	50	Truck	90		
Spain	Olive Cake	100	Truck	180	Boat - Europe	1000
Spain	Grape Cake	40	Truck	180	Boat - Europe	1000
Spain	Eucalyptus Pellet	45	Truck	180	Boat - Europe	1000
Greece	Olive Cake	110	Truck	50	Boat - Europe	1500
Greece	Grape Cake	60	Truck	50	Boat - Europe	1500
Latvia (E. Europe)	Pinewood	35	Truck	50	Boat - Europe	2000
Austria (C. Europe)	Pinewood	45	Rail	50	Boat - Europe	2000

USA	Softwood Pellet	108	Truck	200	Boat - World	3000
Australia	Eucalyptus Pellet	108	Truck	100	Boat - World	9000

7.4.2 Modelling methods

For this case, both options 2a and 4b have been assessed against the range of biomass sources. Two scenarios have been applied to each of the 12 biomass sources for this analysis:

- Importing biomass from various international sites to a processing site in the UK
- Conducting pyrolysis at the point of biomass collection and importing charcoal to the UK from various international sources

Two characteristics have been tested with each of these scenarios:

- Profitability and carbon emissions using the standard process conditions outlined in Table 7-7.
- Effect on minimum scale of production when local costs of biomass and transport are applied to both options where biomass or charcoal are shipped. This was performed using the method outlined in section 7.1.3.3 and the inputs outlined in Table 7.1.1.

Table 7-7. General conditions used for process model inputs. Other relevant constants are outlined in Table 7-1

Symbol	Value	Units
M_{briq}	20,000	ton/year
$C_{briq_{sand}}$	0	g/g
$C_{briq_{bm}}$	15	g/g
$C_{briq_{clay}}$	15	g/g
T_{peak}	450	°C

7.4.3 Results

7.4.3.1 Plant performance based on standard conditions

The results for the standard conditions plant with both biomass and charcoal shipping are presented in Figure 7-24 and Figure 7-25. There are several points to note from this chart:

- As expected, carbon emissions are significantly lower when charcoal is shipped than when biomass is shipped.
- Charcoal shipping also has the result of improving financial performance, to the point where sourcing biomass from international sources is economic.
- Economics support the importing of cheaper European agricultural residues
- However, wood residues internationally are more uniform in price. Therefore there appears to be no financial incentive to utilise wood from further away.
- Option 4B is more stable compared to Option 2A, when biomass is imported as the extra shipping cost is absorbed by the increased revenue from the oil by products.

Overall, the profitability decreases with increasing biomass or charcoal transport distance as outlined in Figure 7-21. This indicates that the biomass cost is less significant than shipping costs.

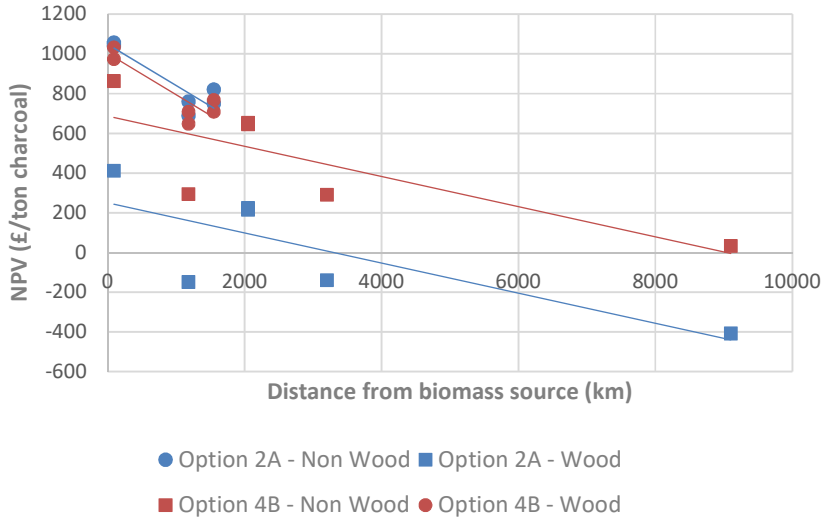


Figure 7-21. NPV per ton of charcoal produced against the distance the biomass has been transported.

7.4.3.2 Minimum profitable scale based on biomass source

Figure 7-22 and Figure 7-23 show the minimum scale required to produce economic charcoal from the biomass and charcoal shipping cases. There observations from this are as follows:

- As shown in section 7.4.3.1, the shipping costs are more significant than biomass costs as can be seen by the dramatic increases in minimum economic scale when biomass is shipped compared to when charcoal is shipped.

- Option 2A is again more affected by these changes due to the lower levels in profit.
- Based on the UK market being a maximum of 30,000 tons of charcoal per year, this analysis suggests that:
    - Option 2A is severely uneconomic when woody charcoal or biomass is sourced outside the EU, and marginally economic when sourced outside the UK as the scale of production is required to be over 30,000 ton per year.
    - Option 4B becomes uneconomic when woody biomass is sourced outside the UK, but if charcoal is produced from woody biomass inside the EU the system can be economic.
    - In all cases, it appears that agricultural residue sourced inside the EU is suitable for both options 2A and 4B.

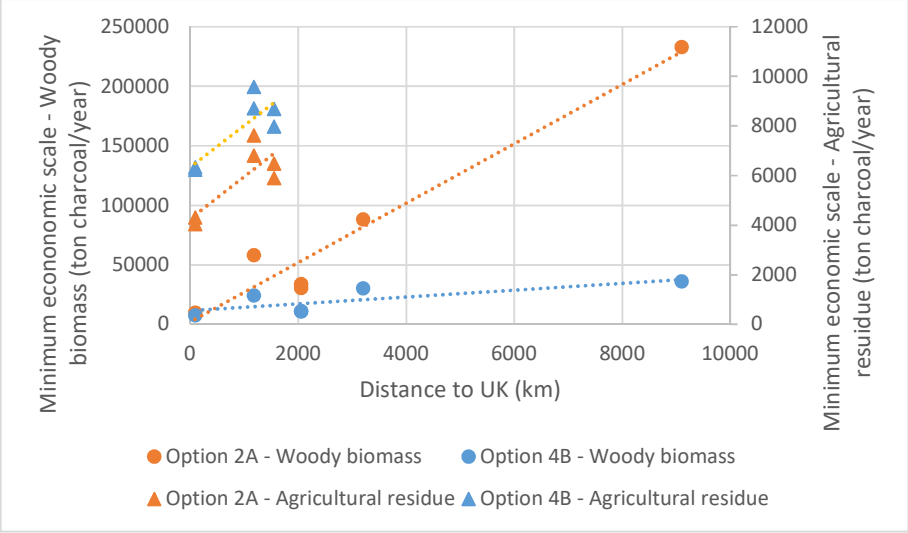


Figure 7-22. Minimum scale of production for biomass shipping case

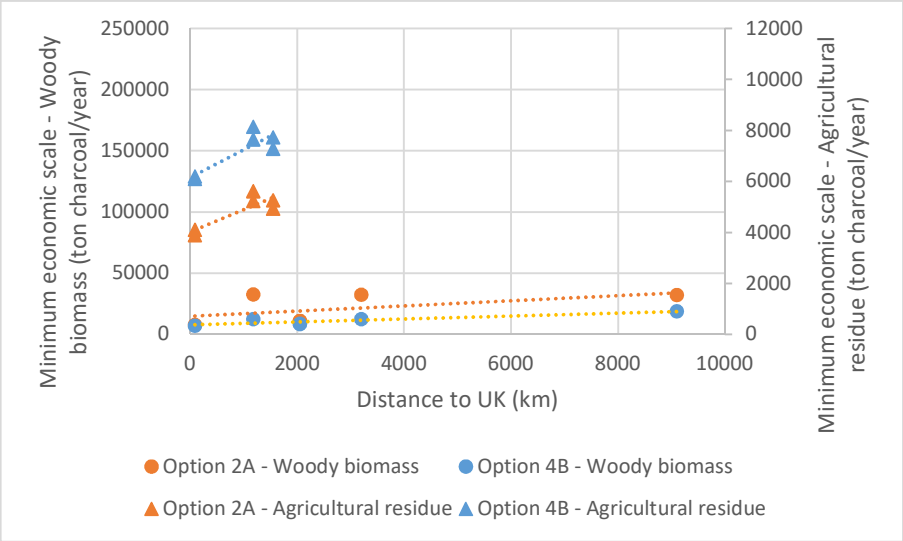


Figure 7-23. Minimum scale of production for charcoal shipping case

7.5 Conclusions

This chapter has covered two main concepts: optimisation of options 2A and 4B for producing charcoal, and; analysis of further process configurations. Conclusions will be presented for these separately.

7.5.1 Optimisation of Options 2A and 4B as charcoal producing systems.

- Option 2A favours high ash non-woody biomass types due to higher retention of raw biomass as charcoal
- Option 4B favours high volatile biomass types due to higher oil yield; which in turn means there is more revenue generated from oil sales and char recovered from atmospheric distillation
- Lower temperature is favoured by both processes due to the higher retention of biomass as charcoal, which lowers the main cost to the process
- The minimum economic scale of production for both options is between 4000 – 7000 Ton/year with no increase in marginal return over approximately 10,000 ton/year.
- Option 2A favours clay addition due to the increase in charcoal yield, while Option 4B economically favours sand addition due to clay utilising oil for this extra charcoal yield. However, it is expected that clay addition is likely to increase the value of the bulk oil so this addition remains recommended by this process.

- Option 4B is still profitable when accounting for 30% error in the cost analysis; while Option 2A is marginal.

7.5.2 Assessment of further charcoal process configurations

- Pre-drying biomass before pyrolysis is recommended, as testing pyrolysis with wet biomass does not have financial benefit.
- Use of a post-pyrolysis clay catalyst system to treat all oil appears beneficial when the clay bed is run at a higher temperature, as a higher level of cracking can be done to the oils producing higher value gas streams for energy production.
- In terms of the biomass source study
    - Option 2A is severely uneconomic when woody charcoal or biomass is sourced outside the EU, and marginally economic when sourced outside the UK
    - Option 4B becomes uneconomic when woody biomass is sourced outside the UK, but if charcoal is produced from woody biomass inside the EU the system can be economic.
    - In all cases, it appears that agricultural residue sourced inside the EU is suitable for both options 2A and 4B.

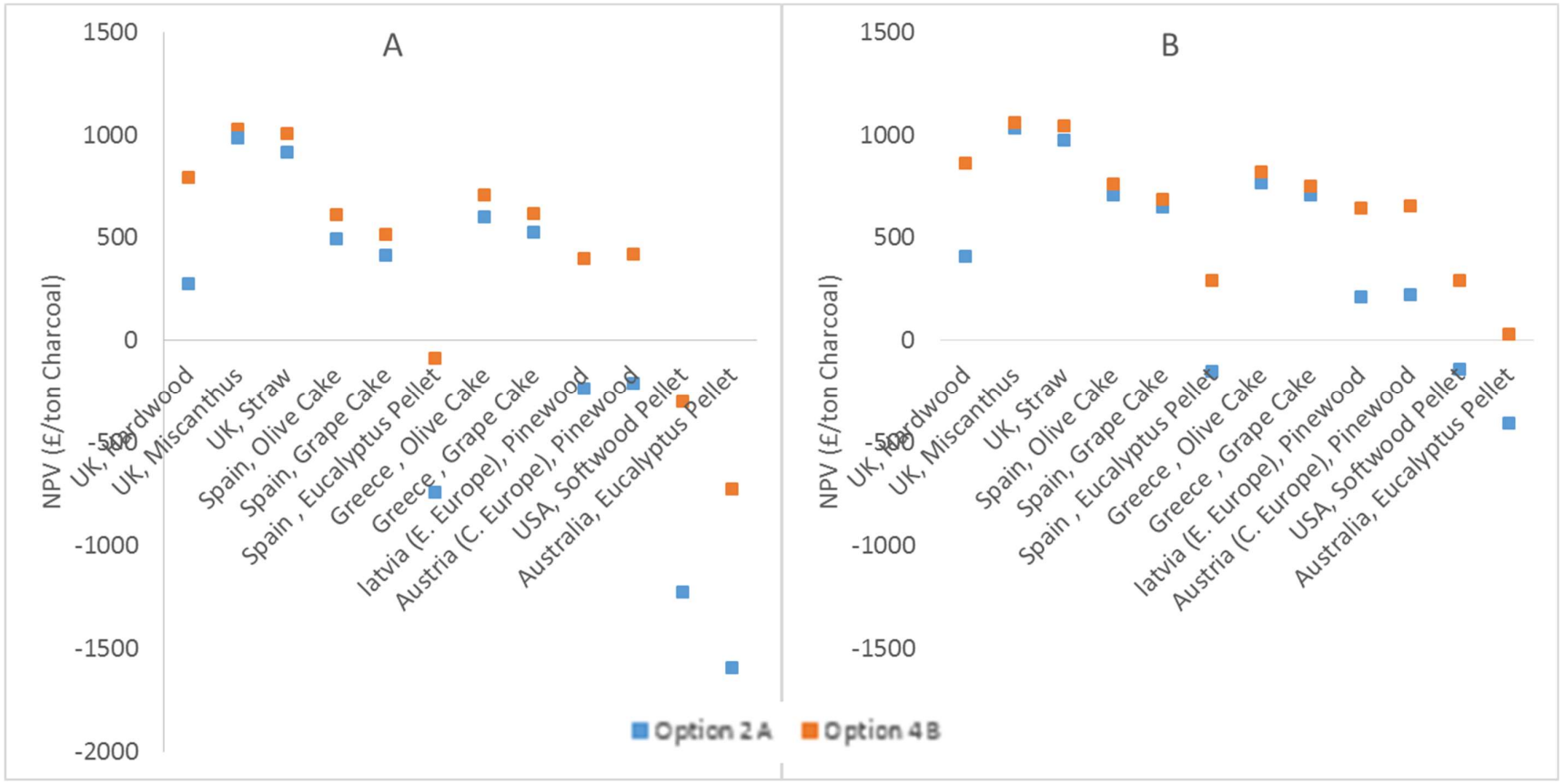


Figure 7-24. Financial results from standard conditions. A) NPV from biomass transport case B) NPV from charcoal transport case

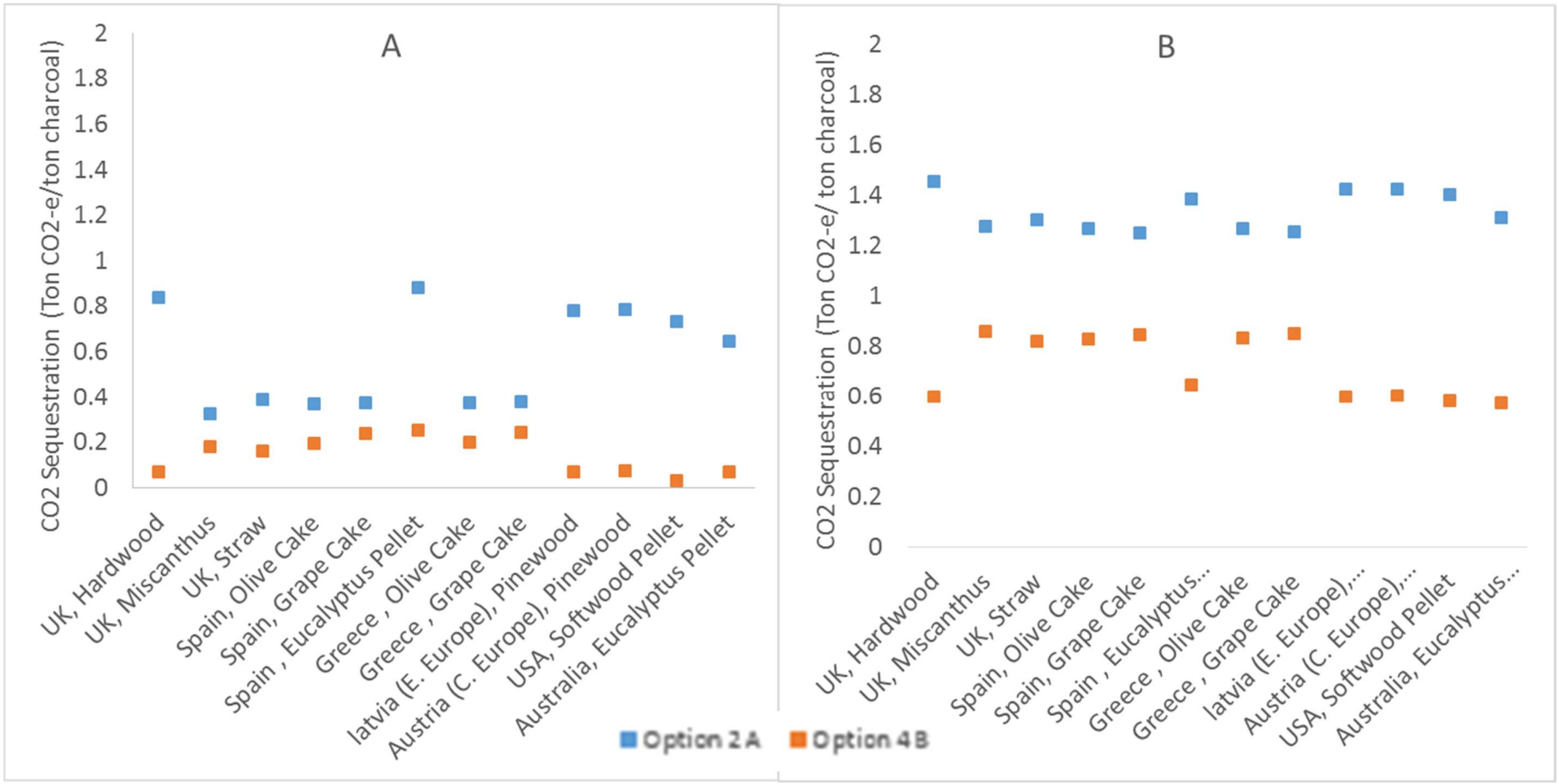


Figure 7-25. Carbon results from standard conditions A) carbon emissions from biomass transport case B) carbon emissions from charcoal transport case

Chapter 8. Conclusions and future work

8.1 Conclusions

This project investigates optimisation of charcoal production, focusing on: experimental slow pyrolysis and yield modelling; charcoal combustion quality testing and modelling, and; techno-economic analysis of the charcoal production process.

8.1.1 Experimental pyrolysis and yield modelling

- Experiments were undertaken at lab and pilot scale on a variety of biomass: pinewood, mixed hardwood, eucalyptus, straw, olive stone and miscanthus, with additives clay minerals, zeolites, dolomite, sand and cement over the temperature range 300 – 900 °C.
    - The work on clay minerals has been published in (Russell *et al.*, 2017a), and shows clay addition can both increase charcoal recovery from biomass and improve the quality of oil by-products produced.
    - Experiments using highly acidic type y zeolite suggests that in the slow pyrolysis regime this catalyst has a similar effect to the lower acid clay minerals. It is speculated that this is because in the slow pyrolysis regime the pores on zeolite are fouled more quickly than expected from fast pyrolysis studies.
    - Sand is inert to the pyrolysis process; while basic cement and dolomite also cause char deposition and oil cracking. However, this is done via a different mechanism which produces more CO_2 and may decrease the value of the gas by-product by lowering its energy density and combustibility.
- Jenkinson (2016) showed that charcoal yield can be based on aromatic carbon and metals concentration of the raw biomass at 800 °C. While not producing a conclusive study, this work has provided evidence this model can be expanded to include temperature dependency.

8.1.2 Charcoal combustion

- Experiments have concluded that BBQ fuel should have the following criteria:
    - Charcoal produced from pyrolysis between 450 – 550 °C
    - Total inert additive and raw biomass concentration should be no higher than 30% wt. of total briquette.
    - Concentration of biomass additive should be no higher than 15% wt.

    - There appears to be no difference if the charcoal origin of the raw biomass is woody or agricultural.
- The results from these experiment have also been used to produce a model to represent the temperature history of a charcoal fire based on the analogy of two first order chemical reactions in series. This has been submitted to Fuel Processing Technology.

8.1.3 Techno-economic modelling

- Increased charcoal yield improves the economics of a BBQ charcoal production system. This can be done by:
    - Having a suitable temperature of pyrolysis as low as possible, which this study has determined to be 450 °C.
    - Addition of clay mineral additive to the pyrolysis process can cause fouling on the mineral surface. This results in higher retention of clay on the catalyst surface, which if added in the correct initial concentration can be utilised as part of the final charcoal product.
- Utilisation of by-product liquid and gas products from the pyrolysis process is important. From 17 initial options, this study has determined that the optimal options are:
    - Utilisation of gas and liquid as process heat with remaining energy being utilised in a steam cycle for electricity production. This has the effect of lowering external energy demand is important both financially and from carbon perspective
    - Production of chemicals from the liquid phase, provided the yield is high enough, specifically mixed phenolic streams, and heat from the gas phase
    - Analysis has shown that the minimum scale of production for these systems is 7000 ton of charcoal per year when the by-products are converted to heat and electricity and 4000 ton per year.
- Addition of clay minerals are important to both of these processes.
    - For the process producing process heat option, the overall heat demand and biomass mass are reduced.
    - For the chemicals option, the quality of the oil is improved reducing the level of upgrading required.

- Process selection between the heat production and chemicals option can be determined on several factors:
    - Biomass types high in ash are more favoured by the heat production process as the majority of revenue comes from charcoal because higher ash content translates to a higher charcoal yield.
    - Biomass types with low ash and therefore higher volatiles or fixed carbon are more suited to chemical production, as more of the higher value chemical products is produced.
    - The heat production option generally is more carbon efficient, due to the lower levels of external heat demand. This may be improved if it can be shown that there is a significant carbon offset by the chemicals product.
    - If capital cost is an important factor for process selection, then the heat production option is significantly cheaper due to lower process complexity
    - Biomass sources closer to charcoal end consumer are favoured by both charcoal production processes as shipping costs and carbon emissions are much higher from these sources.

8.2 Future work

- This work has shown that the universal model for charcoal yield prediction could be expanded for temperature dependency and makes a case for future work to be done to further develop the model.
- There are several areas where the findings from the catalysis work can be expanded
    - Pilot work can be expanded to make larger batches of the oils from clay pyrolysis for further characterisation to allow their true value to allow its true value to be determined
    - Pilot work could also be expanded to develop the oil extinction process flow. For this system regeneration of the clay bed needs to be tested out further.
    - A potential process flow also allows an excess of clay mineral added to the pyrolysis system. This can be done to allow higher levels of oils cracking and introduce clay as an indirect heat carrier. Energy efficiency of the process of indirect heating via natural gas

combustion against the heating of clay and then contacting with biomass could be tested out or modelled.

- The fire model developed as part of this work could be expanded to be valid for more uses. The main use CPL could have for this is developing it for simulation of standard home heating fuels. The method to do this would be as follows:
    - Combust a range of fuels used for home heating in the BBQ grill system, but this time run the testing at a range of extraction air flow rates. This will allow one source of error – mass transfer effects – to be minimised and the differences between the fires to be attributed to the fuels.
    - Fit model parameters based on these new experiments, including accounting for mass transfer effects
    - Run the same fuels through standardised home fire test system and method, and use the new model to fit results.
    - A CFD/FEM could also be applied to this system to allow further validation and determination of key variables
- Process simulation work can be expanded to include optimisation of the pyrolysis kiln design. This can be done via selection of the kiln system and unsteady state modelling of flows to optimise retention times and contacting in catalytic slow pyrolysis systems. A model could also be developed to better determine the effect of using an ex-situ catalytic bed for clay mineral catalysis.
- More detailed techno economic modelling could be developed. The aim of this would be two-fold:
    - Improving cost estimates and supply chain optimisation
    - Upgrading the carbon balance to a full life cycle model to determine the true environmental impact of the BBQ charcoal system.

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Appendix 1. Experimental runs and results for Chapter 3

Preliminary HTF testing

- Preliminary experiment. These were carried out to test the effect of changing well studied conditions on the biomass available to this project at the start of experiments. This was done to allow the selection of pyrolysis conditions for future test work.
    - These were completed in a horizontal tube furnace (HTF) which was not suitable for the majority of the experimental work for this project, as it only allowed determination of charcoal properties

Method

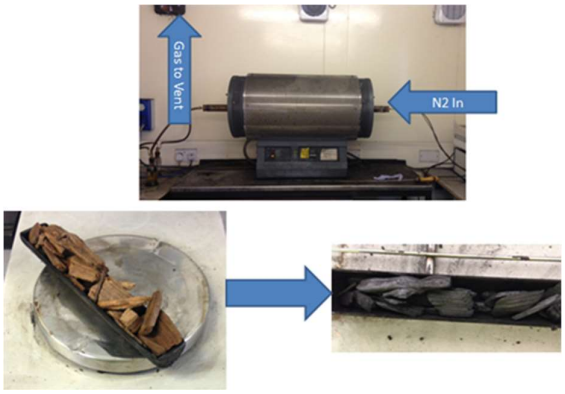


Figure A- 1. Schematic of horizontal tube furnace (HTF) used for preliminary experiments

- Biomass was charged into a crucible (10-20g, depending on the bulk density of the biomass)
    - Eucalyptus wood (properties Table 3-1) was used for pyrolysis
        - Moisture content 25%
    - Two size ranges were selected, based on the smallest dimension of the chips, as measured by veneer callipers: 10 mm and 20 mm
        - This could not be tested in the main experiment as the Gray King tube was too small
- Pyrolysis was performed under the following conditions:
    - Peak temperature 300, 400, 500, 600, 700 °C
    - Heating rate of 10, 20, 30 °C/min
    - Residence time at peak temperature of 1, 5 10 mins

- A constant flow of N2 at 1 l/min was passed through the system.
- Condensable components in the gas stream were removed in two room temperature water traps
    - The relative high temperature of this stream and small condensable gas flow relative to the flow of N_2, and large lengths of un-insulated pipe meant oils yield determination was difficult to impossible.
- Charcoal was recovered and mass weighed for yield determination. Proximate analysis was perfumed to determine the charcoal quality

Results

- Effect of particle size
    - Key results are presented in Figure A- 2. It can be seen that there is negligible difference between the two particle sizes, as confirmed with ANOVA testing the null hypothesis that the means are equal, which was true at α=0.05. These findings agree with the analysis done in Anderson *et al.* (2005) which suggest that for wood chips in the size range 16<x<45 mm that pyrolysis is completed in 10 minutes at 400°C.

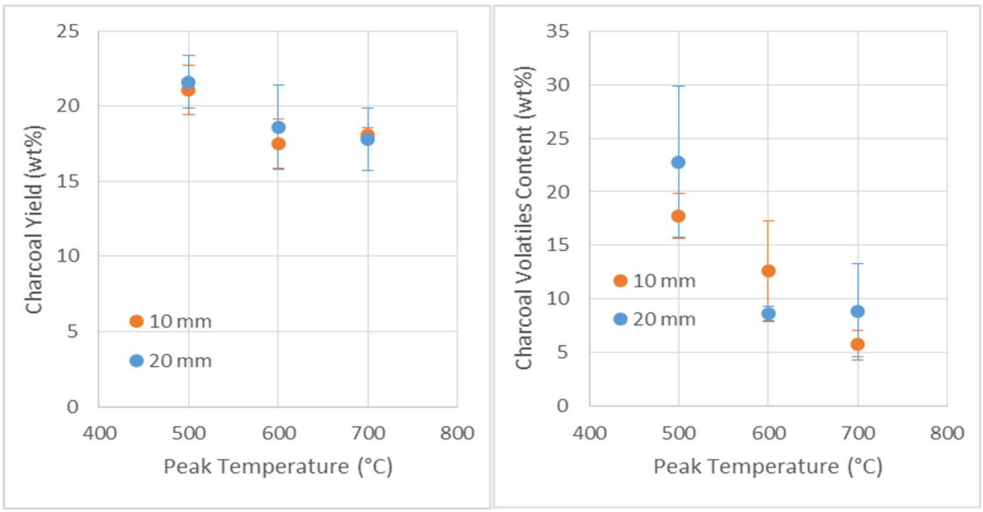


Figure A- 2 Comparison of 10 and 20 mm particles

- Effect of heating rate

Several references show increased heating rate lowers the production of charcoal, producing higher non-condensable gas. Williams *et al.* (1996) look at various heating rates within slow pyrolysis temperature ranges. From TGA testing to show the maximum temperature of weight loss, they speculate that the hemi-cellulose component of things (or compounds which carbonise at lower temperatures) are

more likely to volatise than carbonise under these different regimes. Mohanty *et al.* (2013) goes on to characterise the charcoal from this and shows that the HHV is generally higher from slow pyrolysis and due to the level of C-C cross linkage produced from each heating regime (effects in volatiles, fixed carbon, ash not really seen). (Chen *et al.*, 2014) showed that there was an increase in CH_4 production with the lower char yield in 50 g experiments.

- The results from this experiment, presented in Figure A- 3 indicate that there is some reduction in charcoal yield, but this is not greatly significant.

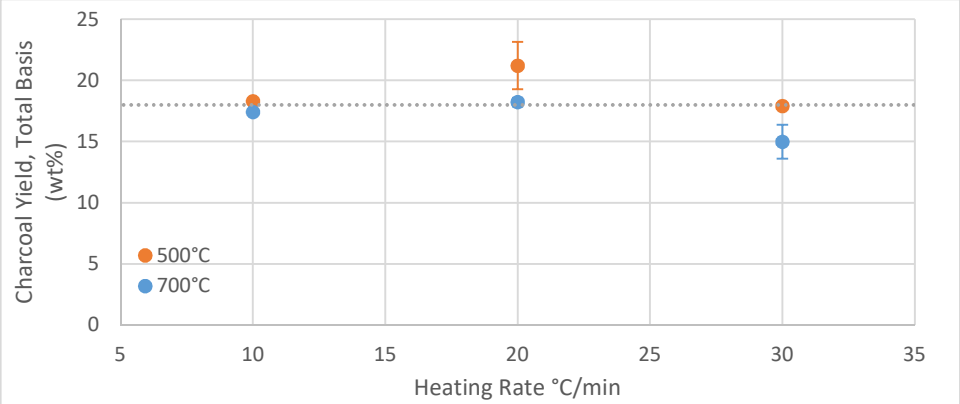


Figure A- 3 Effect of heating rate on charcoal yield

- Effect of residence time
  - Key results are presented in Figure A- 4. What can be seen from this is that there is little effect due to increasing residence time. What can be seen, however, is that there is a decrease in the error band around the yield with increasing residence time.
    Because of this, it was decided to go with the standard time for complete slow pyrolysis of 1 hour residence time.

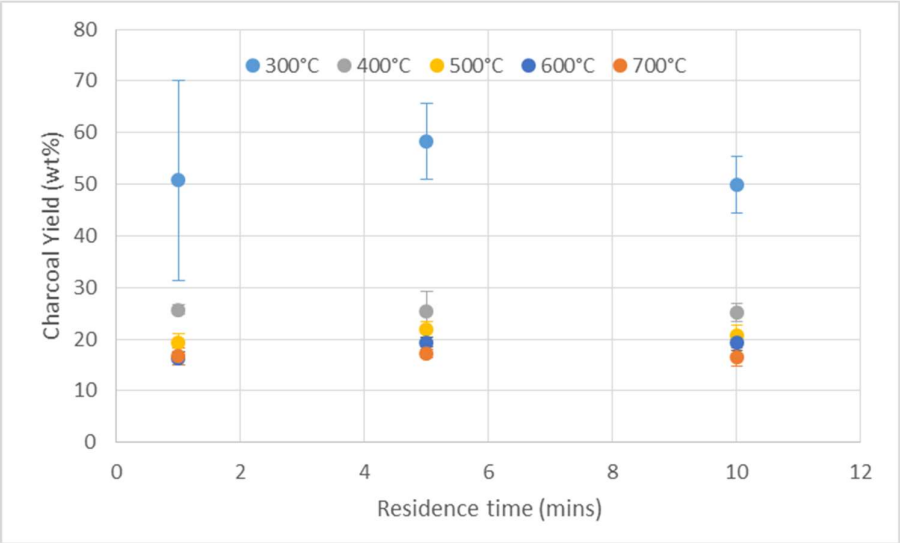


Figure A- 4 Charcoal yield against heating rate at 300 -700 °C.

1. Comparison of HTF with Gray King Assay

- Comparison of results using the HTF with the Gray King method used for the rest of the project. The Gray King pyrolysis was seen as a better way of assessing biomass types for this experimental work as it allowed the collection of slow pyrolysis oil and therefore determination of gas yield as well.

Method

- Pyrolysis experiments were completed in both the HTF system discussed in this appendix 1.1 and the Gray King pyrolysis as outlined in Section 3.2.2.

Results

- The key result for this experiment is presented in Figure A- 5, which shows agreement between the two furnaces.

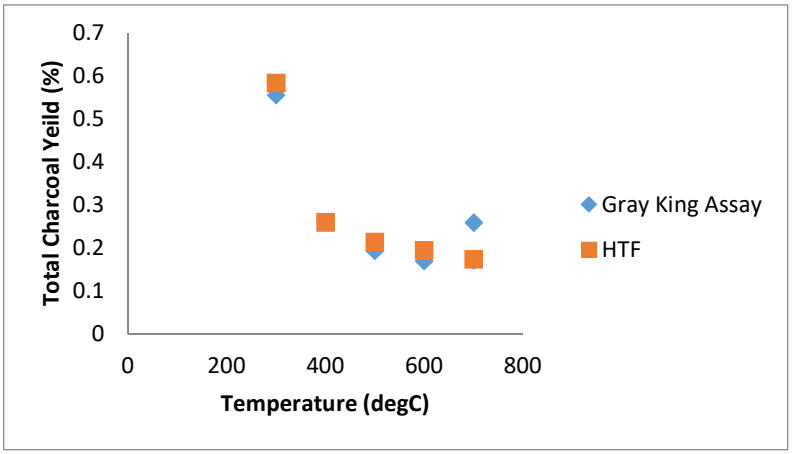


Figure A- 5 Comparison of Gray King pyrolysis and HTF furnace

2. Laboratory Biomass Only Experimental Runs and Results

1. Pinewood		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
300	3	49.93	0.79	35.27	1.53	14.79	0.74	50.03	0.79	35.48	1.54	14.49	0.75	1.10	0.41	48.00
400	3	31.84	1.90	50.50	5.19	17.66	4.06	31.86	1.90	50.80	5.22	17.34	4.09	2.70	0.55	20.40
500	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80	0.90	0.77	11.00
600	3	29.55	2.46	48.15	3.34	22.30	1.20	29.51	2.46	48.44	3.36	22.05	1.21	0.90	0.75	4.80
700	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80	0.80	0.78	3.30
900	3	26.82	1.49	47.11	0.30	26.08	1.79	26.65	1.48	47.39	0.30	25.96	1.78	2.35	1.24	1.67

2. Olive Cake		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
300	1	50.55	0.00	31.62	0.00	17.83	0.00	46.13	0.00	34.00	0.00	19.87	0.00	2.00	13.40	29.20
400	2	46.63	7.82	33.55	4.82	19.82	3.01	42.41	7.12	36.07	5.18	21.51	1.94	1.08	15.41	16.56
500	5	43.69	5.79	32.43	5.51	23.88	1.32	39.38	5.22	34.87	5.92	25.75	1.46	1.61	16.18	9.07
700	6	40.05	6.40	31.90	5.46	28.02	2.28	36.66	5.90	33.26	5.87	30.08	1.93	1.00	16.93	1.07

3. Straw		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
300	1	44.26	0.00	38.82	0.00	16.92	0.00	41.20	0.00	41.74	0.00	17.06	0.00	0.20	13.44	29.18
400	2	36.18	0.37	44.93	0.20	18.89	0.17	31.63	0.32	48.31	0.22	20.06	0.11	0.50	18.68	23.39
500	2	31.93	0.25	43.33	2.02	24.74	2.27	27.61	0.21	46.59	2.17	25.80	2.39	0.50	19.57	17.30
600	1	31.02	0.00	40.29	0.00	28.70	0.00	27.09	0.00	43.32	0.00	29.59	0.00	0.47	18.78	
700	2	28.89	0.05	43.34	0.61	27.78	0.65	23.79	0.04	46.60	0.65	29.62	0.69	0.50	23.42	4.85

4. Eucalyptus		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
300	1	33.62	0.00	55.93	0.00	10.44	0.00	33.45	0.00	56.24	0.00	10.31	0.00	0.36	1.07	32.67
400	1	29.75	0.00	53.02	0.00	17.23	0.00	29.62	0.00	53.32	0.00	17.07	0.00	1.92	1.00	22.36
500	1	24.50	0.00	64.22	0.00	11.28	0.00	24.43	0.00	64.57	0.00	11.00	0.00	1.85	0.84	14.11
600	1	22.07	0.00	60.00	0.00	17.93	0.00	21.97	0.00	60.33	0.00	17.70	0.00	0.40	1.00	4.97
700	2	22.31	1.61	57.33	4.09	20.36	2.48	22.15	1.60	57.65	4.11	20.20	2.52	0.79	1.13	3.07

5. Miscanthus		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
300	1	39.82	0.00	37.22	0.00	22.96	0.00	36.30	0.00	39.60	0.00	24.10	0.00	0.40	14.32	26.35
400	1	34.00	0.00	38.93	0.00	27.07	0.00	30.72	0.00	41.42	0.00	27.86	0.00	0.40	15.07	17.11
500	1	30.78	0.00	38.75	0.00	30.47	0.00	26.53	0.00	41.22	0.00	32.25	0.00	0.40	18.97	9.84
600	1	29.09	0.00	40.55	0.00	30.36	0.00	24.71	0.00	43.14	0.00	32.16	0.00	0.40	20.17	6.11
700	2	30.39	1.57	40.98	2.43	28.63	4.00	26.42	1.36	43.60	2.58	29.98	3.95	0.20	18.29	4.03
900	1	27.86	0.00	40.47	0.00	31.66	0.00	23.64	0.00	43.05	0.00	33.31	0.00	0.51	20.26	1.58

6. Olive Stone		TOTAL YIELD						DAF YIELD						Char Proximate Analysis		
Temp (°C)	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**$C_{mc,char}$**	**$C_{ash,char}$**	**$C_{vol,char}$**
400	1	29.63	0.00	45.90	0.00	24.47	0.00	29.35	0.00	46.08	0.00	24.57	0.00		1.35	
500	1	28.90	0.00	50.18	0.00	20.93	0.00	28.61	0.00	50.38	0.00	21.01	0.00		1.38	
600	1	28.22	0.00	50.21	0.00	21.57	0.00	27.93	0.00	50.41	0.00	21.66	0.00		1.42	
700	1	28.25	0.00	51.86	0.00	19.90	0.00	27.96	0.00	52.07	0.00	19.98	0.00		1.42	

3. Laboratory Biomass Only Experiments – Moisture Content

	400 ° C Pinewood		TOTAL YIELD						Dry Ash Free Yield					
Temp (°C)	$C_{mc,bm}$	Repeat	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
400	0.03	1	31.43	0.00	55.43	0.00	13.14	0.00	31.62	0.00	55.76	0.00	12.61	0.00
400	0.16	3	31.84	1.90	50.50	5.19	17.66	4.06	31.86	1.90	50.80	5.22	17.34	4.09
400	0.52	1	16.00	0.00	74.95	0.00	9.05	0.00	16.10	0.00	75.40	0.00	8.50	0.00

	500 ° C Pinewood		TOTAL YIELD						Dry Ash Free Yield					
Temp (°C)	$C_{mc,bm}$	Repeat	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0.03	1	27.09	0.00	59.36	0.00	13.55	0.00	27.25	0.00	59.72	0.00	13.03	0.00
500	0.16	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	0.52	1	15.17	0.00	76.02	0.00	8.81	0.00	15.26	0.00	76.48	0.00	8.26	0.00

	700 ° C Pinewood		TOTAL YIELD						Dry Ash Free Yield					
Temp (°C)	$C_{mc,bm}$	Repeat	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
700	0.03	1	22.70	0.00	58.55	0.00	18.75	0.00	22.83	0.00	58.90	0.00	18.26	0.00
700	0.16	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	0.52	1	20.15	0.00	60.49	0.00	19.36	0.00	21.67	0.00	65.05	0.00	13.29	0.00

	500 °° C Olive Cake				TOTAL YIELD				Dry Ash Free Yield					
Temp (°C)	**$C_{mc,bm}$**	**Repeat**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**
500	0	1	32.57	0.00	23.24	0.00	44.19	0.00	35.02	0.00	24.99	0.00	39.99	0.00
500	0.16	5	43.69	5.79	32.43	5.51	23.88	1.32	39.38	5.22	34.87	5.92	25.75	1.46
500	0.32	1	22.10	0.00	57.99	0.00	19.92	0.00	23.76	0.00	62.35	0.00	13.89	0.00

4. Pilot Plant Biomass Only Experiments

		Charcoal Quality		
Biomass Type	**Temp (°C)**	**Charcoal Yield**	**Charcoal Volatiles Content**	**Charcoal Ash Content**
Pinewood	400	25.66	25.76	0.52
Pinewood	550	19.82	10.76	0.55
Pinewood	700	17.06	4.54	3.00
Hardwood	400	23.80	17.94	1.20
Hardwood	550	20.82	10.41	1.67
Hardwood	700	14.65	3.40	4.50
Olive Cake	400	49.77	47.20	10.40
Olive Cake	550	26.40	12.50	17.00
Olive Cake	700	22.30	6.90	15.40
Straw	400	34.00	49.40	10.80
Straw	550	25.51	16.46	19.83
Straw	700	11.80	15.54	22.19

Appendix 2. Experimental Runs and Results for Chapter 4 – Catalytic Pyrolysis

1. Additive Screening Experiment

Granular Clay + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	**Cadd**	**Count**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**
400	0	0	31.84	1.90	50.50	5.19	17.66	4.06	31.86	1.90	50.80	5.22	17.34	4.09
400	40	1	59.15	0.00	33.31	0.00	7.54	0.00	32.11	0.00	55.84	0.00	12.05	0.00
400	30	1	51.14	0.00	39.00	0.00	9.86	0.00	30.39	0.00	56.05	0.00	13.57	0.00
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	30	2	49.92	0.25	33.51	1.38	16.57	1.13	28.63	0.36	48.16	1.99	23.21	1.63
500	40	1	57.54	0.00	32.81	0.00	9.65	0.00	29.41	0.00	55.01	0.00	15.58	0.00
500	60	1	72.80	0.00	17.21	0.00	9.99	0.00	32.19	0.00	43.28	0.00	24.53	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	30	1	47.46	0.00	35.12	0.00	17.42	0.00	25.10	0.00	50.47	0.00	24.43	0.00
700	40	1	54.79	0.00	32.30	0.00	12.91	0.00	24.79	0.00	54.16	0.00	21.05	0.00
700	60	1	70.97	0.00	16.05	0.00	12.99	0.00	27.58	0.00	40.36	0.00	32.06	0.00

Pow. Gran. Clay + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
400	0	0	31.84	1.90	50.50	5.19	17.66	4.06	31.86	1.90	50.80	5.22	17.34	4.09
400	10	1	39.23	0.00	48.22	0.00	12.55	0.00	32.68	0.00	53.90	0.00	13.42	0.00
400	20	1	44.72	0.00	40.12	0.00	15.16	0.00	31.09	0.00	50.45	0.00	18.46	0.00
400	40	1	60.20	0.00	31.89	0.00	7.91	0.00	33.87	0.00	53.48	0.00	12.65	0.00
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	10	1	38.23	0.00	59.35	0.00	2.43	0.00	31.55	0.00	66.34	0.00	2.11	0.00
500	20	1	45.93	0.00	36.74	0.00	17.34	0.00	32.61	0.00	46.20	0.00	21.20	0.00
500	30	1	54.08	0.00	34.73	0.00	11.19	0.00	34.61	0.00	49.91	0.00	15.48	0.00
500	40	1	62.70	0.00	22.07	0.00	15.22	0.00	38.07	0.00	37.01	0.00	24.92	0.00
500	60	1	78.15	0.00	11.54	0.00	10.31	0.00	45.65	0.00	29.02	0.00	25.33	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	10	1	38.63	0.00	44.31	0.00	17.06	0.00	32.01	0.00	49.53	0.00	18.47	0.00
700	20	1	47.48	0.00	37.28	0.00	15.25	0.00	34.55	0.00	46.88	0.00	18.57	0.00
700	30	1	55.10	0.00	29.54	0.00	15.36	0.00	36.08	0.00	42.46	0.00	21.47	0.00
700	40	1	67.51	0.00	20.88	0.00	11.61	0.00	46.12	0.00	35.01	0.00	18.87	0.00
700	50	1	64.56	0.00	21.25	0.00	14.19	0.00	29.30	0.00	42.75	0.00	27.95	0.00
700	60	1	75.30	0.00	16.14	0.00	8.56	0.00	38.48	0.00	40.60	0.00	20.92	0.00

Iron Oxide + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	30	1	44.77	0.00	41.02	0.00	14.22	0.00	21.22	0.00	58.95	0.00	19.83	0.00
500	60	1	68.02	0.00	23.66	0.00	8.32	0.00	20.18	0.00	59.52	0.00	20.31	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	30	1	41.13	0.00	43.60	0.00	15.27	0.00	15.99	0.00	62.67	0.00	21.34	0.00
700	60	1	64.16	0.00	25.10	0.00	10.74	0.00	10.46	0.00	63.13	0.00	26.41	0.00

HSM5 Zeolite + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	30	1	47.49	0.00	39.76	0.00	12.75	0.00	25.14	0.00	57.14	0.00	17.72	0.00
500	30	1	44.82	0.00	44.49	0.00	10.69	0.00	21.30	0.00	63.94	0.00	14.76	0.00
500	60	1	70.68	0.00	18.63	0.00	10.69	0.00	26.87	0.00	46.85	0.00	26.28	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	30	1	45.95	0.00	38.12	0.00	15.93	0.00	22.92	0.00	54.79	0.00	22.29	0.00
700	60	1	73.62	0.00	16.68	0.00	9.69	0.00	34.26	0.00	41.96	0.00	23.77	0.00

HSM5-Zeolite + Olive			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	30	1	52.66	0.00	30.30	0.00	17.04	0.00	38.62	0.00	51.64	0.00	9.74	0.00
500	60	1	72.35	0.00	17.95	0.00	9.70	0.00	36.83	0.00	53.53	0.00	9.64	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	30	1	51.65	0.00	30.79	0.00	17.56	0.00	37.23	0.00	52.95	0.00	9.82	0.00
700	60	1	76.89	0.00	13.22	0.00	9.89	0.00	50.84	0.00	39.78	0.00	9.38	0.00

Portland Cement + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	10	3	33.26	3.00	51.02	9.54	15.72	3.86	26.00	2.11	51.46	10.66	16.97	7.31
500	30	2	48.47	0.50	40.59	0.39	10.95	0.11	26.54	0.72	58.33	0.57	15.13	0.16
500	40	1	56.36	0.00	36.46	0.00	7.18	0.00	27.43	0.00	61.13	0.00	11.44	0.00
500	60	2	71.39	0.52	21.19	0.84	7.42	0.32	28.64	1.32	53.30	2.12	18.05	0.80
600	0	3	29.55	2.46	48.15	3.34	22.30	1.20	29.51	2.46	48.44	3.36	22.05	1.21
600	30	1	51.57	0.00	33.34	0.00	15.09	0.00	31.00	0.00	47.91	0.00	21.08	0.00
600	60	1	77.68	0.00	13.54	0.00	8.78	0.00	44.48	0.00	34.06	0.00	21.47	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	30	1	47.84	0.00	32.44	0.00	19.72	0.00	25.64	0.00	46.63	0.00	27.73	0.00
700	40	1	56.26	0.00	30.70	0.00	13.04	0.00	27.26	0.00	51.47	0.00	21.26	0.00
700	60	1	73.42	0.00	17.80	0.00	8.78	0.00	33.75	0.00	44.77	0.00	21.47	0.00

Ben. Clay + Sand + Pine				Total Yield						Dry Ash Free Yield					
Temp (°C)	C_{clay}	C_{snad}	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	0	40	1	58.00	0.00	33.77	0.00	8.23	0.00	26.03	0.00	59.95	0.00	14.02	0.00
500	10	40	1	57.08	0.00	34.07	0.00	8.85	0.00	9.17	0.00	72.58	0.00	18.24	0.00
500	20	40	1	56.06	0.00	35.03	0.00	8.91	0.00	-16.42	0.00	93.28	0.00	23.13	0.00
500	30	40	1	55.54	0.00	33.52	0.00	10.94	0.00	-57.25	0.00	119.01	0.00	38.23	0.00
700	30	0	1	47.84	0.00	32.44	0.00	19.72	0.00	25.64	0.00	46.63	0.00	27.73	0.00
700	0	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	0	40	1	58.87	0.00	28.00	0.00	13.13	0.00	25.59	0.00	51.06	0.00	23.35	0.00
700	20	40	1	55.51	0.00	30.37	0.00	14.12	0.00	-21.11	0.00	83.09	0.00	38.02	0.00
700	10	40	1	57.87	0.00	28.61	0.00	13.52	0.00	8.40	0.00	62.62	0.00	28.98	0.00
700	30	40	1	55.54	0.00	30.02	0.00	14.44	0.00	-61.55	0.00	109.49	0.00	52.06	0.00
500	0	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	10	30	1	69.89	16.89	22.38	13.04	7.73	3.85	30.64	5.17	51.67	5.16	17.70	0.01
500	20	20	1	74.81	21.55	16.90	16.03	8.29	5.52	38.48	10.84	39.60	12.92	21.91	2.08
500	25	25	1	68.34	0.00	23.13	0.00	8.54	0.00	34.55	0.00	48.24	0.00	17.20	0.00
500	30	10	1	60.49	0.00	27.17	0.00	12.34	0.00	33.38	0.00	46.22	0.00	20.40	0.00

Sand + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80
500	30	1	51.16	0.00	37.38	0.00	11.46	0.00	27.31	0.00	56.09	0.00	16.60	0.00
500	20	1	42.07	0.00	43.99	0.00	13.95	0.00	25.61	0.00	56.94	0.00	17.45	0.00
500	40	1	58.94	0.00	29.81	0.00	11.25	0.00	27.72	0.00	52.92	0.00	19.37	0.00
500	60	1	74.97	0.00	19.06	0.00	5.97	0.00	32.10	0.00	52.16	0.00	15.74	0.00
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80
700	40	1	58.87	0.00	28.00	0.00	13.13	0.00	25.59	0.00	51.06	0.00	23.35	0.00
700	50	1	72.72	0.00	13.58	0.00	13.70	0.00	39.70	0.00	30.31	0.00	29.99	0.00
700	90	1	95.88	0.00	1.31	0.00	2.81	0.00	52.24	0.00	15.35	0.00	32.41	0.00

Dolomite + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev
500	0	1	29.86	0.00	44.34	0.00	25.79	0.00	3004.45	0.00	44.61	0.00	25.34	0.00
500	10	1	47.00	0.00	35.60	0.00	17.40	0.00	4135.93	0.00	39.79	0.00	18.85	0.00
500	20	1	53.00	0.00	30.60	0.00	16.40	0.00	4149.90	0.00	38.48	0.00	20.02	0.00
500	30	1	59.88	0.00	26.95	0.00	13.17	0.00	4294.37	0.00	38.73	0.00	18.33	0.00
500	40	1	68.60	0.00	19.80	0.00	11.60	0.00	4795.44	0.00	33.20	0.00	18.85	0.00
500	50	1	78.00	0.00	14.00	0.00	8.00	0.00	5633.80	0.00	28.17	0.00	15.49	0.00
500	60	1	78.86	0.00	14.96	0.00	6.18	0.00	4744.32	0.00	37.61	0.00	14.94	0.00

Type Y Zeolite + Pine			Total Yield						Dry Ash Free Yield					
Temp (°C)	**Cadd**	**Count**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**
500	0	1	29.86	0.00	44.34	0.00	25.79	0.00	3004.45	0.00	44.61	0.00	25.34	0.00
500	8	1	32.85	0.00	52.36	0.00	14.78	0.00	2749.83	0.00	57.01	0.00	15.49	0.00
500	27	1	47.91	0.00	33.26	0.00	18.83	0.00	2903.13	0.00	45.70	0.00	25.27	0.00
500	38	1	61.93	0.00	29.42	0.00	8.64	0.00	3856.47	0.00	47.95	0.00	13.48	0.00
500	49	1	68.93	0.00	16.46	0.00	14.61	0.00	3983.90	0.00	32.19	0.00	27.97	0.00

1.1 Zeolite and Dolomite Liquid Analysis

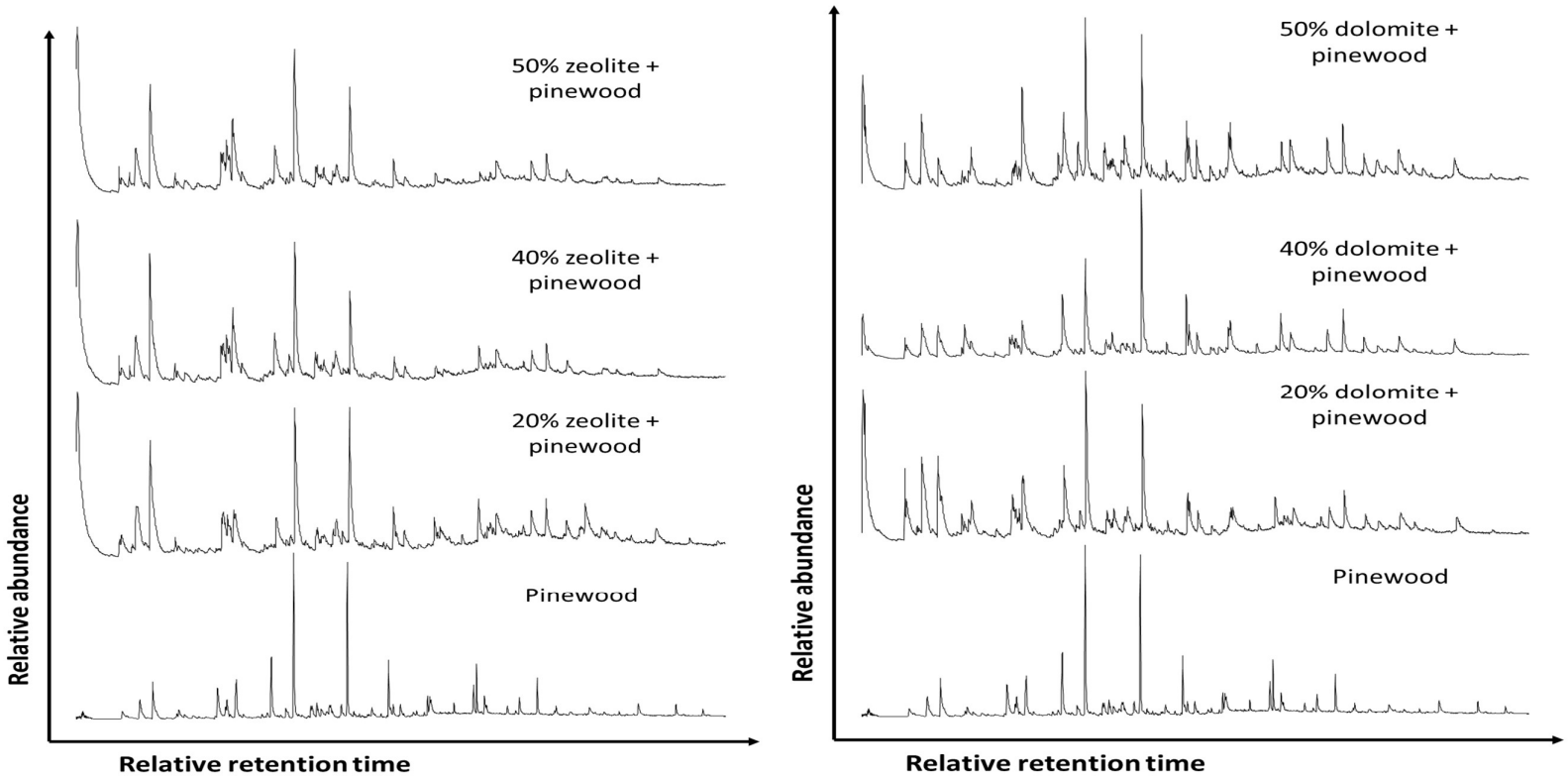


Figure A- 6. GC-MS output from zeolite and dolomite + pinewood experiment at 500 °C. For peak identification see Figure 4-17.

1.2 Bentonite Clay Detailed Experimentation

1. Pinewood			Total Yield						Dry Ash Free Yield						Proximate			
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev	Cmc	Cash	Cvol	$C_{mc,oil}$
300	0	3	49.93	0.79	35.27	1.53	14.79	0.74	50.03	0.79	35.48	1.54	14.49	0.75	1.10	0.41	48.00	
300	5	1	60.22	0.00	32.80	0.00	6.98	0.00	57.84	0.00	34.82	0.00	7.35	0.00	1.14	13.5	34.73	
300	30	1	71.04	0.00	18.61	0.00	10.35	0.00	56.71	0.00	27.86	0.00	15.43	0.00	1.56	21.0	27.65	
300	40	1	80.15	0.00	13.20	0.00	6.65	0.00	64.87	0.00	23.40	0.00	11.73	0.00	0.34	41.2	22.99	
300	70	1	92.89	0.00	4.01	0.00	3.10	0.00	73.72	0.00	14.85	0.00	11.43	0.00	1.00	71.7	22.13	
400	0	3	31.84	1.90	50.50	5.19	17.66	4.06	31.86	1.90	50.80	5.22	17.34	4.09	2.70	0.55	20.40	57
400	10	2	42.17	2.85	43.15	4.30	14.67	1.44	35.53	3.30	48.16	4.88	16.31	1.58	4.61	11.7	19.78	55
400	20	1	47.94	0.00	38.71	0.00	13.36	0.00	34.29	0.00	48.90	0.00	16.81	0.00				64
400	30	1	56.20	0.00	31.62	0.00	12.18	0.00	36.51	0.00	45.88	0.00	17.61	0.00				68
400	40	1	63.26	0.00	25.02	0.00	11.72	0.00	37.56	0.00	42.55	0.00	19.88	0.00				73
400	50	2	72.08	1.43	18.37	0.95	9.55	0.48	43.12	3.41	37.47	2.26	19.42	1.15	0.07	59.2	14.05	
400	60	1	78.71	0.00	12.62	0.00	8.68	0.00	45.19	0.00	32.51	0.00	22.30	0.00				78
500	0	5	30.16	2.75	46.65	3.59	23.20	4.79	30.11	2.75	46.93	3.61	22.97	4.80	0.90	0.77	11.00	58
500	10	1	42.18	0.00	36.76	0.00	21.06	0.00	35.67	2.46	40.93	0.00	23.40	0.00	1.2	13.7	9.8	60
500	20	1	47.82	0.00	35.11	0.00	17.07	0.00	34.26	1.60	44.28	0.00	21.46	0.00	0.0	29.8	9.9	70
500	30	2	57.13	1.75	26.08	1.77	16.78	0.03	38.48	2.51	37.47	2.55	24.05	0.04	0.3	51.1	9.4	68
500	40	1	64.22	0.00	20.56	0.00	15.22	0.00	40.00	2.51	34.51	0.00	25.49	0.00	0.7	63.1	7.9	74
500	50	1	74.66	0.00	10.53	0.00	14.80	0.00	48.94	2.51	21.25	0.00	29.81	0.00	0.9	70.8	8.8	
500	60	2	79.37	0.18	7.89	0.15	12.75	0.34	47.94	2.50	19.92	0.39	32.14	0.85	1.1	78.3	7.8	88
700	0	4	26.12	1.60	52.07	2.78	21.82	1.78	26.07	1.60	52.38	2.80	21.55	1.80	0.80	0.78	3.30	61
700	5	1	29.70	0.00	48.68	0.00	21.61	0.00	26.18	0.00	51.16	0.00	22.65	0.00				
700	9	2	37.60	1.09	36.68	3.40	25.72	2.31	31.36	1.59	40.39	3.97	28.25	2.38	0.53	17.4	2.41	62
700	20	3	45.15	1.03	32.16	1.38	22.69	1.22	32.00	1.26	39.90	1.75	28.09	1.48	0.31	54.4	2.60	68
700	25	1	46.85	0.00	33.24	0.00	19.92	0.00	29.92	0.00	43.86	0.00	26.22	0.00				

700	30	4	51.00	2.79	27.30	4.26	21.69	2.32	30.15	4.32	38.92	5.91	30.92	3.78	0.23	60.3	2.70	69
700	40	2	63.16	0.13	18.04	0.92	18.81	1.05	39.43	0.59	29.68	1.33	30.89	1.92	0.38	67.2	3.21	
700	50	3	70.57	2.63	12.02	1.42	17.41	1.35	42.46	5.21	23.52	2.82	34.01	2.68	0.20	75.2	3.31	
700	60	2	77.04	1.49	5.20	1.30	17.76	0.20	44.13	3.64	12.66	3.16	43.21	0.48	0.15	80.4	3.52	78
900	0	3	26.82	1.49	47.11	0.30	26.08	1.79	26.65	1.48	47.39	0.30	25.96	1.78				
900	5	1	34.68	0.00	36.58	0.00	28.74	0.00	31.43	0.00	38.44	0.00	30.13	0.00				
900	20	1	41.86	0.00	36.14	0.00	22.00	0.00	28.05	0.00	44.76	0.00	27.18	0.00				

2. Olive Cake			Total Yield						Dry Ash Free Yield						Proximate			
Temp (°C)	**Cadd**	**Count**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**	**Cmc**	**Cvol**	**C_{ash}**	**$C_{mc,oil}$**
400	0	2	46.63	7.82	33.55	4.82	19.82	3.01	42.41	7.12	36.07	5.18	21.51	1.94	1.08	15.41	16.56	66
400	10	2	55.91	0.39	25.87	0.82	18.22	0.43	54.75	0.42	30.96	0.96	14.29	0.54				
400	30	1	66.59	0.00	19.47	0.00	13.94	0.00	55.66	0.00	30.23	0.00	14.11	0.00	1.0	51.0	13.4	
400	50	1	80.15	0.00	7.88	0.00	11.97	0.00	64.63	0.00	17.03	0.00	18.34	0.00	1.0	70.2	11.0	
400	70	1	91.31	0.00	-0.31	0.00	9.00	0.00	76.37	0.00	-1.09	0.00	24.72	0.00	1.0	77.0	10.9	
500	0	5	43.69	5.79	32.43	5.51	23.88	1.32	39.38	5.22	34.87	5.92	25.75	1.46	1.61	16.18	9.07	61
500	10	3	52.24	1.22	26.23	2.91	21.53	1.73	50.37	1.39	31.39	3.45	18.23	2.10				
500	30	4	65.58	3.80	19.06	2.07	15.37	1.87	54.60	5.92	29.30	3.21	16.10	2.91	1.0	54.3	7.8	
500	50	3	78.55	1.88	6.54	1.68	14.91	0.68	61.33	4.05	14.09	3.61	24.58	1.51	1.0	65.9	7.8	
500	69	5	90.75	2.93	0.24	2.54	9.00	1.27	74.39	10.67	0.92	9.00	24.68	4.79	1.0	83.5	8.0	
700	0	6	40.05	6.40	31.90	5.46	28.02	2.28	36.66	5.90	33.26	5.87	30.08	1.93	1.00	16.93	1.07	63
700	10	3	50.94	4.01	22.89	2.70	26.17	1.58	49.22	4.67	27.20	3.16	23.57	1.84				
700	30	4	60.68	1.89	16.57	2.48	22.75	1.51	48.09	2.87	25.04	3.73	26.87	2.31	0.53	62.12	0.58	
700	50	3	72.89	0.77	6.59	1.22	20.52	1.03	50.96	1.51	13.75	2.53	35.29	2.12	0.45	80.85	1.67	
700	70	3	88.15	1.51	-6.87	6.55	18.72	8.02	66.35	4.93	-23.80	22.65	57.45	27.50	0.10	88.51	2.99	

3. Straw			Total Yield						Dry Ash Free Yield						Proximate		
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev	Cmc	Cvol	C_{ash}
400	0	2	36.18	0.37	44.93	0.20	18.89	0.17	31.63	0.32	48.31	0.22	20.06	0.11	0.50	18.68	23.39
400	10	2	43.21	0.20	40.54	0.49	16.25	0.30	39.75	0.23	48.38	0.59	11.87	0.36	0.50	23.76	21.60
400	60	1	82.29	0.00	5.14	0.00	12.56	0.00	60.22	0.00	13.75	0.00	26.03	0.00	0.50	80.67	13.03
400	70	1	89.15	0.00	1.17	0.00	9.68	0.00	68.92	0.00	4.15	0.00	26.93	0.00			
500	0	2	31.93	0.25	43.33	2.02	24.74	2.27	27.61	0.21	46.59	2.17	25.80	2.39	0.50	19.57	17.30
500	10	2	41.80	0.55	36.58	1.27	21.62	0.72	37.88	0.65	43.78	1.52	18.34	0.86			
500	30	1	56.68	0.00	25.77	0.00	17.55	0.00	40.66	0.00	39.78	0.00	19.56	0.00	0.36	47.66	12.16
500	50	1	72.02	0.00	12.40	0.00	15.58	0.00	46.86	0.00	26.89	0.00	26.25	0.00	3.37	67.36	12.03
500	70	1	87.60	0.00	2.31	0.00	10.09	0.00	62.57	0.00	8.37	0.00	29.06	0.00			
700	0	2	28.89	0.05	43.34	0.61	27.78	0.65	23.79	0.04	46.60	0.65	29.62	0.69	0.50	23.42	4.85
700	10	1	38.67	0.00	34.77	0.00	26.56	0.00	34.57	0.00	41.36	0.00	24.07	0.00			
700	30	1	52.39	0.00	25.26	0.00	22.35	0.00	35.36	0.00	38.29	0.00	26.35	0.00	0.50	50.48	2.81
700	50	2	68.70	0.76	10.53	2.27	20.77	1.51	41.69	1.59	22.15	4.78	36.16	3.18	0.28	82.19	59.44

4. Eucalyptus			Total Yield						Dry Ash Free Yield						Proximate		
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev	Cmc	Cvol	C_{ash}
400	0	1	29.75	0.00	53.02	0.00	17.23	0.00	29.62	0.00	53.32	0.00	17.07	0.00	1.92	1.00	22.36
400	20	1	46.16	0.00	40.40	0.00	13.44	0.00	33.32	0.00	50.45	0.00	16.23	0.00			
400	30	1	53.88	0.00	32.14	0.00	13.98	0.00	34.94	0.00	45.72	0.00	19.33	0.00			
400	40	1	63.28	0.00	27.06	0.00	9.66	0.00	39.82	0.00	44.76	0.00	15.42	0.00			
500	0	1	24.50	0.00	64.22	0.00	11.28	0.00	24.43	0.00	64.57	0.00	11.00	0.00	1.85	0.84	14.11
500	10	1	31.89	0.00	53.31	0.00	14.80	0.00	25.57	0.00	58.69	0.00	15.74	0.00	1.66	8.07	11.34
500	20	3	39.30	1.48	46.53	4.03	14.17	2.56	26.49	1.81	56.77	4.92	16.74	3.12	0.33	22.7	9.62
500	30	1	44.11	0.00	38.70	0.00	17.19	0.00	23.79	0.00	53.15	0.00	23.06	0.00	0.23	50.2	9.83
500	40	1	54.88	0.00	32.73	0.00	12.39	0.00	29.45	0.00	51.58	0.00	18.97	0.00	0.00	0.00	0.00

500	50	1	63.40	0.00	25.66	0.00	10.95	0.00	32.32	0.00	47.83	0.00	19.85	0.00	0.40	68.1	9.10
500	60	1	73.90	0.00	17.09	0.00	9.02	0.00	40.69	0.00	39.18	0.00	20.13	0.00			
700	0	2	22.31	1.61	57.33	4.09	20.36	2.48	22.15	1.60	57.65	4.11	20.20	2.52	0.79	1.13	3.07
700	10	1	28.51	0.00	51.42	0.00	20.07	0.00	22.25	0.00	56.32	0.00	21.42	0.00	0.43	24.3	2.97
700	20	1	35.47	0.00	49.03	0.00	15.50	0.00	22.64	0.00	59.20	0.00	18.16	0.00	0.27	41.5	3.47
700	30	1	45.11	0.00	35.87	0.00	19.02	0.00	26.36	0.00	48.48	0.00	25.16	0.00	0.27	56.1	5.82
700	40	1	56.29	0.00	27.60	0.00	16.11	0.00	30.45	0.00	44.27	0.00	25.28	0.00	0.23	65.0	3.60

5. Miscanthus			Total Yield						Dry Ash Free Yield					
Temp (°C)	**Cadd**	**Count**	**$Y_{char,total}$**	**Stdev**	**$Y_{liquid,total}$**	**Stdev**	**$Y_{gas,total}$**	**Stdev**	**$Y_{char,DAF}$**	**Stdev**	**$Y_{liquid,DAF}$**	**Stdev**	**$Y_{gas,DAF}$**	**Stdev**
400	0	1	34.00	0.00	38.93	0.00	27.07	0.00	30.72	0.00	41.42	0.00	27.86	0.00
400	10	1	37.63	0.00	38.15	0.00	24.22	0.00	32.00	0.00	45.49	0.00	22.50	0.00
400	18	1	53.20	0.00	21.64	0.00	25.16	0.00	44.54	0.00	28.60	0.00	26.86	0.00
400	40	1	67.78	0.00	17.12	0.00	15.10	0.00	47.21	0.00	31.44	0.00	21.35	0.00
500	0	1	30.78	0.00	38.75	0.00	30.47	0.00	26.53	0.00	41.22	0.00	32.25	0.00
500	10	1	42.85	0.00	32.71	0.00	24.45	0.00	38.28	0.00	38.97	0.00	22.75	0.00
500	20	1	51.01	0.00	26.33	0.00	22.66	0.00	40.18	0.00	35.57	0.00	24.24	0.00
500	30	1	57.81	0.00	22.57	0.00	19.62	0.00	40.71	0.00	35.13	0.00	24.15	0.00
500	40	1	64.68	0.00	15.96	0.00	19.36	0.00	41.74	0.00	29.20	0.00	29.06	0.00
700	0	2	30.39	1.57	40.98	2.43	28.63	4.00	26.42	1.36	43.60	2.58	29.98	3.95
700	10	1	41.09	0.00	30.89	0.00	28.02	0.00	36.64	0.00	36.57	0.00	26.79	0.00
700	30	1	54.03	0.00	20.06	0.00	25.90	0.00	36.17	0.00	30.65	0.00	33.18	0.00
700	40	1	61.34	0.00	14.73	0.00	23.93	0.00	37.39	0.00	26.28	0.00	36.33	0.00

6. Olive Stone			Total Yield						Dry Ash Free Yield						Proximate			
Temp (°C)	Cadd	Count	$Y_{char,total}$	Stdev	$Y_{liquid,total}$	Stdev	$Y_{gas,total}$	Stdev	$Y_{char,DAF}$	Stdev	$Y_{liquid,DAF}$	Stdev	$Y_{gas,DAF}$	Stdev	Cmc	Cvol	C_{ash}	$C_{mc,oil}$
400	0	1	29.63	0.00	45.90	0.00	24.47	0.00	29.35	0.00	46.08	0.00	24.57	0.00	11.30	0.40	1.35	
400	10	1	33.14	0.00	45.53	0.00	21.33	0.00	26.22	0.00	50.51	0.00	23.27	0.00				
400	18	1	47.41	0.00	30.18	0.00	22.41	0.00	36.49	0.00	36.67	0.00	26.84	0.00				
400	40	1	62.30	0.00	23.82	0.00	13.88	0.00	38.68	0.00	39.00	0.00	22.32	0.00				
500	0	1	28.90	0.00	50.18	0.00	20.93	0.00	28.61	0.00	50.38	0.00	21.01	0.00	11.30	0.40	1.38	
500	10	1	36.29	0.00	43.01	0.00	20.70	0.00	30.05	0.00	47.50	0.00	22.46	0.00				
500	20	1	43.99	0.00	36.46	0.00	19.55	0.00	31.54	0.00	44.83	0.00	23.63	0.00				
500	30	1	50.78	0.00	31.99	0.00	17.23	0.00	31.95	0.00	44.48	0.00	23.56	0.00				
500	40	1	57.87	0.00	24.81	0.00	17.32	0.00	32.76	0.00	39.83	0.00	27.41	0.00				
700	0	1	28.25	0.00	51.86	0.00	19.90	0.00	27.96	0.00	52.07	0.00	19.98	0.00	11.30	0.40	1.42	
700	10	1	34.77	0.00	41.53	0.00	23.71	0.00	28.75	0.00	45.61	0.00	25.64	0.00				
700	30	1	47.35	0.00	29.95	0.00	22.70	0.00	28.39	0.00	40.96	0.00	30.65	0.00				
700	40	1	54.74	0.00	23.91	0.00	21.35	0.00	29.34	0.00	37.54	0.00	33.12	0.00				

1.3 Liquid GC-MS from olive cake + clay experiment

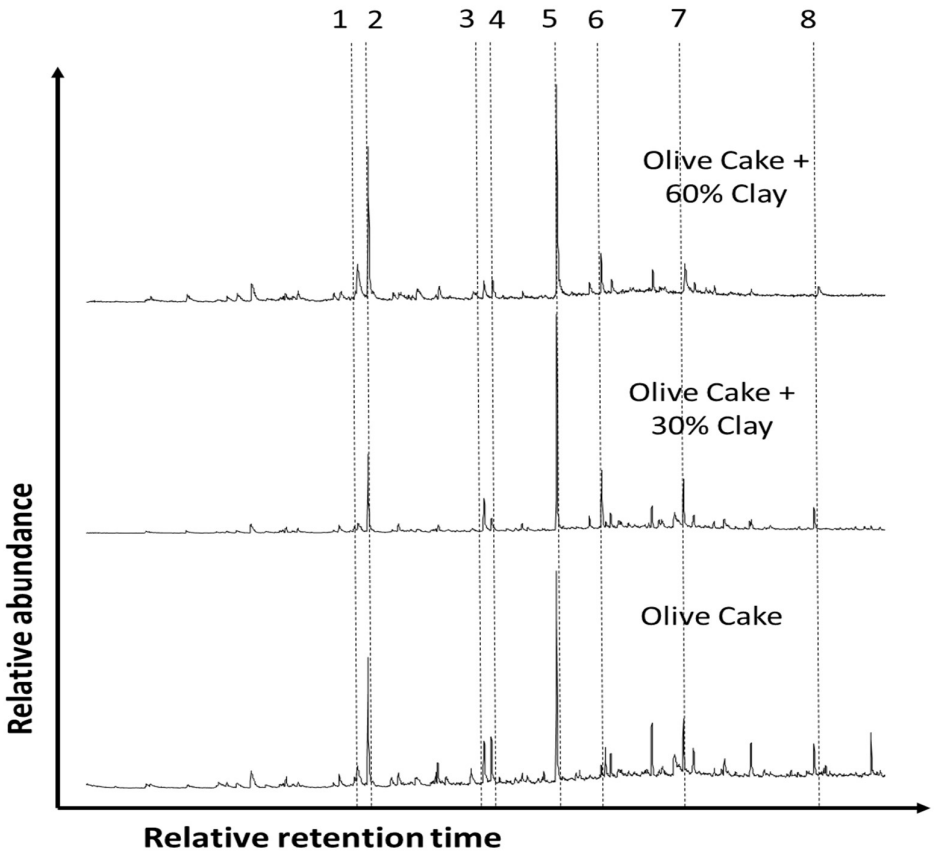


Figure A- 7. Olive cake GC-MS for clay additive experiment.

Peak assignments:

1) Phenol 2) Methoxyphenol 3) Diannhydromannitol 4) 4 ethyl 2 methoxyphenol 5) 2,6 dimethoxyphenol 6) 2 methoxy 4 propyl phenol 7) 4 hydroxy 3 methoxyphenol propane 8) butane tryhydroxymethoxy phenol.

2. Moisture Content Experiments

Dry Pine + Clay			Total Yield			Dry Ash Free Yield		
Temp (°C)	**Cadd**	**$C_{mc,bm}$**	**$Y_{char,total}$**	**$Y_{liquid,total}$**	**$Y_{gas,total}$**	**$Y_{char,DAF}$**	**$Y_{liquid,DAF}$**	**$Y_{gas,DAF}$**
400	0	0.03	31.43	55.43	13.14	31.62	55.76	12.61
400	30	0.03	60.24	23.22	16.54	43.46	33.37	23.17
500	0	0.03	27.09	59.36	13.55	27.25	59.72	13.03
500	30	0.03	52.84	32.78	14.37	32.83	47.12	20.05
500	60	0.03	73.34	15.95	10.72	33.54	40.10	26.36
700	0	0.03	22.70	58.55	18.75	22.83	58.90	18.26
700	30	0.03	54.26	17.59	28.15	34.86	25.28	39.86
700	60	0.03	77.87	4.40	17.73	44.94	11.06	44.00

Wet Pine + Clay			Total Yield			Dry Ash Free Yield		
Temp (°C)	**Cadd**	**$C_{mc,bm}$**	**$Y_{char,total}$**	**$Y_{liquid,total}$**	**$Y_{gas,total}$**	**$Y_{char,DAF}$**	**$Y_{liquid,DAF}$**	**$Y_{gas,DAF}$**
500	0	0.52	15.17	76.02	8.81	15.26	76.48	8.26
500	10	0.52	25.49	66.05	8.47	17.31	73.83	8.86
500	30	0.52	42.48	47.32	10.20	17.93	68.01	14.06
500	60	0.52	68.36	24.46	7.18	21.02	61.53	17.45
500	80	0.52	85.06	10.11	4.83	25.48	50.86	23.67
700	0	0.52	13.51	74.95	11.54	13.60	75.40	11.00
700	60	0.52	73.18	15.71	11.11	33.15	39.51	27.34
700	30	0.52	45.91	40.58	13.51	22.87	58.32	18.81

Wet Olive + Clay			Total Yield			Dry Ash Free Yield		
Temp (°C)	**Cadd**	**$C_{mc,bm}$**	**$Y_{char,total}$**	**$Y_{liquid,total}$**	**$Y_{gas,total}$**	**$Y_{char,DAF}$**	**$Y_{liquid,DAF}$**	**$Y_{gas,DAF}$**
500	0	0.32	22.10	57.99	19.92	23.76	62.35	13.89
500	30	0.32	48.39	37.98	13.63	28.25	58.35	13.41
500	40	0.32	56.37	29.77	13.86	29.34	53.34	17.32
500	50	0.32	64.24	23.22	12.54	30.62	49.93	19.45
500	60	0.32	71.71	18.65	9.63	31.49	50.15	18.36
500	70	0.32	78.39	12.59	9.02	30.06	45.13	24.82
500	80	0.32	86.18	5.16	8.66	33.22	27.75	39.03
700	0	0.32	20.15	60.49	19.36	21.67	65.05	13.29
700	30	0.32	50.30	29.75	19.95	31.18	45.71	23.12
700	60	0.32	75.50	8.15	16.35	41.68	21.91	36.41
700	80	0.32	93.40	-4.46	11.06	72.04	-23.98	51.94

3. Oil Recycle Experiments.

Oil Recycle Experiment			Non- Recycle Comparison		
Temperature	Conc Clay (wt%.eq)	Increase in Charcoal Yield	Temperature	Wt% Clay	Increase in Charcoal Yield
500	49.13	6.87	500	0	0
500	58.11	7.21	500	10	3.42
500	28.40	4.32	500	20	4.64
500	18.65	3.05	500	30	4.83
500	10.68	5.28	500	40	6.45
			500	50	8.00
			500	60	9.00

3.1Oil Recycle experiment liquid analysis

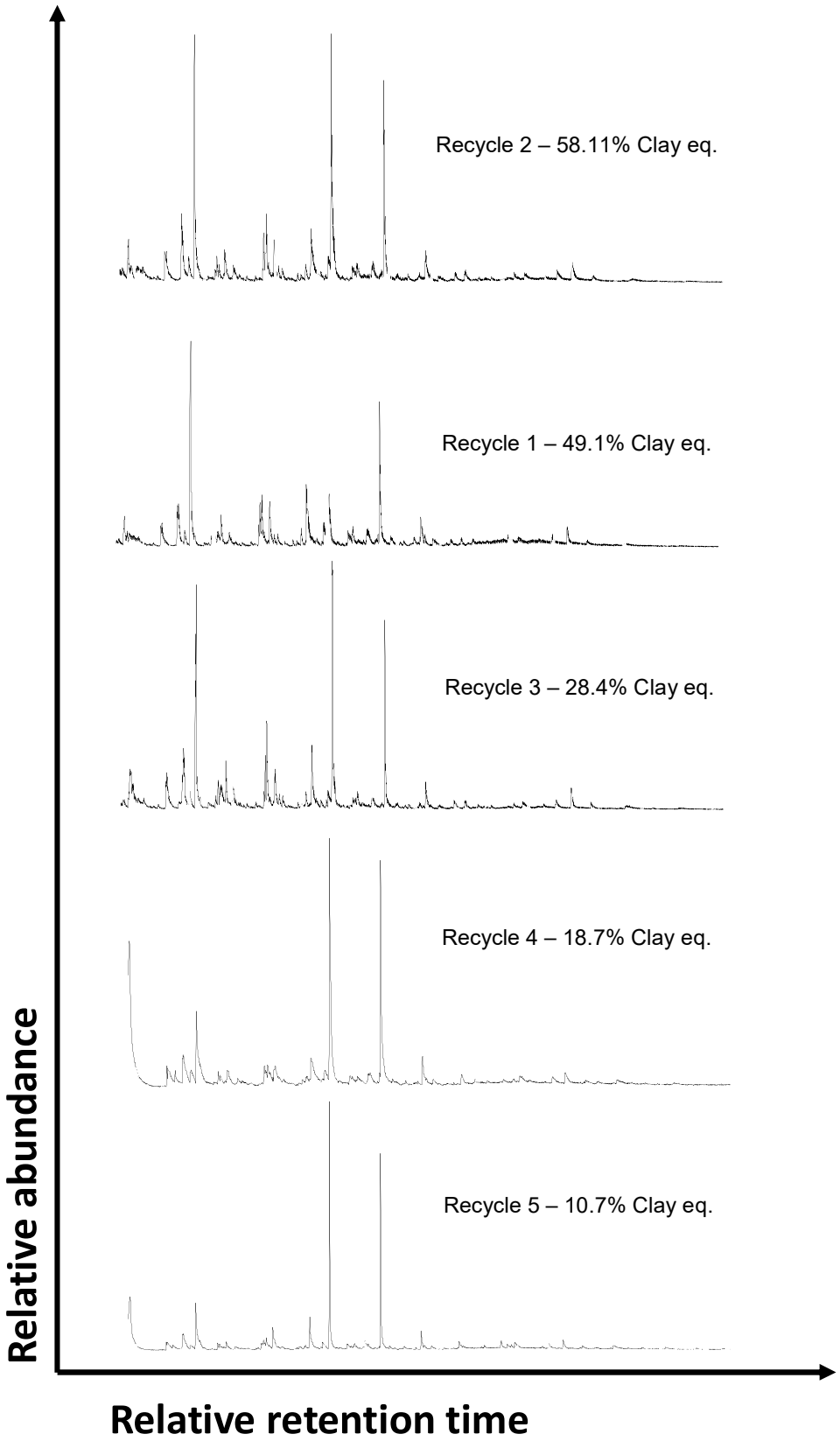


Figure A- 8. GC-MS curves from recycle experiment. For peak identification see Figure 4-17.

4. Biomass + Clay Pilot Plant Experiments

				Charcoal Quality	
Biomass Type	**C_{clay}**	**Temp (°C)**	**Charcoal Yield**	**Charcoal Volatiles Content**	**Charcoal Ash Content**
Pinewood	0	400	25.66	25.76	0.52
Pinewood	40	400	46.99		
Pinewood	0	550	19.82	10.76	0.55
Pinewood	20	550	31.56	58.00	7.10
Pinewood	40	550	41.16	82.10	6.60
Pinewood	0	700	17.06	4.54	3.00
Pinewood	40	700	33.33		

Appendix 3. Experimental Runs and Results for Chapter 5 – BBQ Modelling

1. Briquette Properties – Replicate Samples

Pyrolysis Conditions			Briquette Components (wt%)					Briquette Proximate Analysis (wt%)			Observations
Date	**Biomass**	**Temp (°C)**	$C_{raw\ bm}$	C_{sand}	$C_{raw\ clay}$	$C_{pyro\ clay}$	C_{binder}	C_{ash}	$C_{Volatiles}$	$C_{fixed\ Carbon}$	
07/07/2015	Pinewood	400						1.2%	31.7%	67.1%	Smoke
24/08/2015	Pinewood	400						1.1%	31.2%	67.7%	Smoke
avg	Pinewood	400					5	1.2%	31.5%	67.4%	
07/07/2015	Hardwood	400					5	1.4%	30.5%	68.1%	Smoke
24/08/2015	Hardwood	400					5				Smoke
avg	Hardwood	400					5	1.4%	30.5%	68.1%	
05/10/2015	Straw	400					5	11.7%	48.6%	39.7%	Smoke
17/09/2015	Straw	400					5	11.3%	48.2%	40.5%	Smoke
avg	Straw	400					5	11.5%	48.4%	40.1%	
03/09/2015	Straw	550					5	18.8%	21.0%	60.2%	
24/05/2016	Straw	550					5	18.3%	21.1%	60.6%	
24/05/2016	Straw	550					5	17.7%	20.5%	61.8%	
avg	Straw	550					5	18.3%	20.9%	60.9%	
17/09/2015	Straw	700					5	21.0%	19.2%	59.8%	Smoulder
05/10/2015	Straw	700					5	21.0%	17.9%	61.1%	Smoulder
avg	Straw	700					5	21.0%	18.6%	60.5%	
09/10/2015	Pinewood	550		30			5	36.6%	14.4%	49.0%	

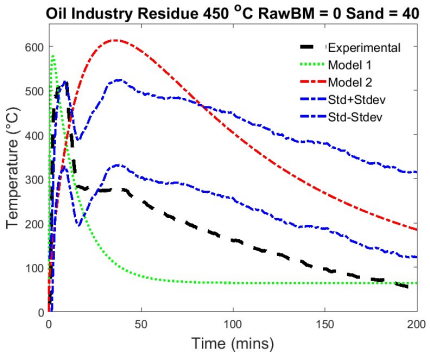
11/03/2016	Pinewood	550	30	5	24.4%	10.4%	65.2%	
avg	Pinewood	550	30	5	30.5%	12.4%	57.1%	
25/05/2016	Straw	550	30	5	45.1%	18.1%	36.8%	
25/05/2016	Straw	550	30	5	43.5%	14.5%	42.0%	
avg	Straw	550	30	5	44.3%	16.3%	39.4%	
31/05/2016	Straw	400	30	5	29.4%	35.2%	35.4%	Smoke
31/05/2016	Straw	400	30	5	36.4%	24.8%	38.8%	Smoke
avg	Straw	400	30	5	32.9%	30.0%	37.1%	
26/05/2015	Pinewood	550		5	2.0%	11.0%	87.0%	
14/03/2016	Pinewood	550		5				
avg	Pinewood	550		5	2.0%	11.0%	87.0%	
23/04/2015	Olive Cake	700		5				
29/04/2015	Olive Cake	700		5	16.7%	19.9%	63.4%	
avg	Olive Cake	700		5	16.7%	19.9%	63.4%	
01/04/2016	Pinewood	550	20	5	17.6%	13.2%	69.3%	
09/06/2016	Pinewood	550	20	5	17.6%	13.2%	69.3%	
09/06/2016	Pinewood	550	20	5	17.6%	13.2%	69.3%	
avg	Straw	550		5	17.6%	13.2%	69.3%	

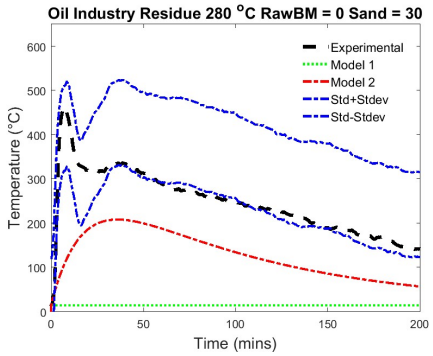
2. Briquette Properties – Single Samples

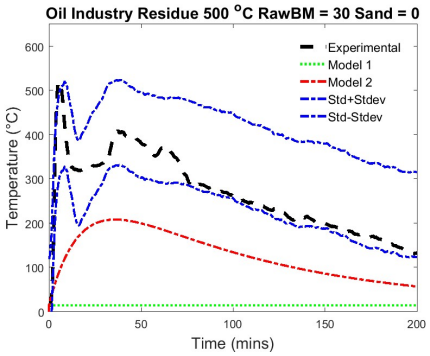
Pyrolysis Conditions			Briquette Components					Briquette Proxmiate Analysis (wt%, as received)			Observations
Date	**Biomass**	**Temp (°C)**	**$C_{raw\ bm}$**	**C_{sand}**	**$C_{raw\ clay}$**	**$C_{pyro\ clay}$**	**C_{binder}**	**C_{ash}**	**$C_{Volatiles}$**	**$C_{fixed\ Carbon}$**	
23/04/2015	Olive Cake	400					5	7.3%	60.5%	28.0%	Smoke
29/04/2015	Olive Cake	550					5	16.7%	25.3%	16.5%	
07/05/2015	Olive Cake	400		30			5				Smoke
07/05/2015	Olive Cake	700	30				5				Smoulder
01/07/2015	Pinewood	700					5	2.5%	19.9%	22.0%	
01/07/2015	Hardwood	550					5	1.6%	7.9%	30.5%	
03/09/2015	Hardwood	700					5	2.2%	9.6%	15.5%	Smoulder
04/09/2015	Hardwood	550		30			5	36.6%	8.8%	54.6%	
09/10/2015	Straw	550		30			5	43.7%	11.9%	44.4%	
12/10/2015	Straw	550	25	30			5	26.2%	30.2%	43.6%	
12/10/2015	Pinewood	550	25	30			5	29.7%	22.9%	47.4%	
05/11/2015	Straw	400		70			5	75.0%	14.4%	10.6%	Smoke
05/11/2015	Straw	400		50			5	54.2%	24.7%	21.1%	Smoke
03/02/2016	Olive Cake	550	20				5	14.1%	29.5%	56.4%	
03/02/2016	Olive Cake	550	40				5	11.4%	45.4%	43.2%	
08/02/2016	Olive Cake	550		20			5	14.1%	29.5%	56.4%	
08/02/2016	Olive Cake	550		40			5	11.4%	45.4%	43.2%	
25/02/2016	Olive Cake	550	10				5	15.3%	27.7%	57.0%	

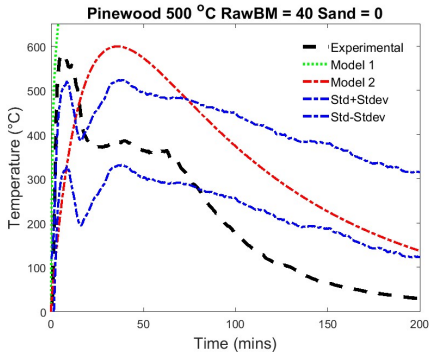
25/02/2016	Olive Cake	550	45				5	9.0%	47.3%	43.7%	
26/02/2016	Olive Cake	550		25			5	33.2%	16.9%	49.9%	
26/02/2016	Olive Cake	550		45			5	56.0%	13.3%	30.7%	
29/02/2016	Olive Cake	550		35			5	45.9%	15.0%	39.1%	
29/02/2016	Olive Cake	550		10			5	23.1%	19.7%	57.2%	
08/03/2016	Pinewood	550					10	36.8%	15.4%	47.8%	
08/03/2016	Pinewood	550	40				5	2.9%	36.1%	61.0%	
09/03/2016	Pinewood	550		10			5	18.3%	11.3%	70.4%	
09/03/2016	Pinewood	550		40			5	45.6%	9.1%	45.3%	
10/03/2016	Pinewood	550	30				5	42.4%	31.9%	25.7%	
10/03/2016	Pinewood	550		20			5	24.4%	10.4%	65.2%	
11/03/2016	Pinewood	550	10				5	7.5%	18.4%	74.1%	
14/03/2016	Pinewood	550	5				5	8.8%	14.5%	76.7%	
22/03/2016	Pinewood	550			20		5	24.4%	12.4%	63.2%	
22/03/2016	Pinewood	550			30		5	32.8%	13.0%	54.2%	
23/03/2016	Pinewood	550				57	5	45.3%	10.8%	43.9%	Smoulder
23/03/2016	Pinewood	550				90	5	72.0%	9.6%	18.4%	Smoulder
01/04/2016	Pinewood	550				30	5	32.0%	11.8%	56.3%	
06/04/2016	Pinewood	550				10	5	7.4%	13.3%	79.4%	
06/04/2016	Pinewood	550				40	5	31.2%	12.3%	56.5%	
17/06/2016	Pinewood	550	15	15			5	22.0%	0.2%	77.8%	
17/06/2016	Pinewood	550	10	10			5	19.0%	17.0%	64.0%	

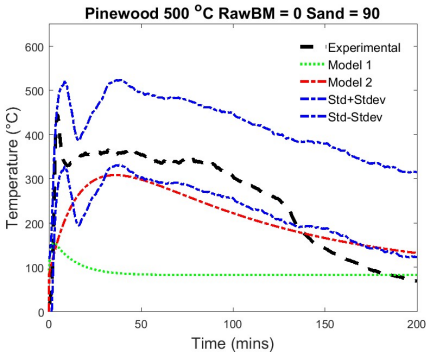
3. All Experimental Run Fits

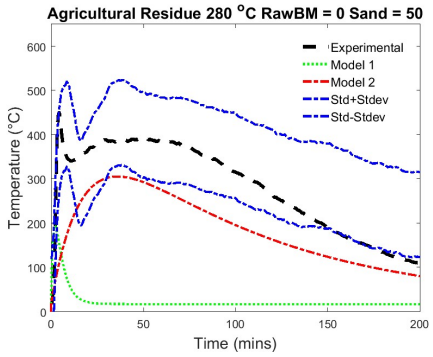


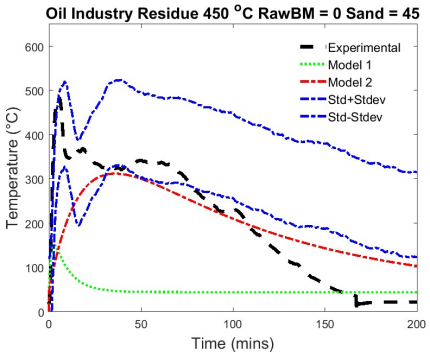


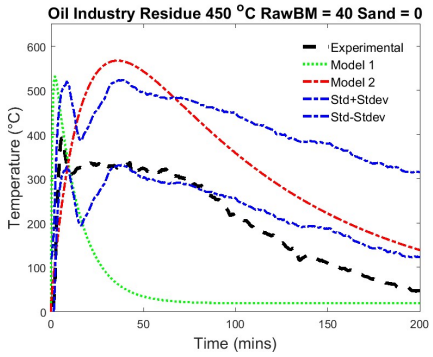


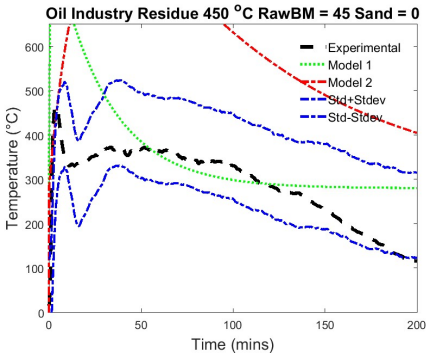


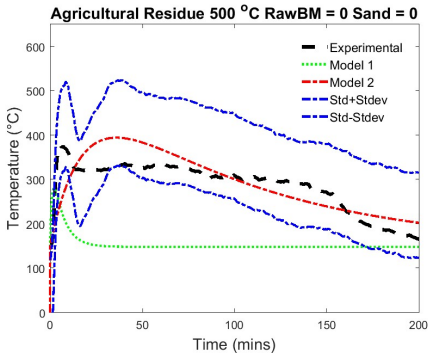


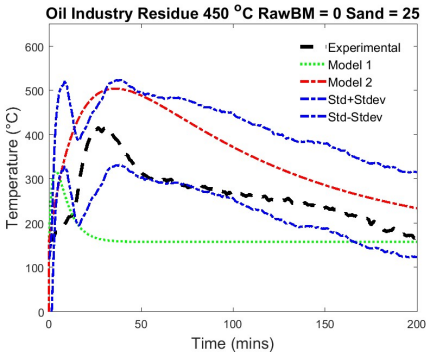


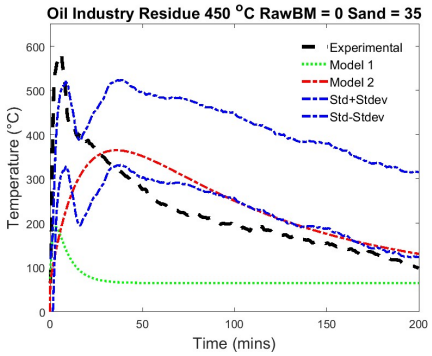


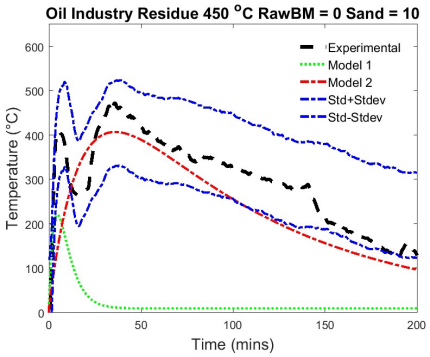


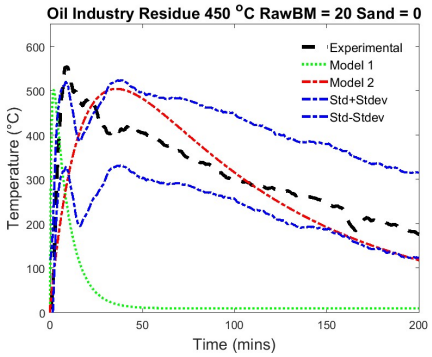

Oil Industry Residue 450 °C RawBM = 45 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

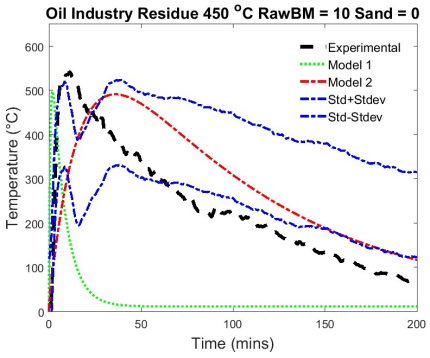

Agricultural Residue 500 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

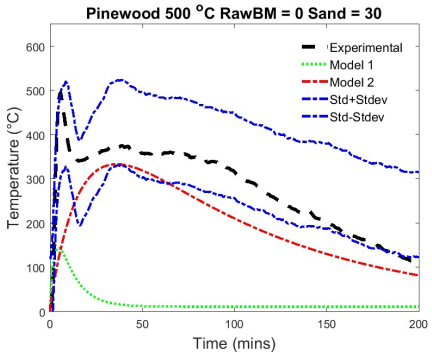

Oil Industry Residue 450 °C RawBM = 0 Sand = 25
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

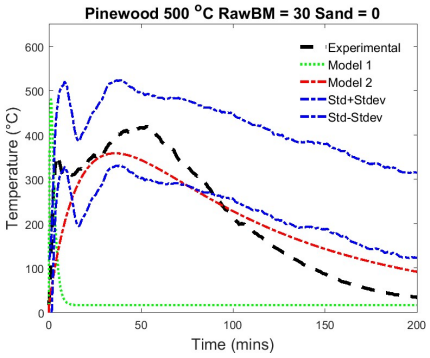

Oil Industry Residue 450 °C RawBM = 0 Sand = 35
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

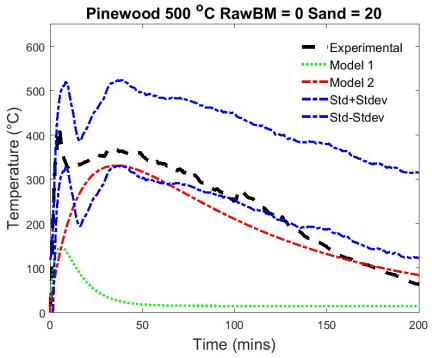

Oil Industry Residue 450 °C RawBM = 0 Sand = 10
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

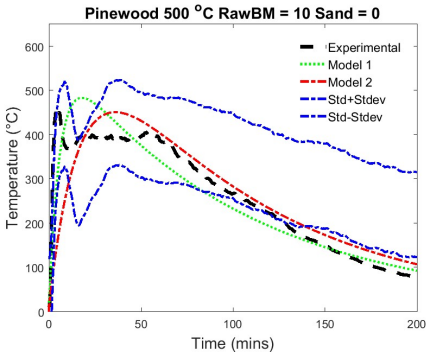

Oil Industry Residue 450 °C RawBM = 20 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

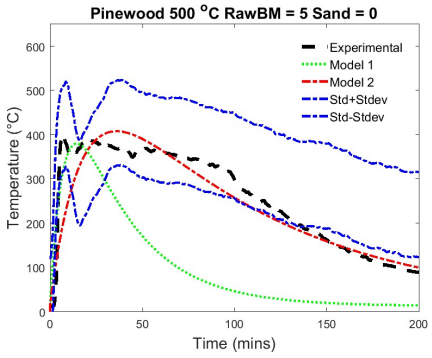

Oil Industry Residue 450 °C RawBM = 10 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

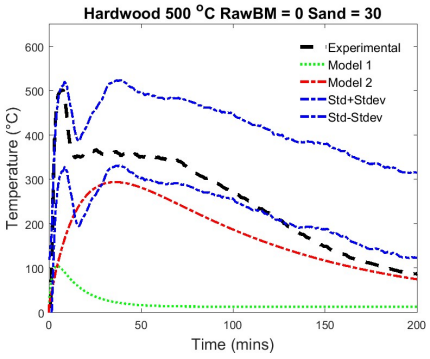

Pinewood 500 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

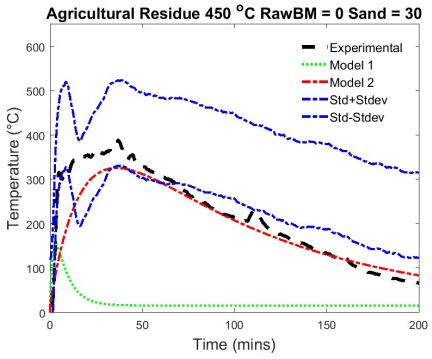

Pinewood 500 °C RawBM = 30 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

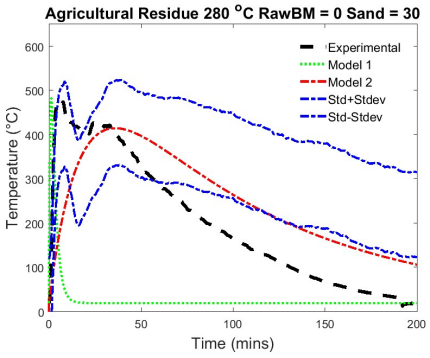

Pinewood 500 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

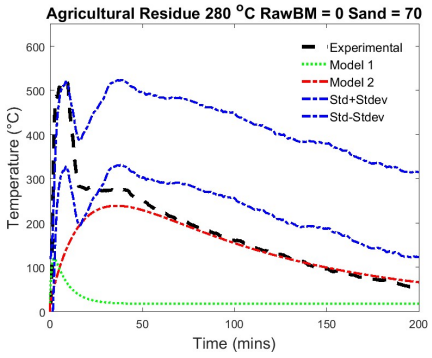

Pinewood 500 °C RawBM = 10 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

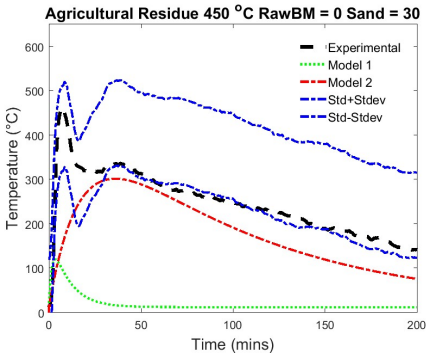

Pinewood 500 °C RawBM = 5 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

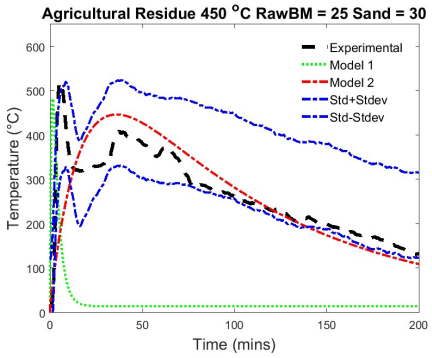

Hardwood 500 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

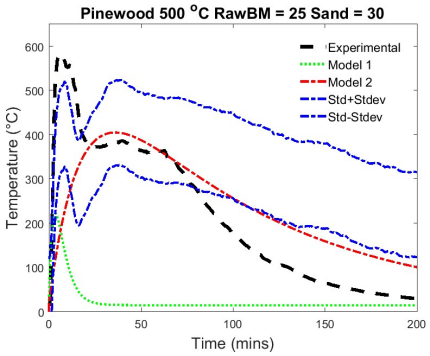

Agricultural Residue 450 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

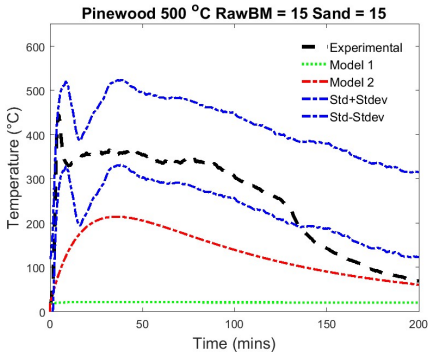

Agricultural Residue 280 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

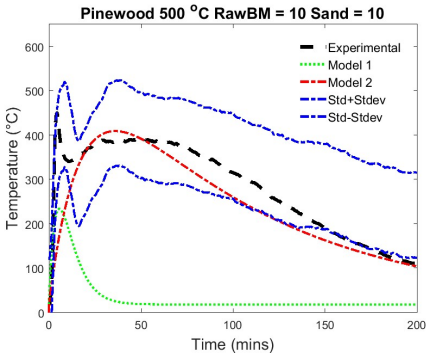

Agricultural Residue 280 °C RawBM = 0 Sand = 70
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

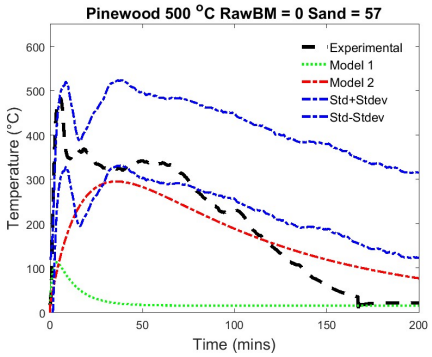

Agricultural Residue 450 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

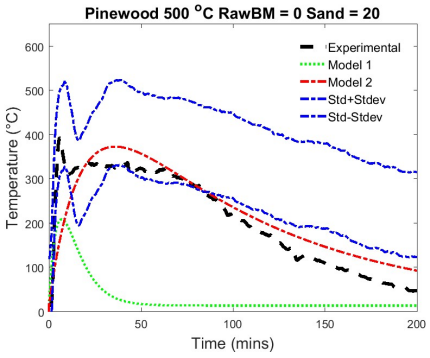

Agricultural Residue 450 °C RawBM = 25 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

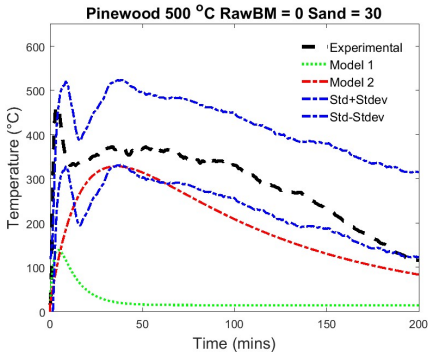

Pinewood 500 °C RawBM = 25 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

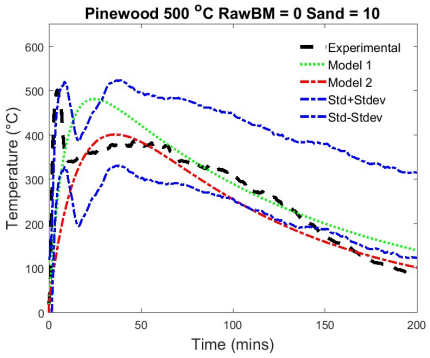

Pinewood 500 °C RawBM = 15 Sand = 15
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

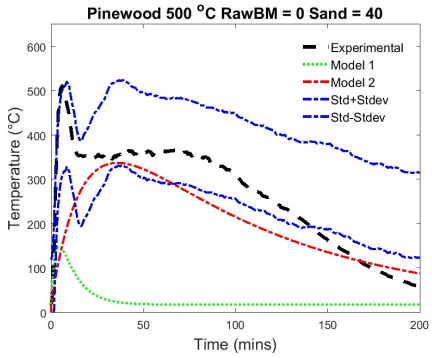

Pinewood 500 °C RawBM = 10 Sand = 10
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

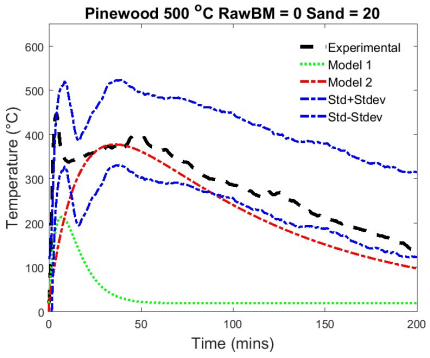

Pinewood 500 °C RawBM = 0 Sand = 57
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

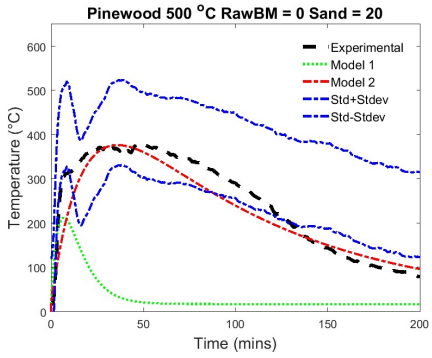

Pinewood 500 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

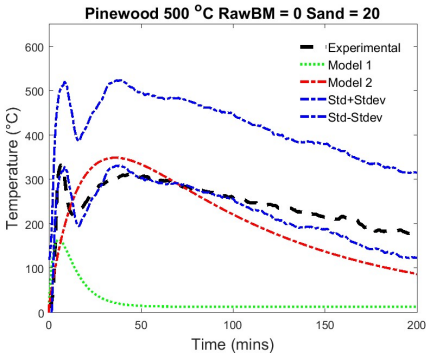

Pinewood 500 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

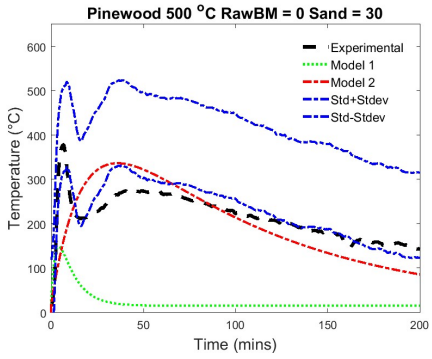

Pinewood 500 °C RawBM = 0 Sand = 10
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

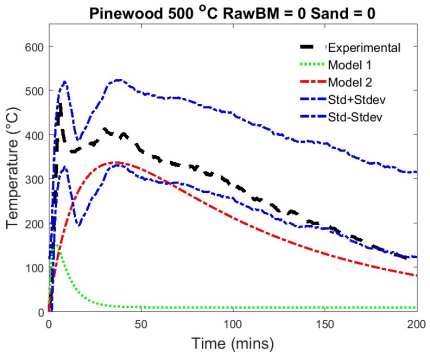

Pinewood 500 °C RawBM = 0 Sand = 40
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

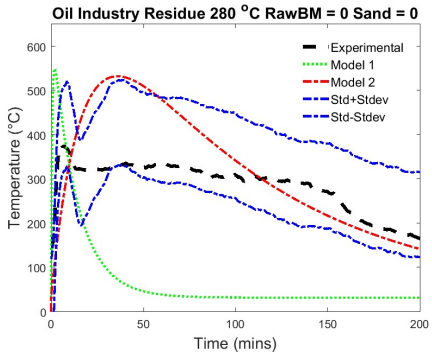

Pinewood 500 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

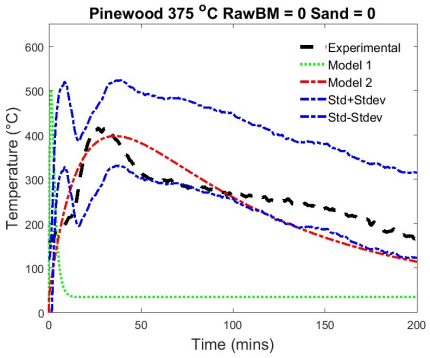

Pinewood 500 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

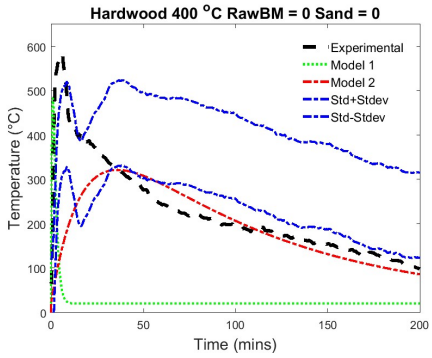

Pinewood 500 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

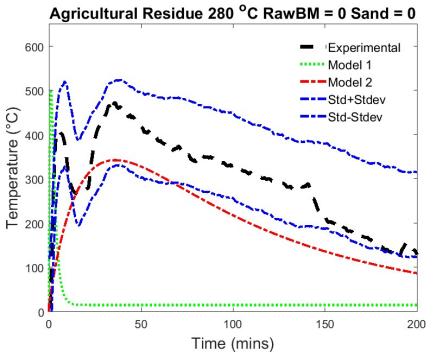

Pinewood 500 °C RawBM = 0 Sand = 30
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

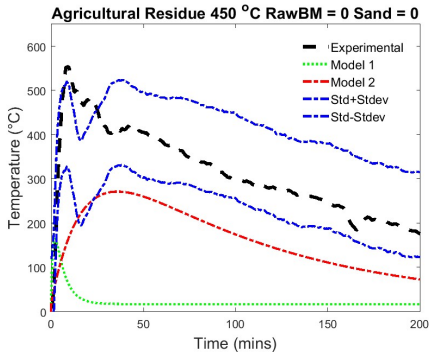

Pinewood 500 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

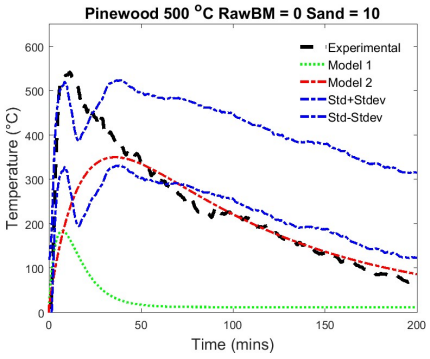

Oil Industry Residue 280 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

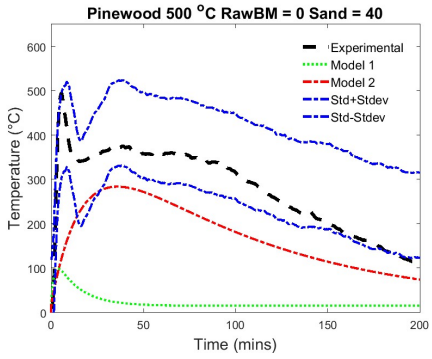

Pinewood 375 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

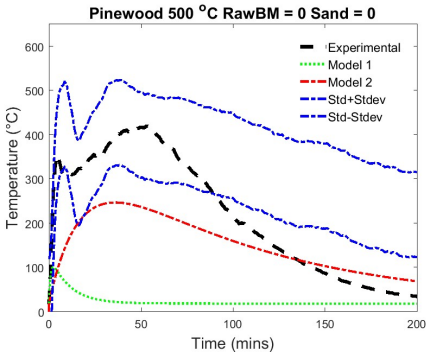

Hardwood 400 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

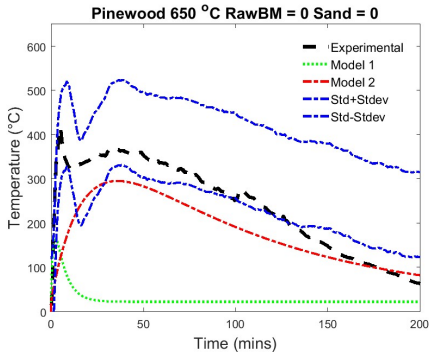

Agricultural Residue 280 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

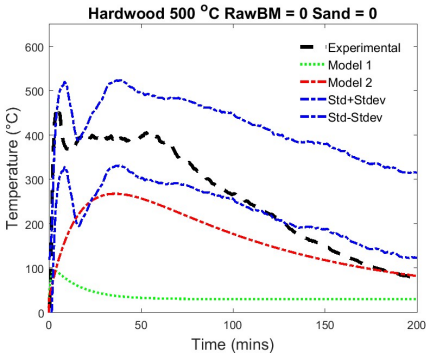

Agricultural Residue 450 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

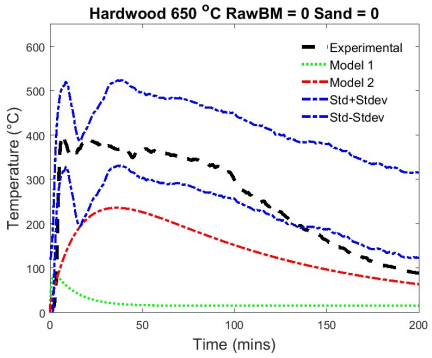

Pinewood 500 °C RawBM = 0 Sand = 10
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

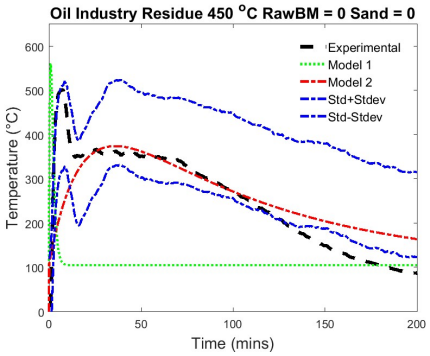

Pinewood 500 °C RawBM = 0 Sand = 40
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

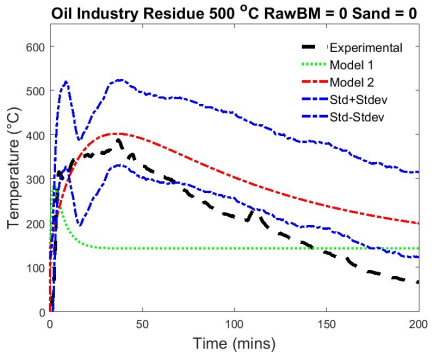

Pinewood 500 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

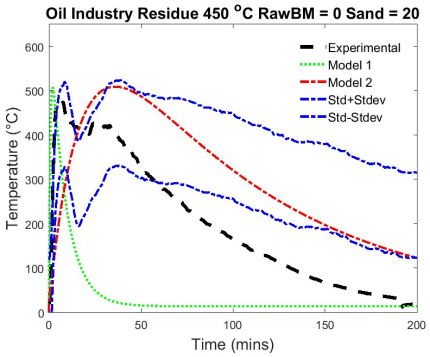

Pinewood 650 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)


Hardwood 500 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

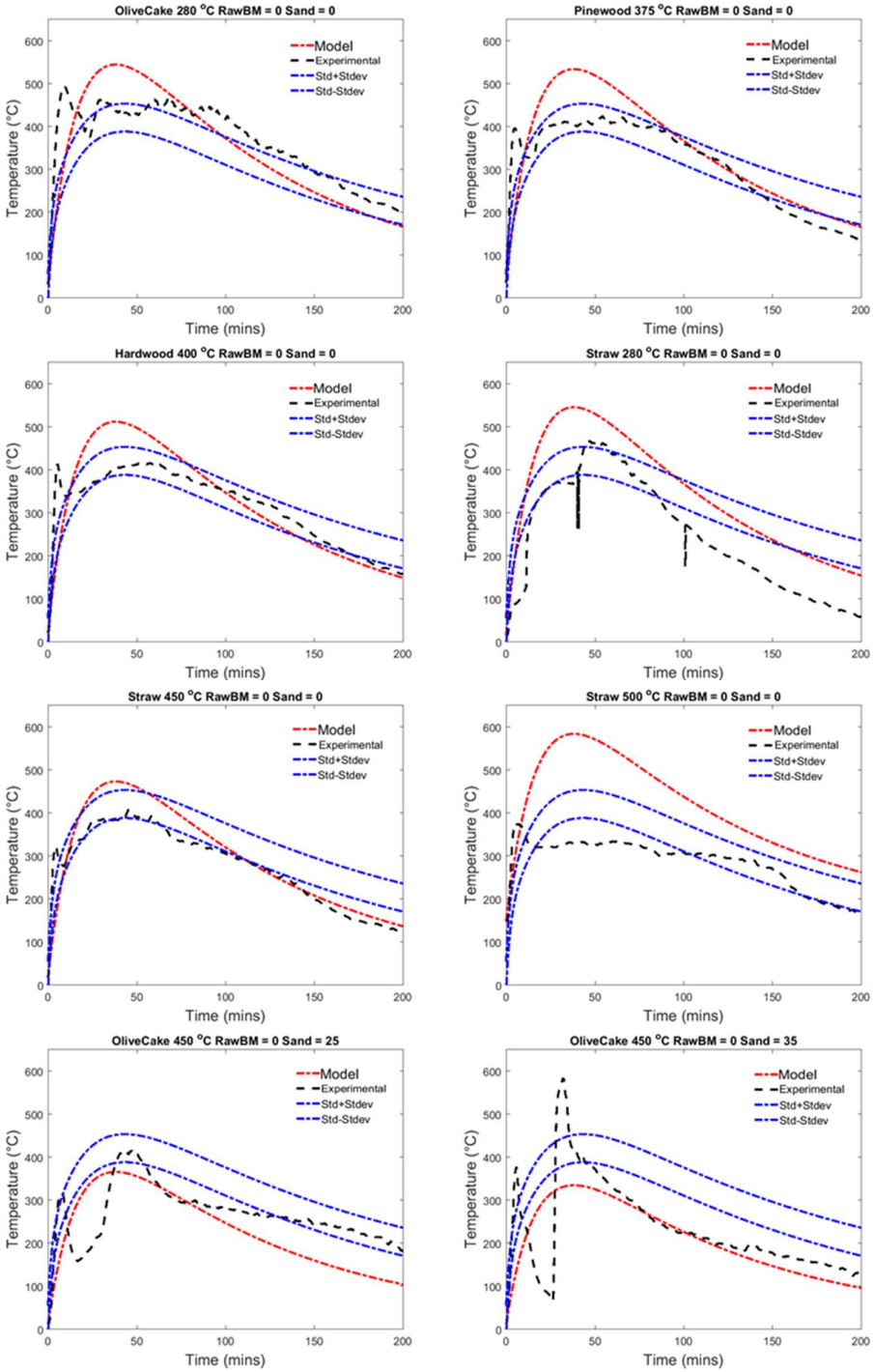

Hardwood 650 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

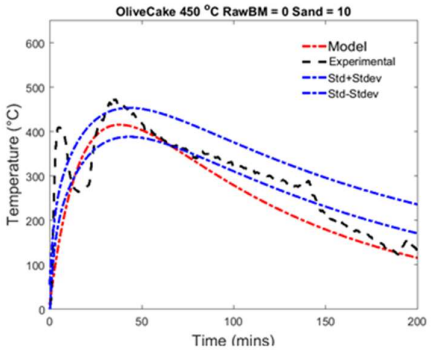

Oil Industry Residue 450 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

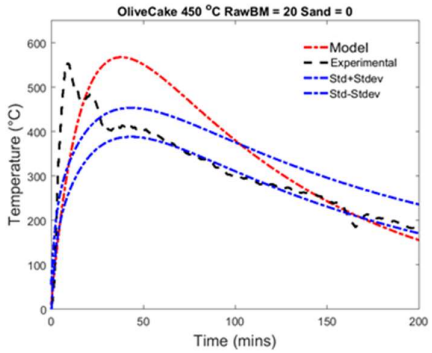

Oil Industry Residue 500 °C RawBM = 0 Sand = 0
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

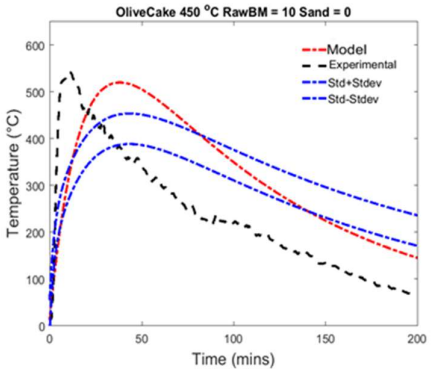

Oil Industry Residue 450 °C RawBM = 0 Sand = 20
Experimental
Model 1
Model 2
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

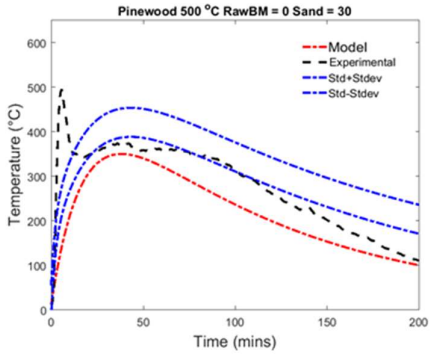
4. Pyrolysis and BBQ integrated model

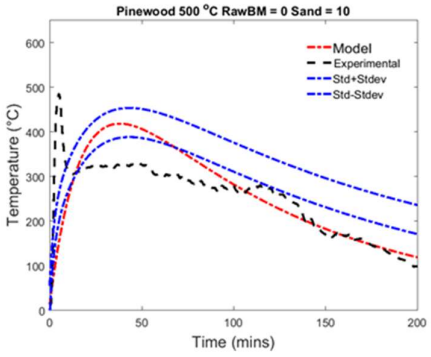


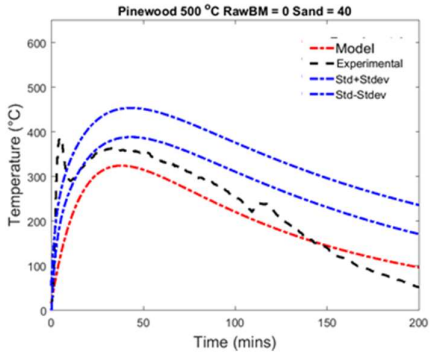

OliveCake 450 °C RawBM = 0 Sand = 10
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

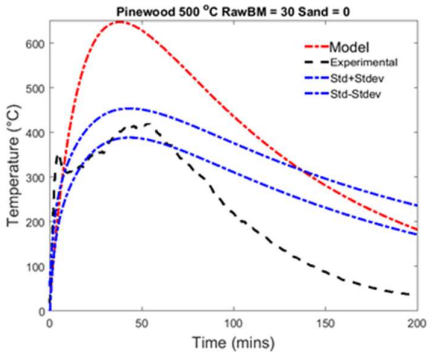

OliveCake 450 °C RawBM = 20 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

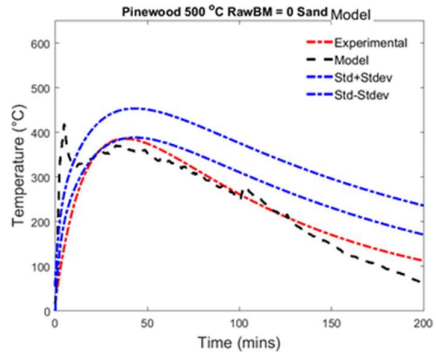

OliveCake 450 °C RawBM = 10 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

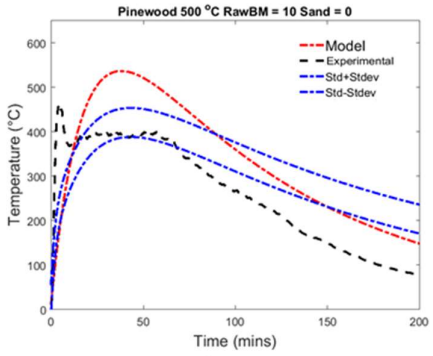

Pinewood 500 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

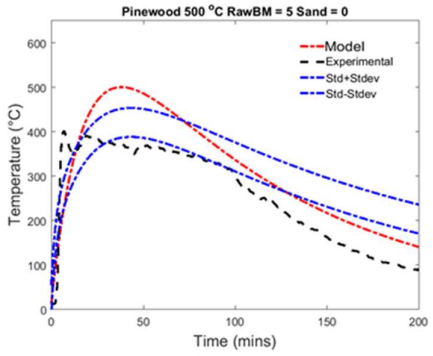

Pinewood 500 °C RawBM = 0 Sand = 10
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

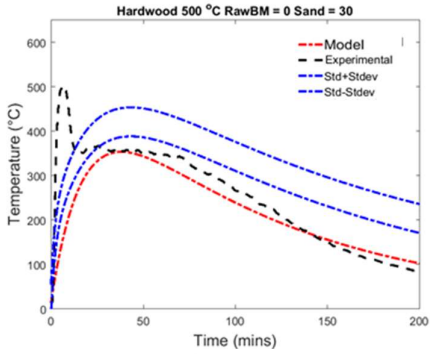

Pinewood 500 °C RawBM = 0 Sand = 40
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

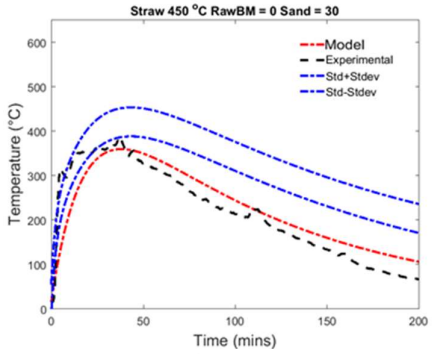

Pinewood 500 °C RawBM = 30 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

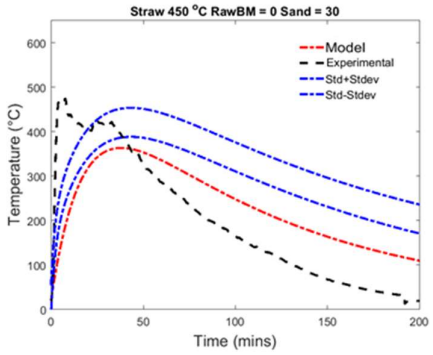

Pinewood 500 °C RawBM = 0 Sand
Model
Experimental
Model
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

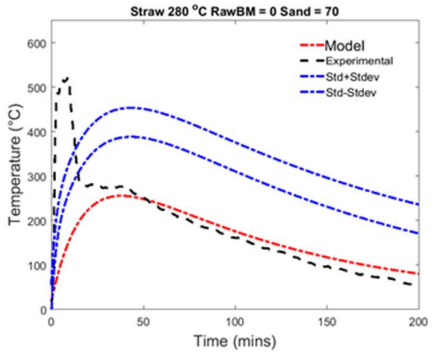

Pinewood 500 °C RawBM = 10 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

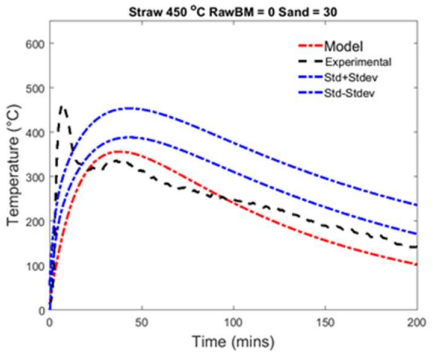

Pinewood 500 °C RawBM = 5 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

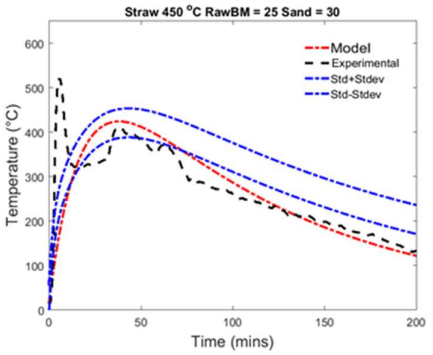

Hardwood 500 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

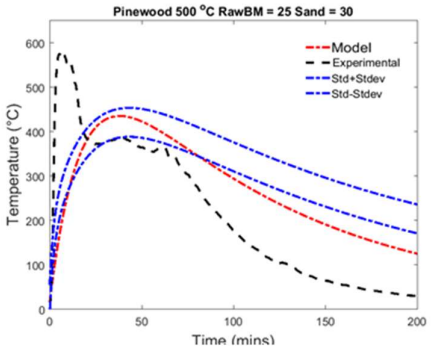

Straw 450 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

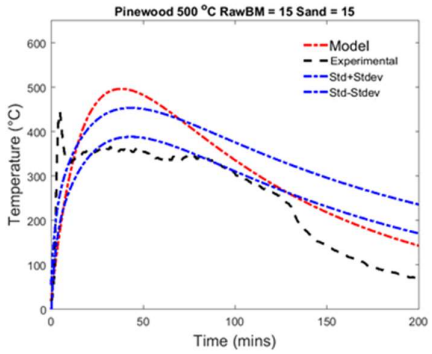

Straw 450 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

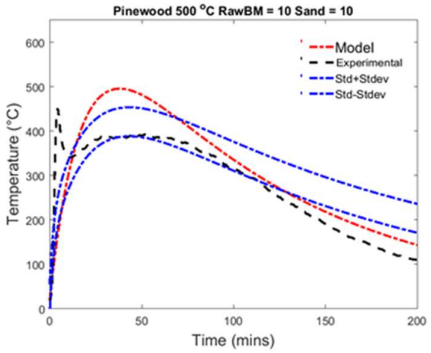

Straw 280 °C RawBM = 0 Sand = 70
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

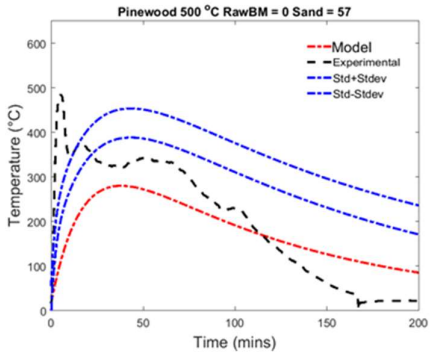

Straw 450 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

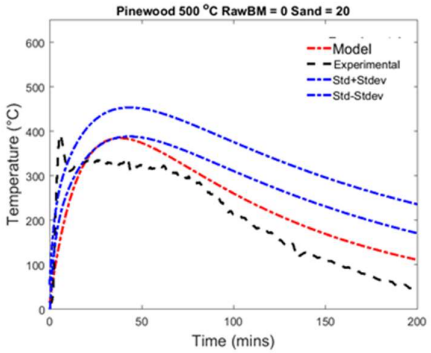

Straw 450 °C RawBM = 25 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

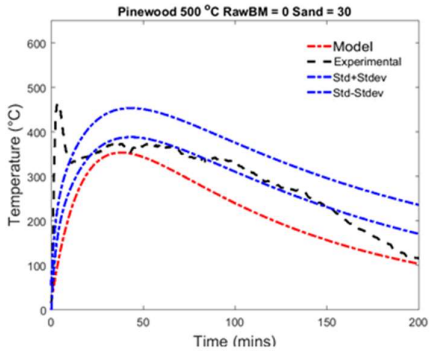

Pinewood 500 °C RawBM = 25 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

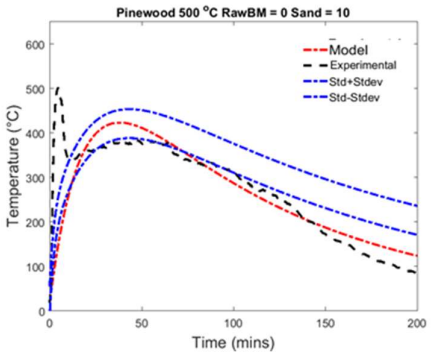

Pinewood 500 °C RawBM = 15 Sand = 15
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

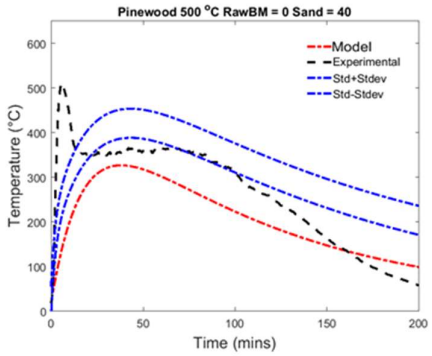

Pinewood 500 °C RawBM = 10 Sand = 10
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

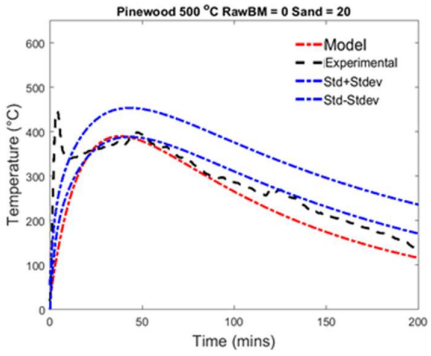

Pinewood 500 °C RawBM = 0 Sand = 57
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

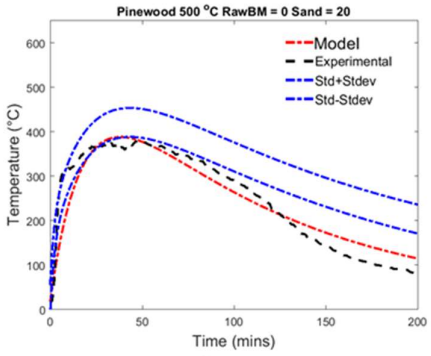

Pinewood 500 °C RawBM = 0 Sand = 20
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

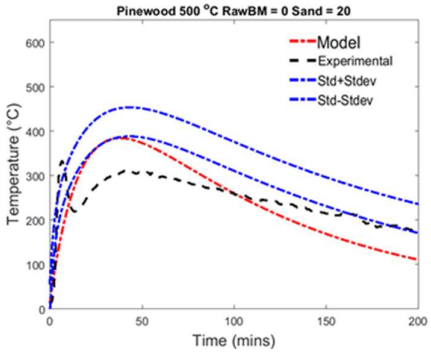

Pinewood 500 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

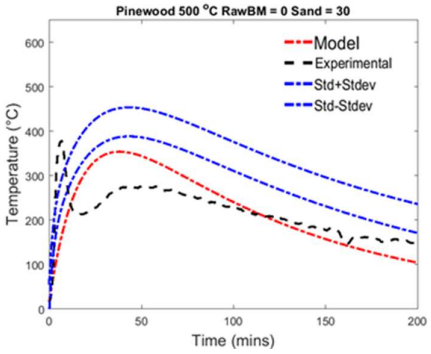

Pinewood 500 °C RawBM = 0 Sand = 10
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

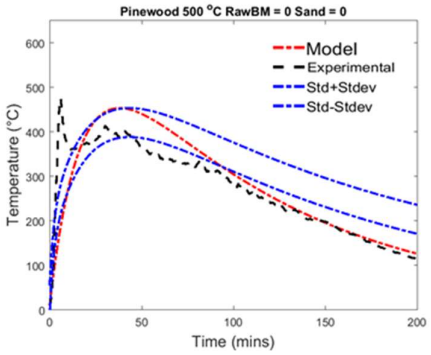

Pinewood 500 °C RawBM = 0 Sand = 40
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)


Pinewood 500 °C RawBM = 0 Sand = 20
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)


Pinewood 500 °C RawBM = 0 Sand = 20
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

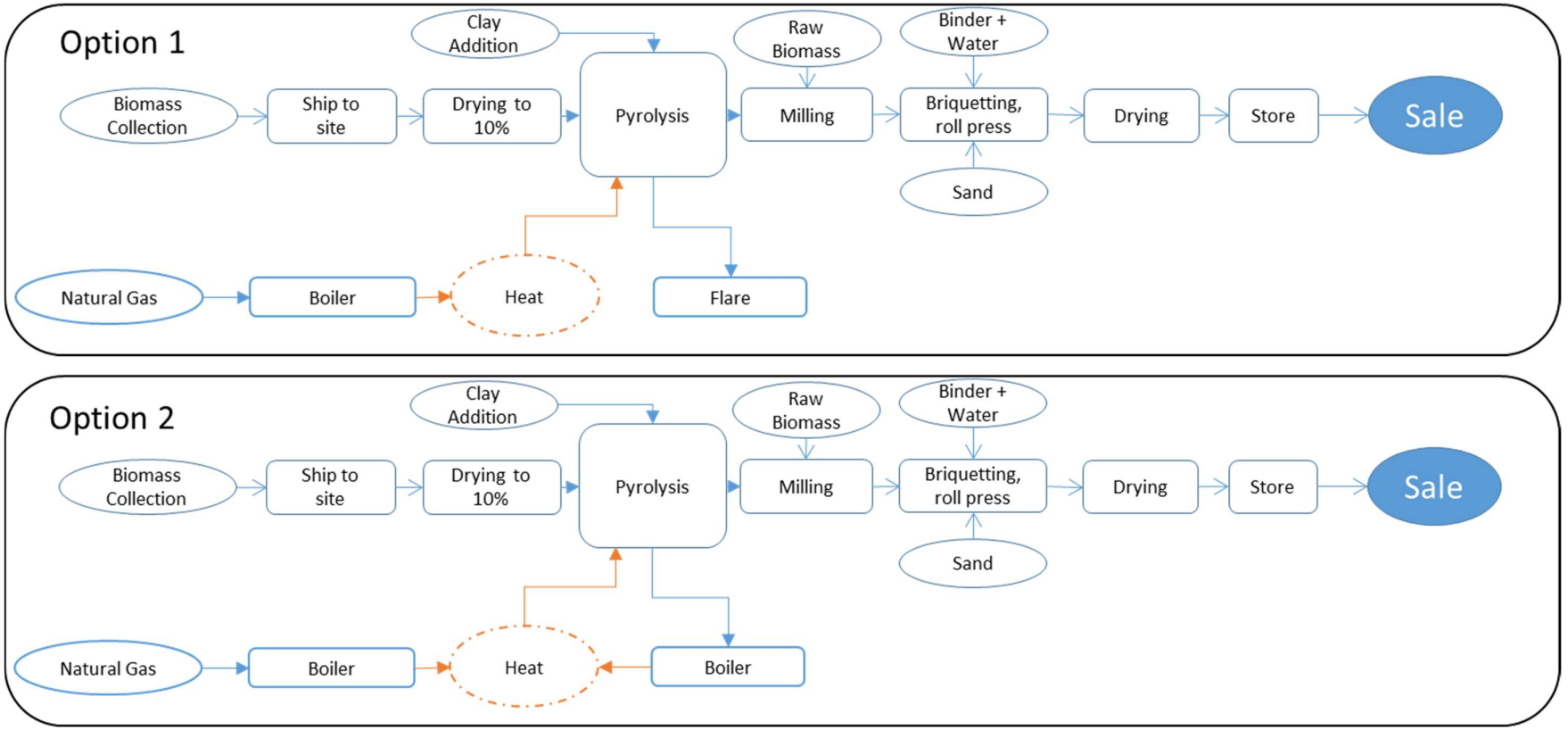

Pinewood 500 °C RawBM = 0 Sand = 20
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

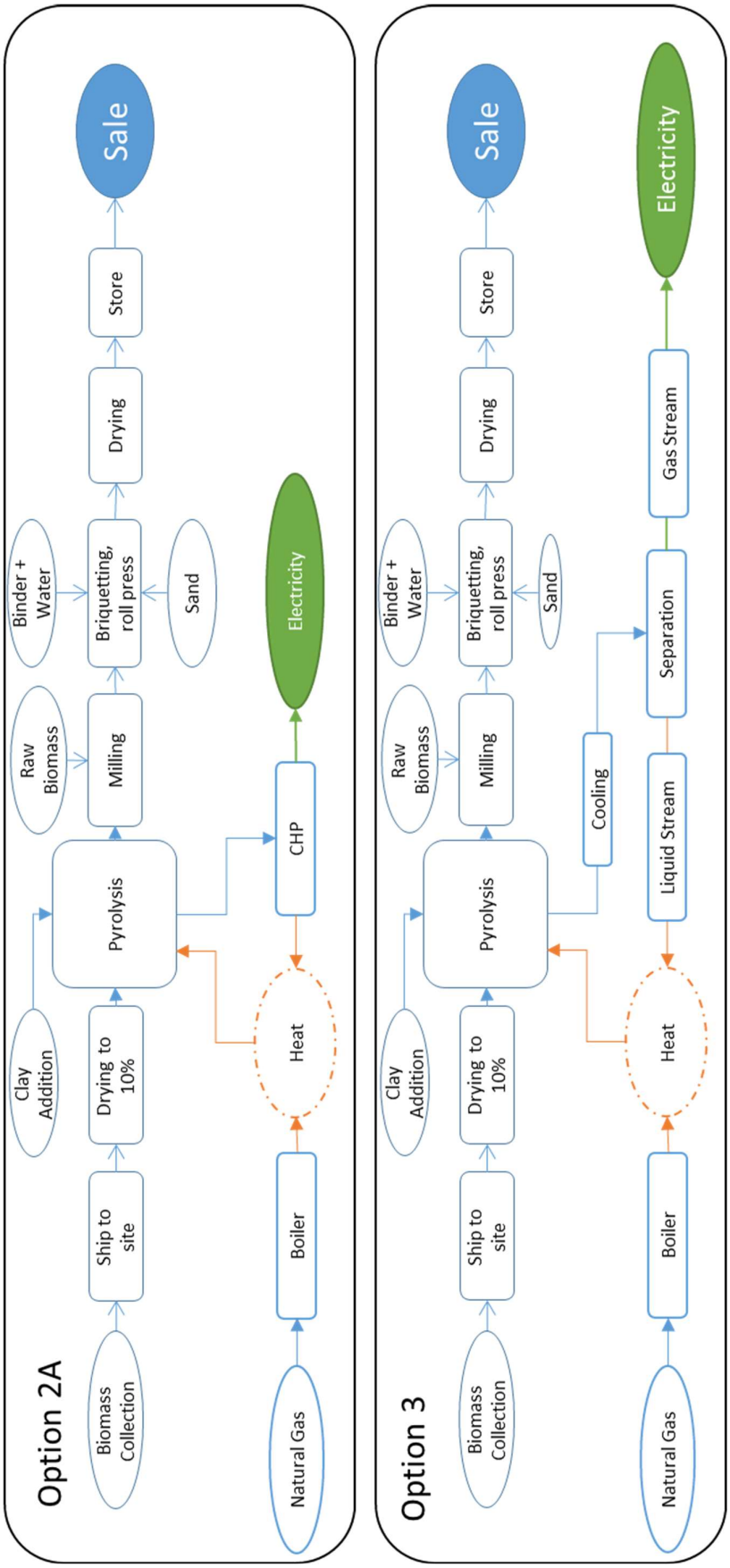

Pinewood 500 °C RawBM = 0 Sand = 30
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

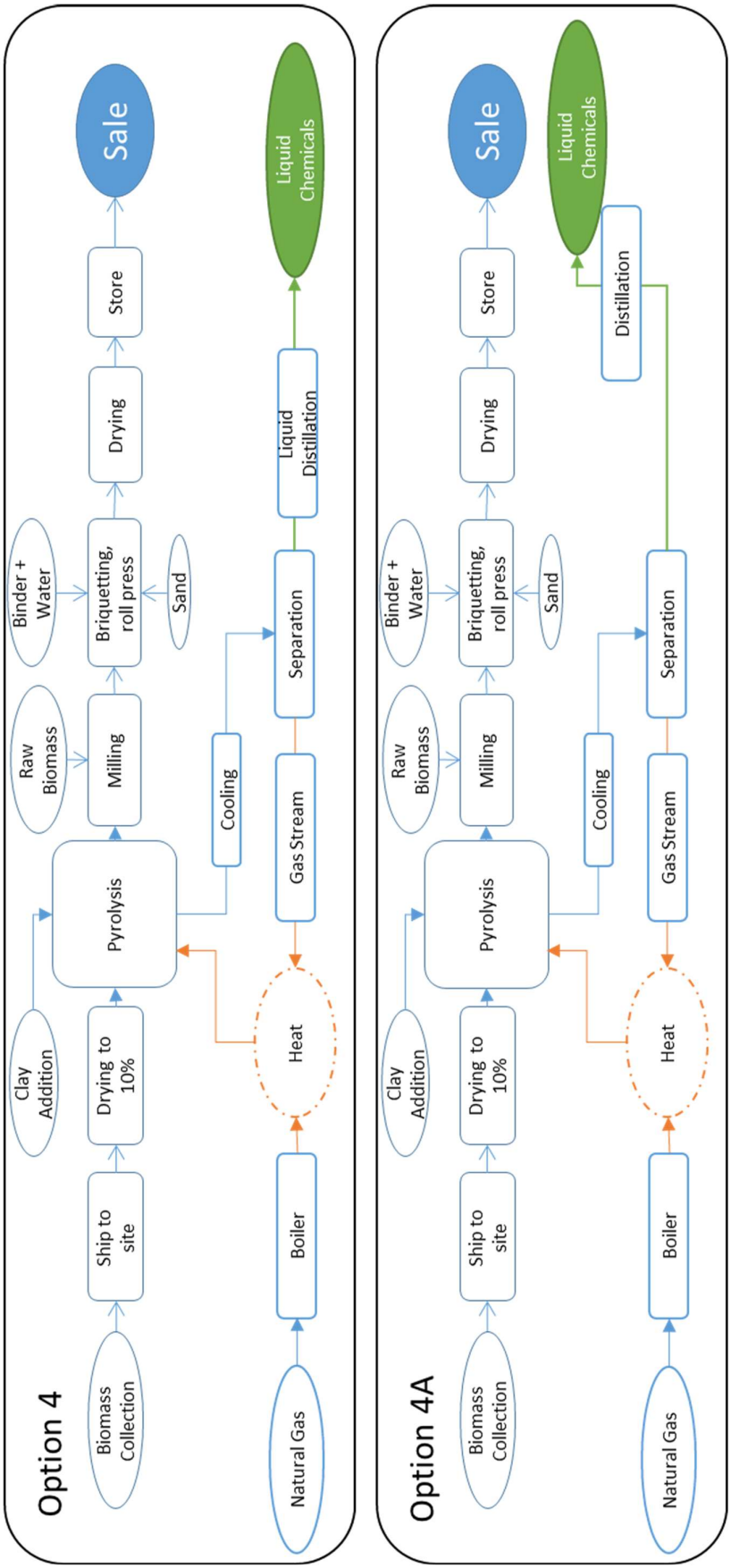

Pinewood 500 °C RawBM = 0 Sand = 0
Model
Experimental
Std+Stdev
Std-Stdev
Temperature (°C)
Time (mins)

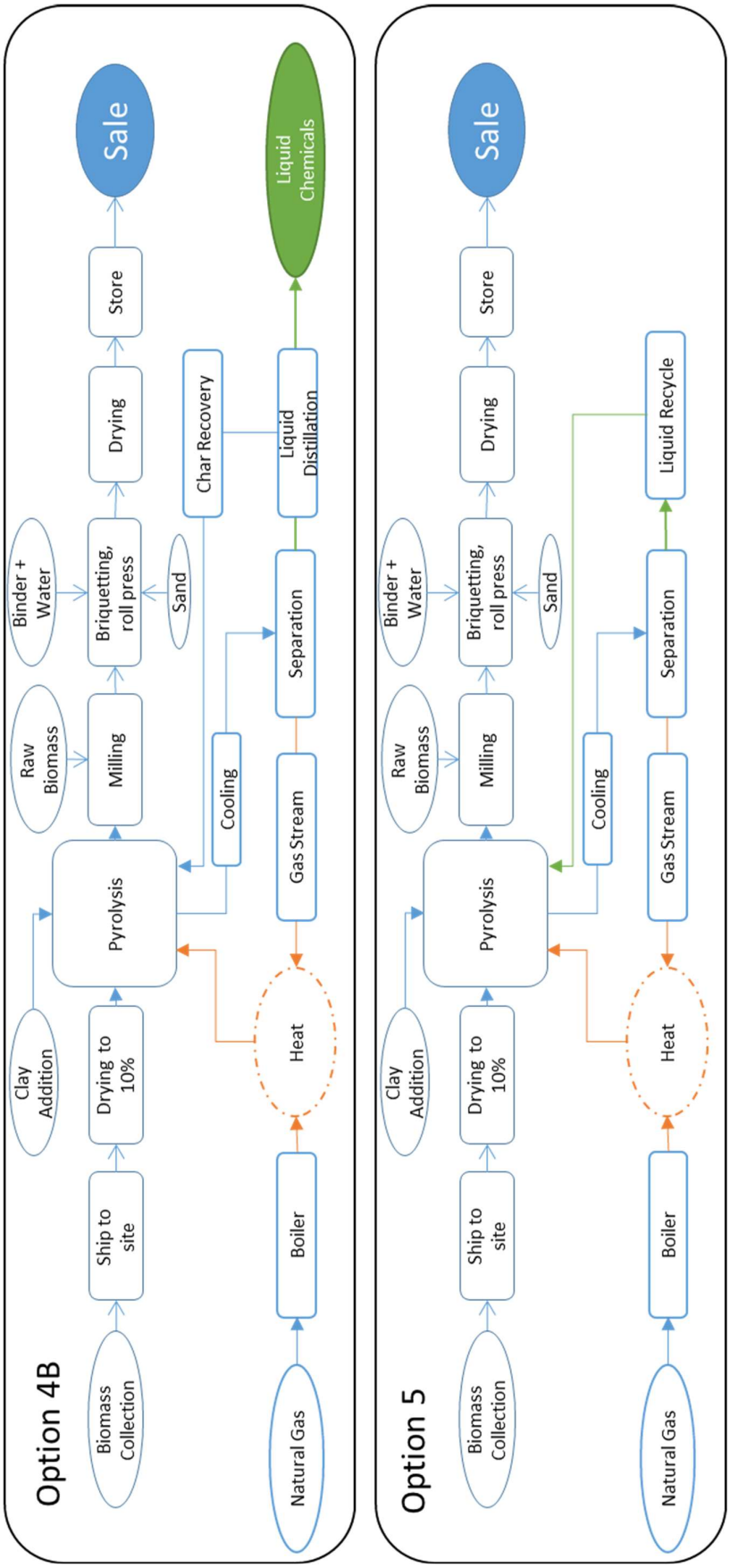
Appendix 4. Additional Information for Chapter 6 –Model Screening

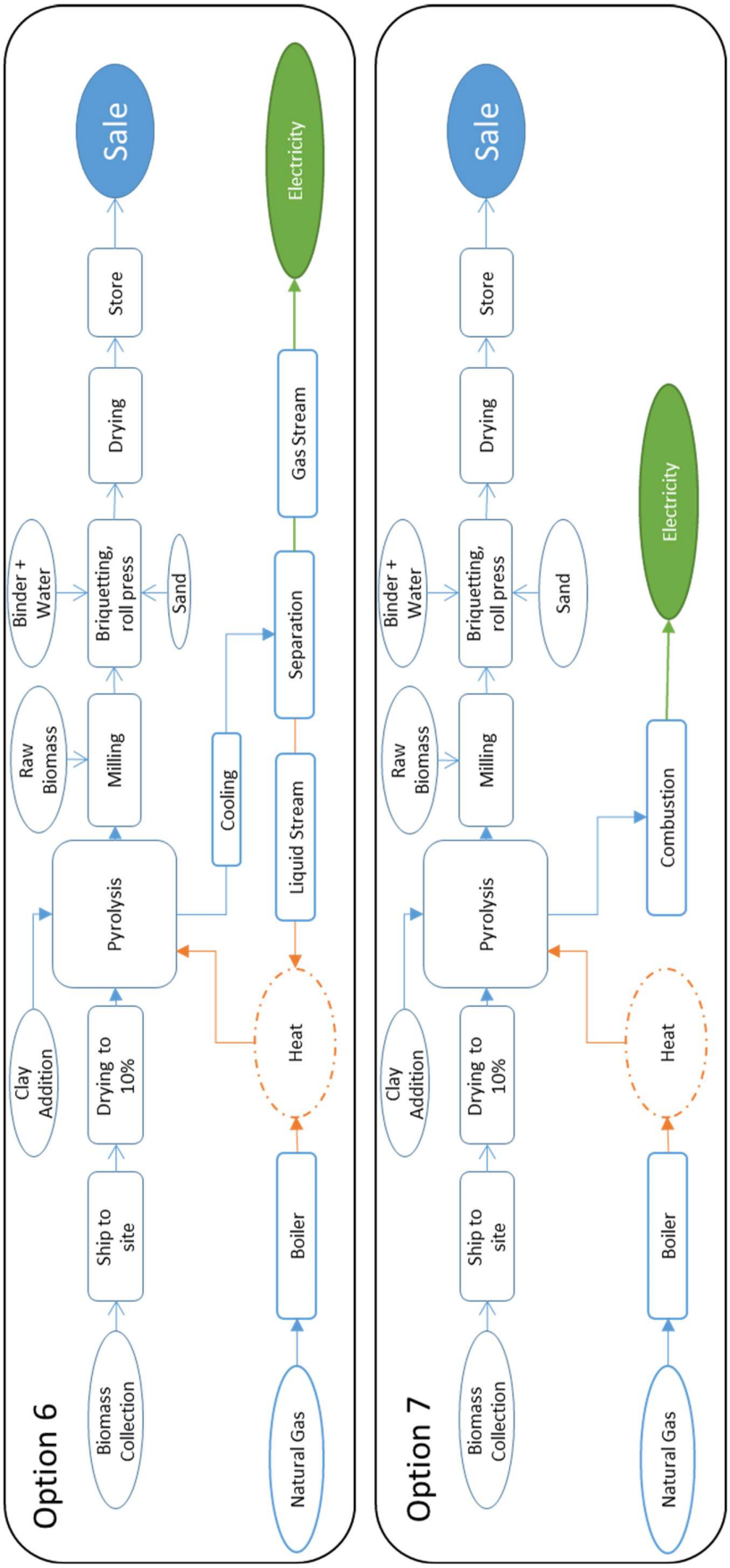
1. Model flow schemes

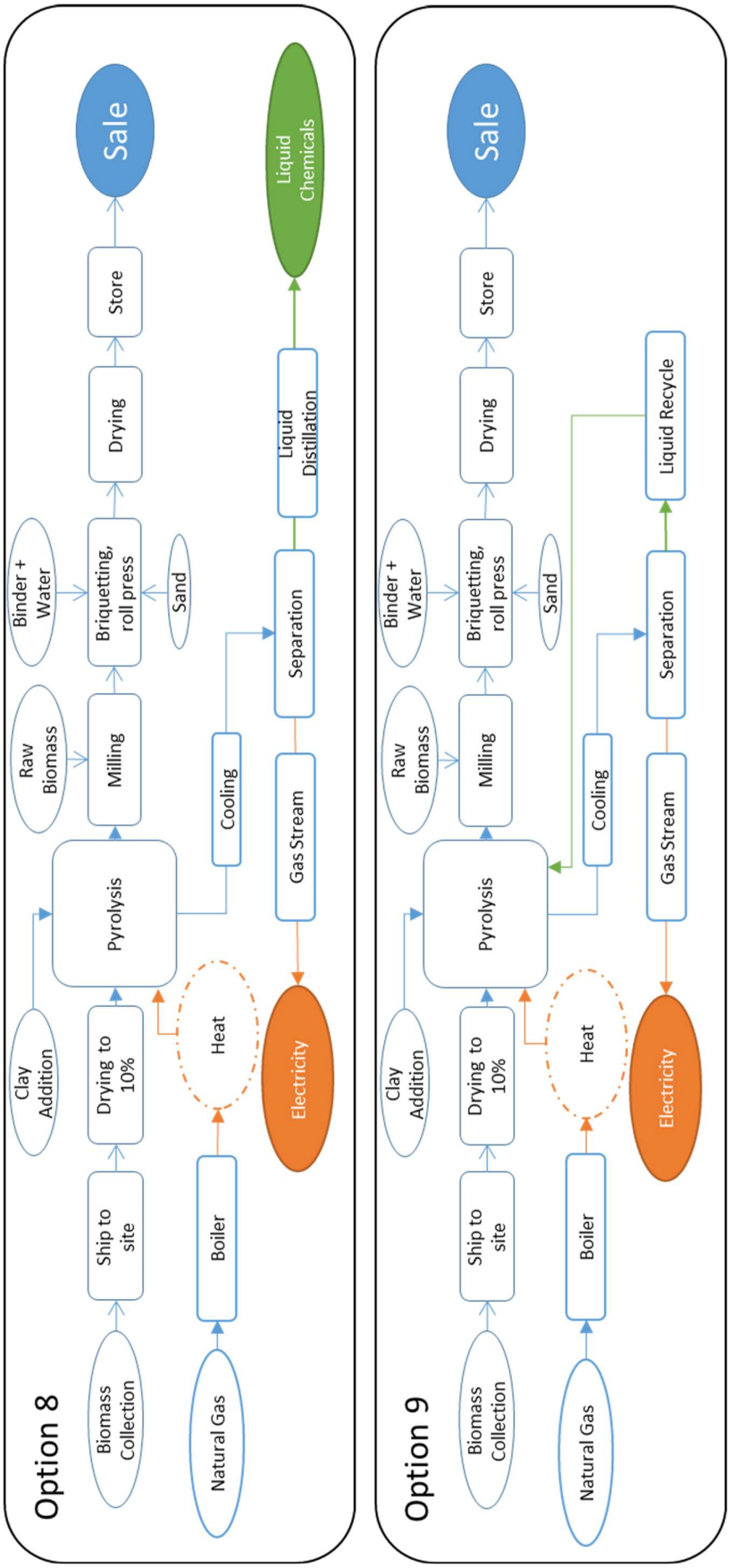


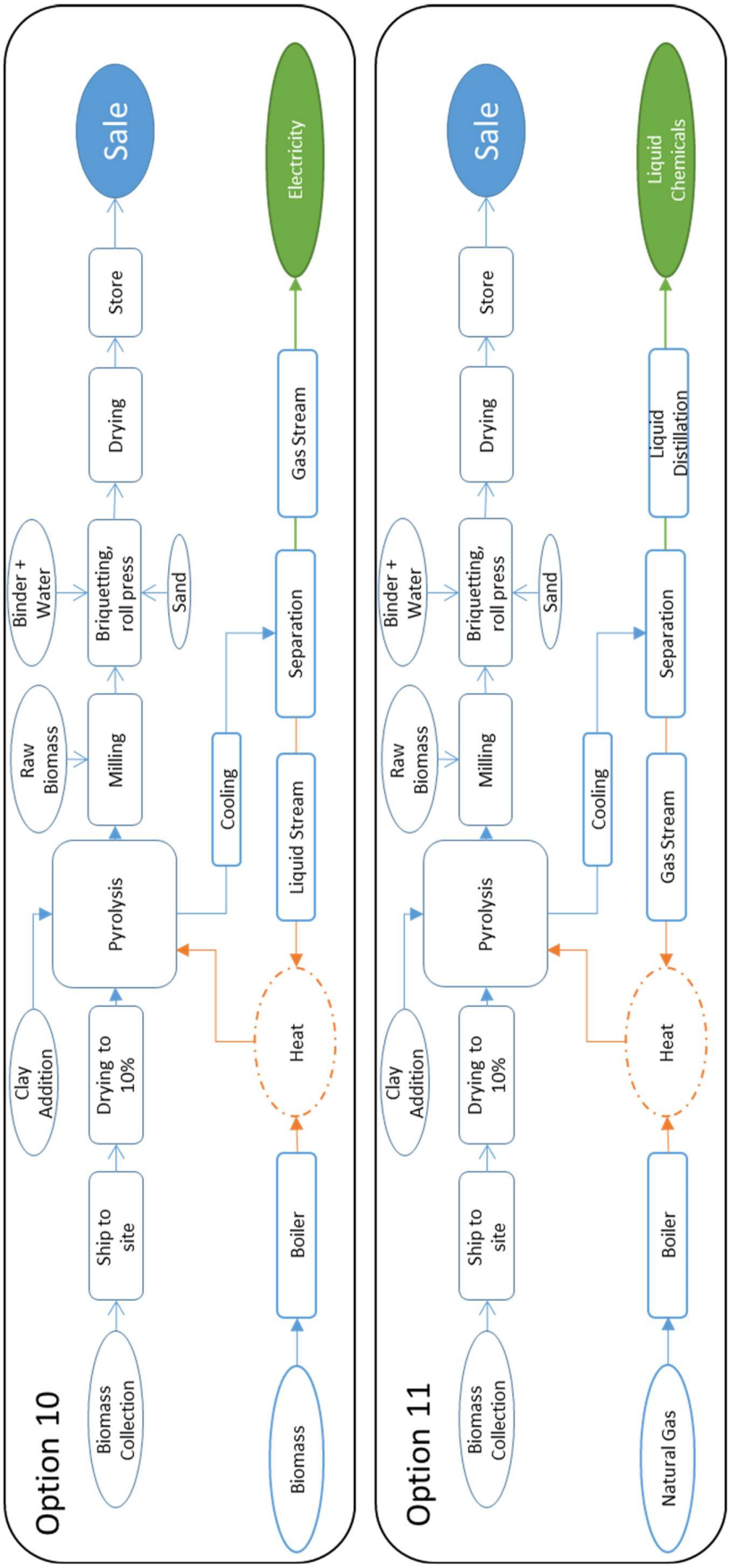

Option 2A
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Natural Gas
Boiler
Heat
Pyrolysis
CHP
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 3
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Natural Gas
Boiler
Heat
Pyrolysis
Cooling
Separation
Liquid Stream
Gas Stream
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale

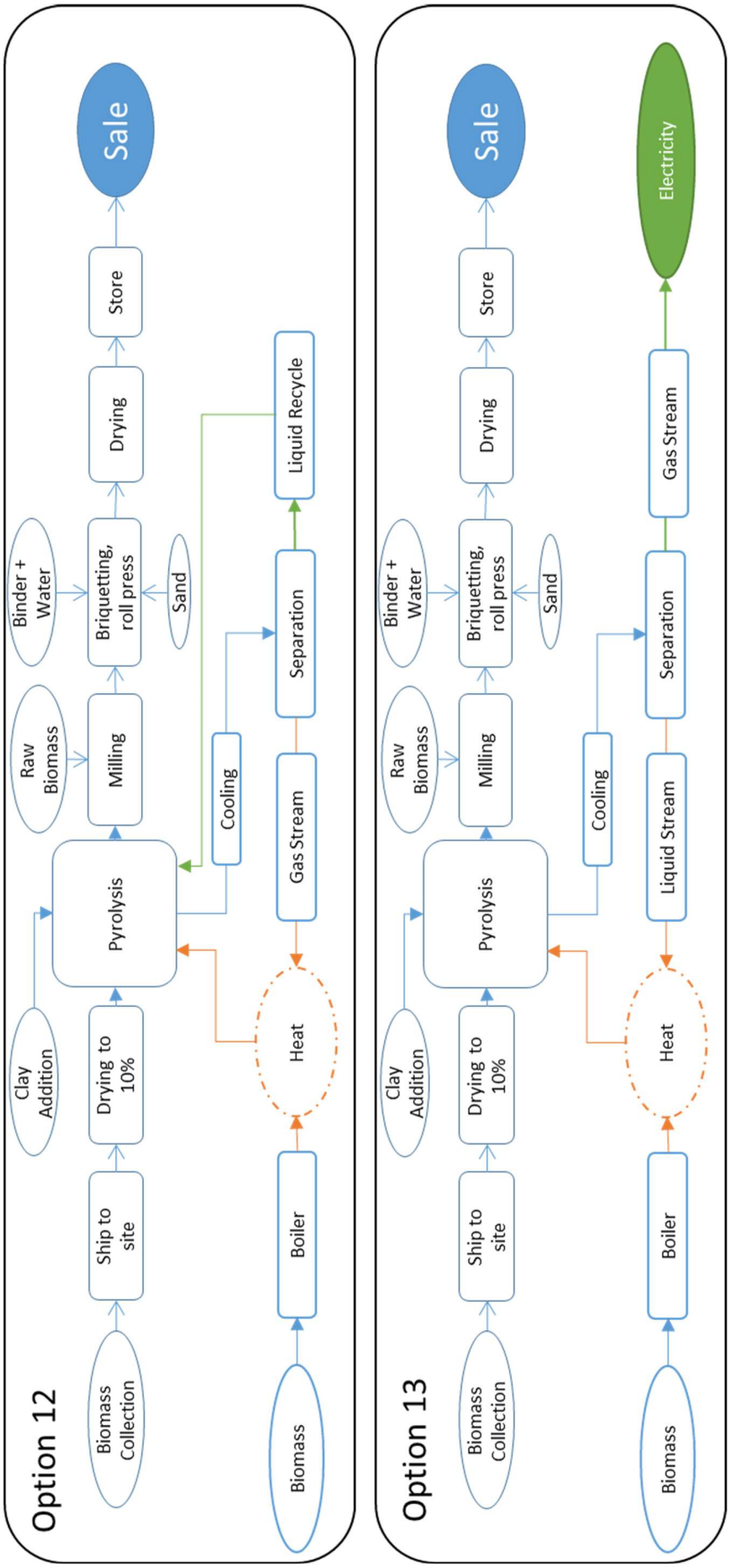

Option 4
Biomass Collection
Natural Gas
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Cooling
Gas Stream
Separation
Liquid Distillation
Liquid Chemicals
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 4A
Biomass Collection
Natural Gas
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Cooling
Gas Stream
Separation
Distillation
Liquid Chemicals
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale

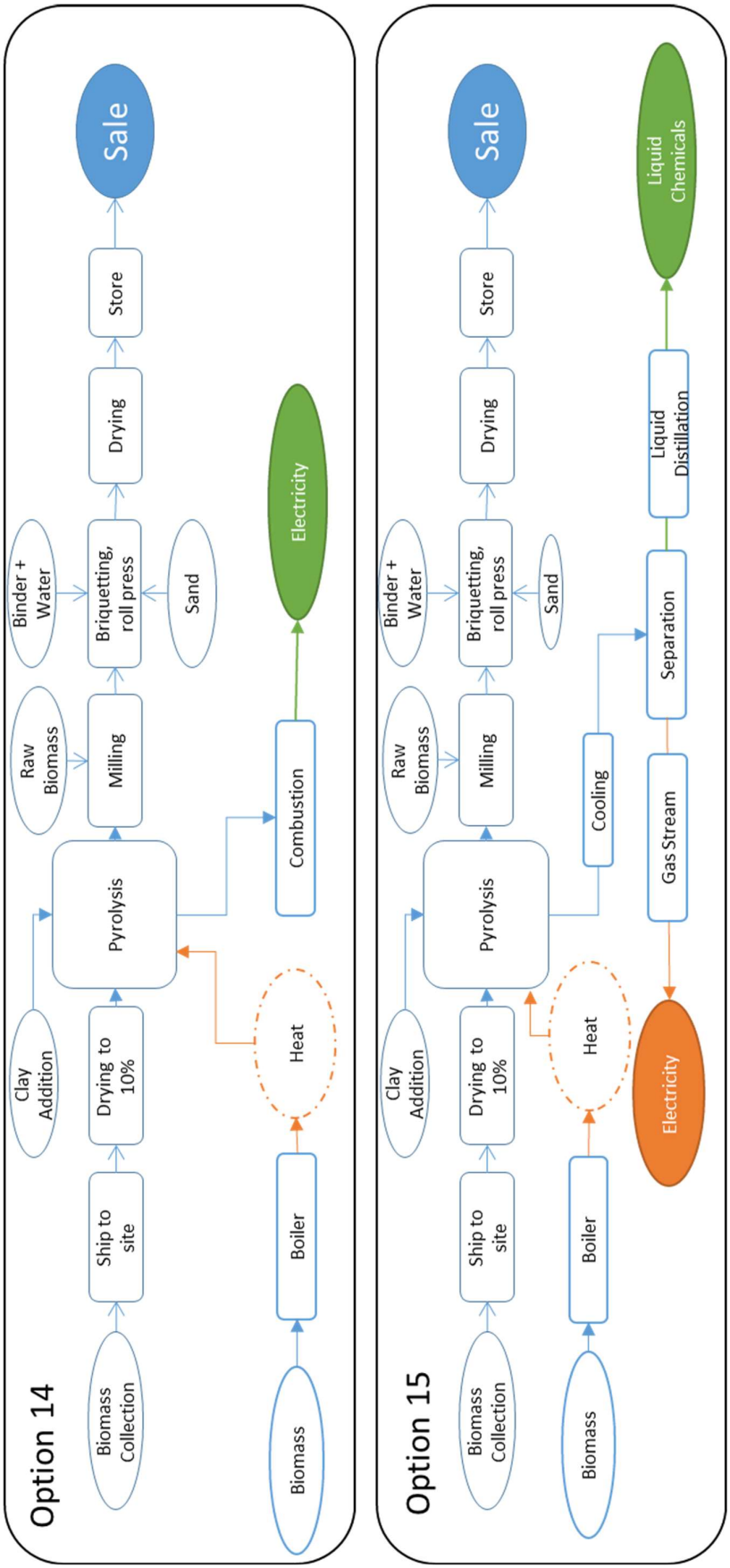

Option 4B
Biomass Collection
Natural Gas
Ship to site
Boiler
Drying to 10%
Heat
Clay Addition
Pyrolysis
Raw Biomass
Milling
Cooling
Gas Stream
Separation
Binder + Water
Briquetting, roll press
Sand
Char Recovery
Liquid Distillation
Liquid Chemicals
Drying
Store
Sale
Option 5
Biomass Collection
Natural Gas
Ship to site
Boiler
Drying to 10%
Heat
Clay Addition
Pyrolysis
Raw Biomass
Milling
Cooling
Gas Stream
Separation
Liquid Recycle
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale

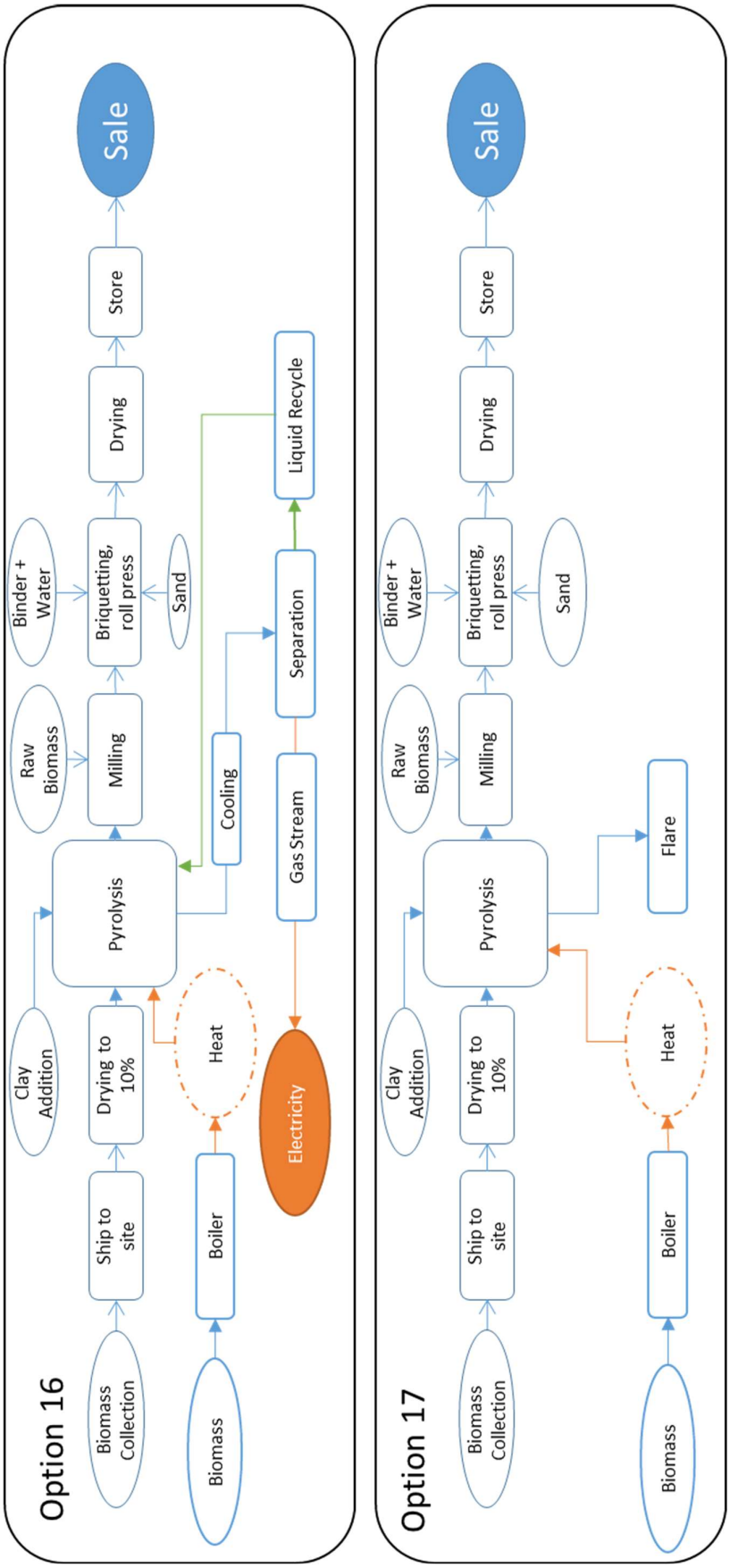

Option 6
Biomass Collection
Natural Gas
Ship to site
Boiler
Clay Addition
Drying to 10%
Heat
Pyrolysis
Cooling
Liquid Stream
Separation
Gas Stream
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 7
Biomass Collection
Natural Gas
Ship to site
Boiler
Clay Addition
Drying to 10%
Heat
Pyrolysis
Combustion
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale


Option 8
Biomass Collection
Natural Gas
Ship to site
Boiler
Drying to 10%
Heat
Clay Addition
Pyrolysis
Cooling
Gas Stream
Electricity
Separation
Liquid Distillation
Liquid Chemicals
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 9
Biomass Collection
Natural Gas
Ship to site
Boiler
Drying to 10%
Heat
Clay Addition
Pyrolysis
Cooling
Gas Stream
Electricity
Separation
Liquid Recycle
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale


Option 10
Biomass
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Cooling
Liquid Stream
Separation
Gas Stream
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 11
Natural Gas
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Cooling
Gas Stream
Separation
Liquid Distillation
Liquid Chemicals
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale


Option 12
Biomass
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Gas Stream
Separation
Liquid Recycle
Cooling
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 13
Biomass
Biomass Collection
Ship to site
Drying to 10%
Clay Addition
Boiler
Heat
Pyrolysis
Liquid Stream
Separation
Gas Stream
Cooling
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Electricity


Option 14
Biomass
Biomass Collection
Ship to site
Boiler
Clay Addition
Drying to 10%
Heat
Pyrolysis
Combustion
Electricity
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 15
Biomass
Biomass Collection
Ship to site
Boiler
Clay Addition
Drying to 10%
Heat
Pyrolysis
Cooling
Separation
Gas Stream
Electricity
Liquid Distillation
Liquid Chemicals
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale


Option 16
Biomass
Biomass Collection
Ship to site
Boiler
Heat
Clay Addition
Drying to 10%
Pyrolysis
Electricity
Gas Stream
Cooling
Separation
Liquid Recycle
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale
Option 17
Biomass
Biomass Collection
Ship to site
Boiler
Heat
Clay Addition
Drying to 10%
Pyrolysis
Flare
Raw Biomass
Milling
Binder + Water
Briquetting, roll press
Sand
Drying
Store
Sale

2. Core Process Model mass and energy balance equations

This section presents the mass and energy balance equations for each stage of the main pyrolysis process. Where required, discussion of calculations for determining sizing parameters for capital costing will be included.

The calculation procedure is as follows:

1) Inputs required by the model, as shown in Table A- 1

Table A- 1 Mass Balance inputs to model

Symbol	Description	Units
M_{briq}	Mass of briquettes produced per year	ton/year
t_{op}	Operating hours per year	h
$C_{briq_{sand}}$	Concentration of sand in briquettes	g/g
$C_{briq_{bm}}$	Concentration of raw biomass added in briquettes	g/g
$C_{briq_{clay}}$	Concentration of clay in briquettes	g/g
$C_{briq_{starch}}$	Concentration of starch in briquettes	g/g
T_{peak}	Temperature of pyrolysis	°C
BM_{type}	Type of biomass – defines proximate analysis	(-)
$C_{bm_{MC\ Raw}}$	Raw biomass moisture content	g/g
$C_{MC_{bm-Dry}}$	Dried biomass moisture content – assumed to be 10%	g/g
Fire Test	PASS	

2) Determine composition of briquette and amount of raw biomass required (Eq A- 1 to Eq A- 7)
3) Using the mass of product briquettes required, multiply this by the additive concentration to determine mass of additive required
4) Then find the mass of charcoal to be used in the briquettes
5) Using the raw and target biomass moisture content, and the expected yield based on the pyrolysis temperatures find the mass of biomass required for pyrolysis
6) Then find the total mass of biomass required by adding the additive biomass and pyrolysis biomass.

$$M_{adds_{sand}} = M_{briq_{kg}} C_{briq_{sand}} \qquad \textit{Eq A- 1}$$

$$M_{adds_{bm}} = M_{briq_{kg}} C_{briq_{bm}} \qquad \textit{Eq A- 2}$$

$$M_{adds_{clay}} = M_{briq_{kg}} C_{briq_{clay}} \quad \textit{Eq A- 3}$$

$$M_{char_{briq}} = M_{briq_{kg}} - M_{adds_{sand}} - M_{adds_{bm}} - M_{adds_{clay}} \quad \textit{Eq A- 4}$$

$$M_{BM_{py_dry}} = \frac{M_{char_{briq}}}{Y_{char}} \quad \textit{Eq A- 5}$$

$$M_{BM_{py}} = \frac{M_{BM_{py_dry}}\left(1 - C_{MC_{bm-RAW}}\right)}{1 - C_{MC_{bm-Dry}}} \quad \textit{Eq A- 6}$$

$$M_{BM_{total}} = M_{BM_{py}} + M_{adds_{bm}} \quad \textit{Eq A- 7}$$

Symbol	Description	Units
$M_{adds_{sand}}$	Mass of sand added to briquettes	kg/h
$M_{adds_{bm}}$	Mass of biomass added to briquettes	kg/h
$M_{adds_{clay}}$	Mass of clay added to briquettes	kg/h
$M_{char_{briq}}$	Mass of char to be produced for the briquettes	kg/h
Y_{char}	Yield of charcoal from dried biomass	
$M_{BM_{py_dry}}$	Mass of dry biomass needed for pyrolysis	kg/h
$M_{BM_{total}}$	Mass of total wet biomass required for pyrolysis	kg/h

7) Biomass then passes through a rotary drier which gets the biomass from raw to dried moisture content. The biomass to be added to the briquette raw is still added at this point so $M_{bm_{Total}}$ is used as the basis for this calculation. This is sized by heat transfer area.

- Calculate the mass balance around the drier: Eq A- 8and Eq A- 9.

$$M_{bm_{dry}} = \frac{M_{bm_{Total}} \cdot \left(1 - C_{bm_{MC\ Raw}}\right)}{\left(1 - C_{bm_{MC\ Dry}}\right)} \quad \textit{Eq A- 8}$$

$$M_{H_2O\ loss_{bm}} = M_{bm_{Total}} - M_{bm_{dry}} \quad \textit{Eq A- 9}$$

Symbol	Description	Units
$M_{bm_{dry}}$	Mass of dried biomass – pyrolysis + raw addition to briquette	kg/h
$M_{H_2O\ loss_{bm}}$	Mass of water loss from biomass drying stage	kg/h

- Determine the energy demand and the heat transfer area required

This has been done based on the following assumptions using Eq A- 10 and Eq A- 11.

- Dryer residence time: $t_{dry} = 1\ hour$

- Temperature of the dryer: $\boldsymbol{T_{dry} = 110°C}$
- Heat transfer coefficient of the dryer: $\boldsymbol{U_{dry} = 1\frac{kW}{m^2h}}$
- Co-current conditions exist in the dryer

$$\boldsymbol{Q_{drier_{bm}} = \left(T_{dryer} - T_{ambient}\right)\left(C_{p_{water}} M_{H_2O\ loss_{bm}} + C_{p_{biomass}} M_{bm_{dry}}\right) + h_{l_{steam}} * M_{steam_{drier}}} \quad \textit{Eq A- 10}$$

$$\boldsymbol{A = \frac{\left(\frac{Q_{drier}}{\frac{3600kW}{kJ}}\right)}{U_{dryer}\left(T_{dryer} - T_{ambient}\right)}} \quad \textit{Eq A- 11}$$

Symbol	Description	Units
$\boldsymbol{Q_{drier_{bm}}}$	Heat required by biomass dryer step	kJ/h
$\boldsymbol{A}$	Area required of rotary drier	m2

8) Calculate the mass and energy balance around the pyrolysis unit. If clay is used, this is added at this stage.

- Determine the pyrolysis yields, as in Eq A- 12 to Eq A- 15.
  - Charcoal mass produced has already been calculated based on the modelled project requirements, so will not be presented here. One assumption has been made to complete the mass balance:
  - There is a 5% loss of charcoal yield as determined by the pilot experimental work (see section 3.3.3)

$$\boldsymbol{M_{oil_{py}} = Y_{oil} M_{BM_{py_dry}}} \quad \textit{Eq A- 12}$$

$$\boldsymbol{M_{water_{py}} = Y_{water} M_{BM_{py_dry}}} \quad \textit{Eq A- 13}$$

$$\boldsymbol{M_{gas_{py}} = Y_{gas} M_{BM_{py_dry}}} \quad \textit{Eq A- 14}$$

$$\boldsymbol{M_{loss} = M_{BM_{py_dry}} - M_{oil_{py}} - M_{water_{py}} - M_{gas_{py}} - M_{char_{briq}}} \quad \textit{Eq A- 15}$$

Symbol	Description	Units
$\boldsymbol{M_{oil_{py}}}$	Mass of oil produced by pyrolysis	kg/h
$\boldsymbol{M_{water_{py}}}$	Mass of water produced by pyrolysis – includes initial moisture	kg/h
$\boldsymbol{M_{gas_{py}}}$	Mass of gas produced by pyrolysis	kg/h

M_{loss}	Mass of loss due to large scale conditions	kg/h

- Determine the energy required for pyrolysis, Eq A- 16.

Two assumptions have been included in this calculation:

- Pyrolysis reactions all occur at: $T_{py-rx} = 260\ °C$. Antal *et al.* (2003) have suggested this is the onset temperature of pyrolysis and having reactions occur at once simplifies this stage of calculation
  - To account for this, a relatively high heat of reaction for pyrolysis has been used $h_{py-rx} = 280\ \frac{kJ}{kg}$ (Antal *et al.*, 2003; Rath *et al.*, 2003)
- When clay is added to the system it can be expected that these reactions will be endothermic. Using this high value for the heat of reaction for the base reaction means that it can be assumed that energy for the cracking reaction is negligible.

$$\begin{aligned} Q_{pyrolysis} = {} & (T_{py-rx} \\ & - T_{ambient})\left(C_{p_{bm}} M_{BM_{py_dry}} \right. \\ & \left. + C_{p_{clay}} M_{add_{clay}}\right) \\ + \Big(& (100 - T_{ambient}) C_{p_{water}} + h_{l_{steam}} \\ & + (T_{peak} - 100) C_{p_{steam}}\Big)(M_{water_{dry\ bm}} \\ & + M_{water_{clay}}) \\ & + h_{py-rx} M_{BM_{py_dry}} \\ + (T_{peak} - T_{py-rx}) & (C_{p_{char}} * M_{briq_{charcoal}} + C_{p_{clay}} M_{clay_{raw}} \\ & + C_{p_{gas}} M_{py_{gas}} + C_{p_{oil}} M_{py_{oil}} \\ & + C_{p_{steam}} M_{water_{py}}) \end{aligned} \qquad \textit{Eq A- 16}$$

Symbol	Description	Units
$Q_{pyrolysis}$	Heat flow required for pyrolysis	kJ/h
C_{p_x}	Heat capacity of substance x – see table below	kJ/kg/K
$h_{l_{steam}}$	Latent heat of steam	kJ/kg
$T_{ambient}$	Ambient temperature – assumed to be 25 °C	°C

Symbol	Description	kJ/kg	References
$H_{nat\ gas}$	heat of combustion of Nat Gas	50000	Steam Tables
H_{oil}	Heat of Combustion of Oil	15000	Bridgwater (2003)

H_{gas}	Heat of Combustion of Gas	37500	Bridgwater (2003)
$C_{p_{water}}$	Specific Heat of Water	4.18	Steam Tables
$C_{p_{oil}}$	Specific Heat of Biooil	4.18	Assumed (water)
$C_{p_{gas}}$	Heat capacity of gas	3	Steam Tables
$C_{p_{sand}}$	Specific heat capacity of sand	1	
$C_{p_{char}}$	Specific heat capacity of char	0.6667	Steam Tables
$C_{p_{bm}}$	Specific heat capacity of biomass	1.76	Antal (2003)
$C_{p_{steam}}$	Specific heat capacity of steam	1.992	Steam Tables
$C_{p_{clay}}$	Specific heat capacity of clay	1	
$h_{l_{oil}}$	Latent heat of Bio-oil	406	Assumed oil – Steam tables
$h_{l_{steam}}$	Latent heat of steam	2206	Steam Tables
h_{py-rx}	heat of pyrolysis	280	Rath (2003) Antal (2003)

9) Determine the mass and energy balance around the milling stage, Eq A-18.

- If biomass or sand are added to the process, they are accounted for now. In reality there may be a mixing stage where the sand may be added in but biomass would be required to go through this mill to ensure it is of the right size range for briquetting. There is no loss assumed on the milling step, however, so the mass balance is straight forward as no other reactions take place.
- The energy demand for milling can be found by Eq A- 17, and requires the assumption that milling energy is $\boldsymbol{E_{gr} = 46\,\frac{kJ}{kg}}$ (Bitra *et al.*, 2009). This over estimates the milling energy as this is for raw biomass in a hammer mill, and not charcoal which is much more brittle.

$$\boldsymbol{Q_{mill} = E_{gr} * \left(M_{char} + M_{adds_{bm}}\right)} \qquad \textbf{\textit{Eq A- 17}}$$

Symbol	Description	Units
Q_{mill}	Energy flow to mill	kJ/h

10) Determine the mass and energy balance around the briquetting stage, Eq A- 18- Eq A- 20.
    - This includes the drying stage, where there is a mass loss.
    - Determine the energy demand for roll pressing

The assumption has been made that:

Briquetting Energy: $\boldsymbol{E_{briquette} = 432\,\frac{kJ}{kg}}$ (FAO, 1990)

$$\boldsymbol{Q_{briq_{electricity}} = E_{briq} * \left(M_{adds_{clay}} + M_{add_{sand}} + M_{add_{bm}} + M_{char_{briq}}\right)} \quad \textit{Eq A- 18}$$

Symbol	Description	Units
$\boldsymbol{Q_{briq_{electricity}}}$	Energy required for briquetting process	kJ/h

11) Determine the mass balance for the final briquette drying step

It is expected that following this stage the briquettes will come out dry, and the mass of final briquettes and the composition of this is already known via assumption (see Table A- 1, Table 6-1). It is also known as is the mass of water added, $\boldsymbol{C_{Binder_{water}}}$,will be 10% of the final mass of briquettes.

$$\boldsymbol{M_{H_2O\ loss_{briq}} = M_{briq_{kg}}\left(C_{Binder_{water}}\right)} \quad \textit{Eq A- 19}$$

Symbol	Description	Units
$\boldsymbol{M_{H_2O\ loss_{briq}}}$	Mass of water lost over briquetting	kg/h

- Determine the heat demand for briquette drying

The same assumptions apply as presented for the biomass drying step presented in step 7.

$$\boldsymbol{Q_{briq_{dry}} = \left(T_{dryer} - T_{ambient}\right)\left(C_{p_{water}} M_{H_2O\ loss_{briq}} + M_{add_{bm}} C_{p_{biomass}} + M_{adds_{clay}} C_{p_{Clay}} + M_{char_{briq}} C_{p_{charcoal}} + M_{add_{sand}} C_{p_{sand}}\right) + h_{l_{steam}} * M_{H_2O\ loss_{briq}}} \quad \textit{Eq A- 20}$$

Symbol	Description	Units
$\boldsymbol{Q_{drier_{bm}}}$	Energy flow to drier	kJ/h

12) Sum the energy demand

- Calculate the electricity demand, Eq A- 21.

It has been assumed that the briquetting and milling energy are electric powered, so these are included here.

$$\boldsymbol{Q_{electricity} = Q_{Mill} + Q_{briq_{electricity}}} \quad \textit{Eq A- 21}$$

Symbol	Description	Units
$Q_{electricity}$	Total electricity demand by process	kJ/h

- Calculate the heat demand, Eq A- 22.

The total heat demand for the system comes from the two drying options and the pyrolysis stage. Later versions of the model assume that there are two grades of process heat – high and low grade heat – but this was used in estimation of usefulness of the heat produced from by-products and not general natural gas demand. When natural gas or biomass is burnt, 60% combustion efficiency has been assumed as a general worst case statement.

$$Q_{heat} = Q_{drier_{bm}} + Q_{pyrolysis} + Q_{briq_{dry}} \qquad \textit{Eq A- 22}$$

Symbol	Description	Units
Q_{heat}	Total heat demand by process	kJ/h

3. Aspen Hysys cost curves and process models developed for screen experiment 4

Unit Operation Costing

Three models were developed to simulate capital costing of unit operations: the rotary drier, hammer mill and tray dryer. These were simple models using the Aspen Costing database, and the outputs are presented in Figure A- 9-Figure A- 11. The base equipment cost was used in costing, due to the factors used for producing the capital cost calculation covering the installation component.

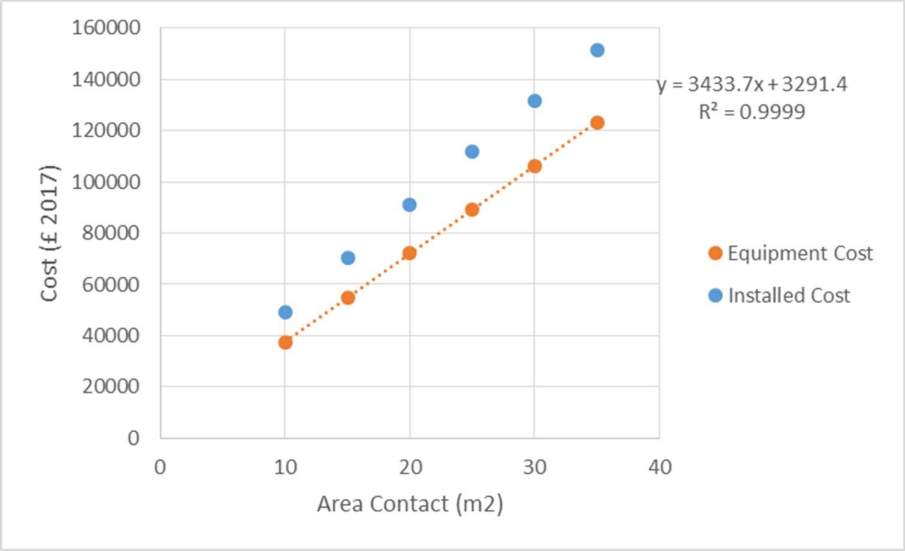


Figure A- 9 Aspen Cost Estimator Capital Cost for a Direct Fired Rotary Drier

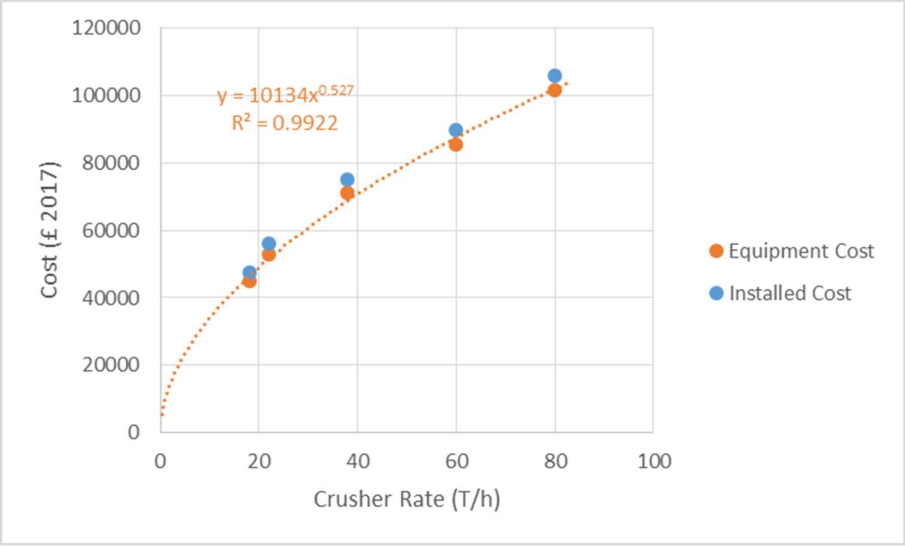


Figure A- 10 Aspen Cost Estimator Capital Cost for a Hammer Mill

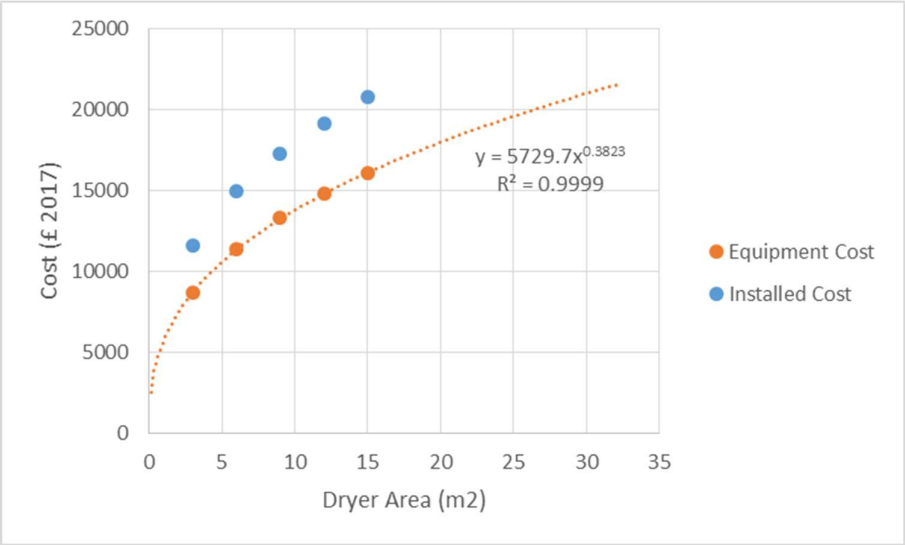


Figure A- 11 Aspen Cost Estimator Capital Cost for a Tray Drier

Aspen Hysys Models

Gas – Liquid Separation by Air then Water Cooler

This model was developed to improve the estimate of the capital cost of both the air and water coolers, and provide a more accurate estimate of the mass of cooling water required.

The system simulated is based on the flow scheme presented in Figure A- 12.

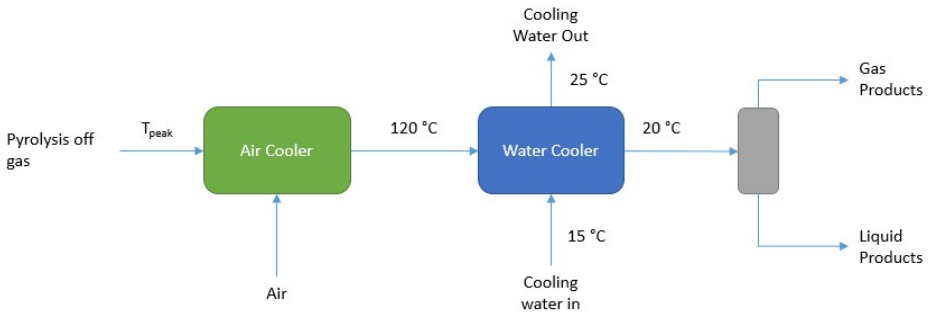


Figure A- 12 Simulation basis for liquid – gas separator model

The following assumptions have been made:

- Cooling water system has a 10 °C pinch
- Oil is 50% phenol (to represent light oil fractions) and 50% olive oil (to represent heavy oil fractions)
    - Simulations with full heavy or light oil changes water flow 10%, so not seen as significant.
- Assuming that the gas composition is 50% CO_2 40% CO and 10% CH_4

- Assuming full C-5 flow changes water demand by 5%, so not seen as significant.
- Assume pyrolysis off gas steam is 50% H_2O.
    - Water flow in off gas is the most significant effect. Likely this over estimates the cooling water demand, but this accounts for error in simulation of other flows.

The mass flow of cooling water was found by running a case study on this model varying the flows of water, oil and gas in the pyrolysis off gas from 500 – 4000 kg/h at 50 kg/h intervals. This was then converted to a correlation using regression analysis in Minitab, which is presented in Eq A- 23.

$$M_{Seperation_{water}} = -38.11 + 127.07M_{water_{py}} + 15.04M_{Oil_{py}} + 5.28M_{gas_{py}} \quad \textit{Eq A- 23}$$

Symbol	Description	Units
$M_{Seperation_{water}}$	Mass flow of cooling water at 15 °C required for separation of gas and liquid	kg/h

The cost curves for the coolers are presented in Figure A- 13and Figure A- 14.

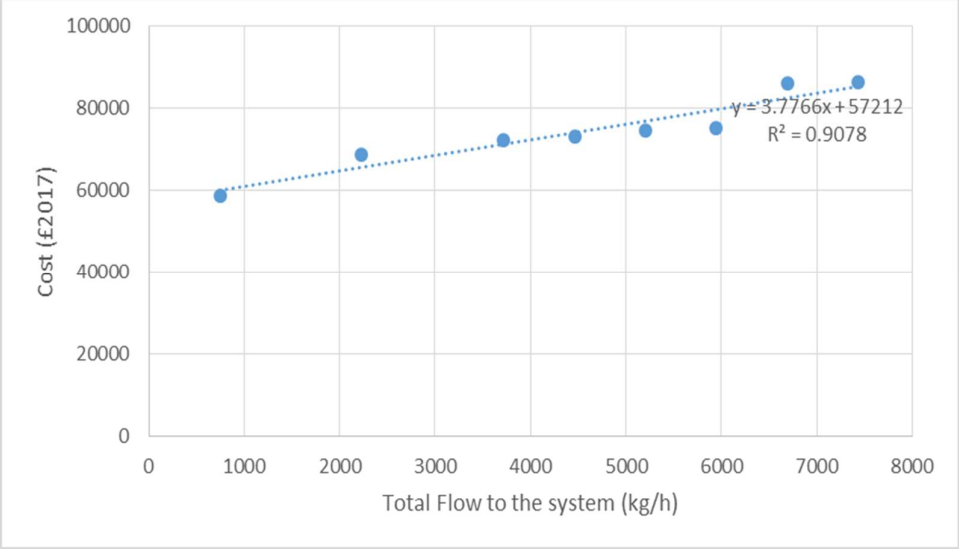


Figure A- 13 Aspen Cost Estimator Capital Cost for the Water Cooler Heat Exchanger

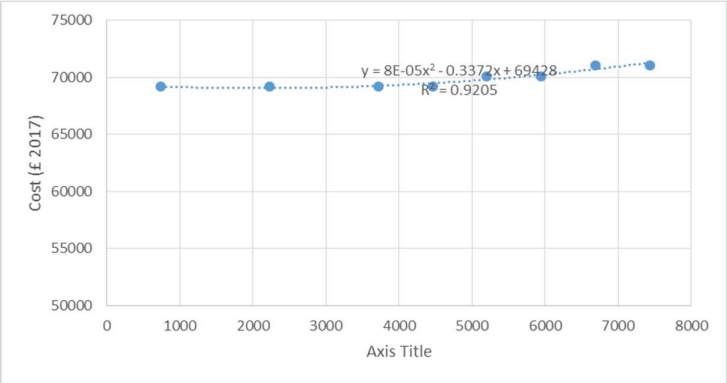


Figure A- 14 Aspen Cost Estimator Capital Cost for an Air Cooler Unit

Distillation Model for Phenol Production

The distillation of bio-oil aims to produce a phenol product and as suggested by Zhang *et al.* (2013) a distillation residue which experiments completed suggest is similar in composition to pet-coke, and can be added back into the pyrolysis. It has been assumed that 50% of the input oil is converted to this pet-coke substance. A modification to the mass of charcoal required for the process

A simulation of this has been produced to estimate the energy requirements from this distillation. This has been approximated by the assumption that the energy requirements can be compared to that of a simple phenol water system which has 15% phenol in water, which again should over-estimate the energy required due to the higher heat capacity of water than oil products. The system modelled is presented in Figure A- 15.

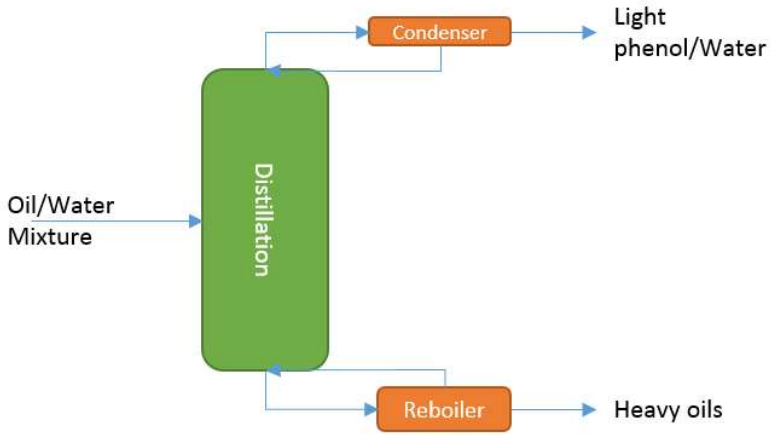


Figure A- 15 Simulation basis for distillation model

A case study was run to determine the condenser and reboiler energy demand over the range of 100 – 5000 kg/h 15% phenol mixture coming into the distillation. The results are presented in Figure A- 16.

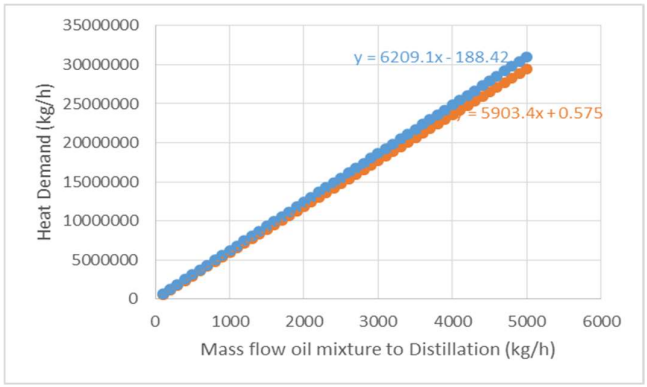


Figure A- 16 Aspen Cost Estimator Capital Cost for a Tray Distillation Column xx stages

Aspen Hysys was also used to produce a capital cost curve as indicated in Figure A-17.

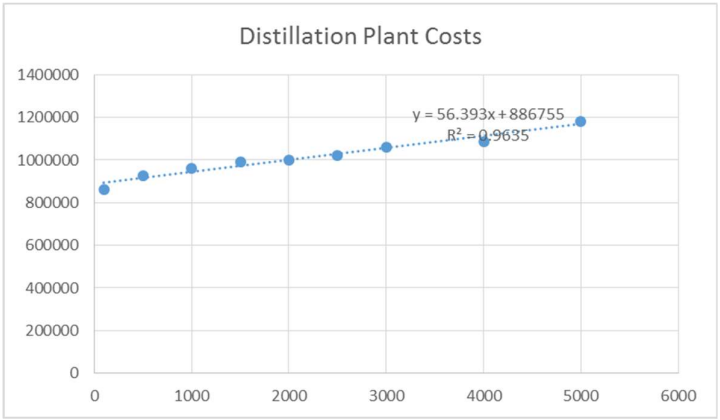


Figure A- 17 Aspen Cost Estimator Capital Cost for a Tray Distillation Column xx stages

Gas Combustion to Produce Heat Case 4

Up to this point in the model, it has been assumed that process heat is just of one grade. With the case of the CHP and boiler system, it has been assumed that the boilers can be optimised to produce high (for the pyrolysis and distillation re-boiler) and low grade streams (for the biomass and briquette drying options), via production of steam.

However the gas stream produced by case 4 after the oil separation, can be expected to provide high grade heat for distillation or pyrolysis and then the hot gas recovered off this can be used for low grade heat to be used in one of the drying stages.

The model used for this is presented in Figure A- 18.

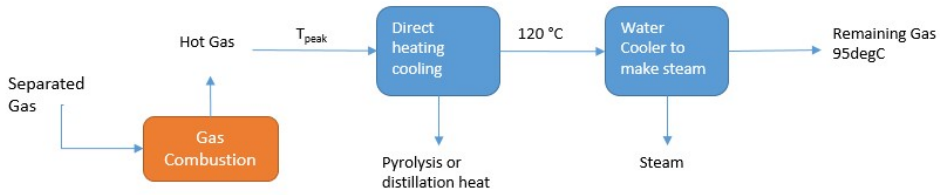


Figure A- 18 Simulation basis for Option 4B gas combustion system

This model was built on the basis of 1 kg of a simple pyrolysis gas composition with a case study controlling the concentration of CO between 30-70%, CH_4 between 0-30% and the balance CO_2. The temperature, Tpeak was varied between 300 -800 °C.

The results were passed to the regression analysis function in Minitab and the results are presented in Eq A- 24 to Eq A- 26. Fits between the regression analysis and the Hysys output are presented in Figure A- 19.

$$H_{high} = 524.7 + 48519.3C_{gas_{CH_4}} + 9947.8C_{gas_{CO}} - 7.0294T_{peak} \quad \textit{Eq A- 24}$$

$$for\ CH_4 < 20\% \ \& \ CO < 40\%$$

$$H_{high} = 19322.1 - 21.92C_{gas_{CH_4}} - 26.2C_{gas_{CO}} - 7.47T_{peak} \quad \textit{Eq A- 25}$$

$$for\ CH_4 > 20\% \ \& \ CO > 40\%$$

$$M_{steam_{gas}} = -0.41 + 0.47C_{gas_{CH_4}} + 0.0064C_{gas_{CO}} + 0.003T_{peak} \quad \textit{Eq A- 26}$$

Symbol	Description	Units
H_{high}	High grade heat output	kJ heat/kg gas
$M_{steam_{gas}}$	Mass of steam generated	kg steam/kg gas
$C_{gas_{CH_4}}$	Concentration CH_4 in the gas stream	g/g
$C_{gas_{CO}}$	Concentration CO in the gas stream	g/g
T_{peak}	Temperature of pyrolysis	°C

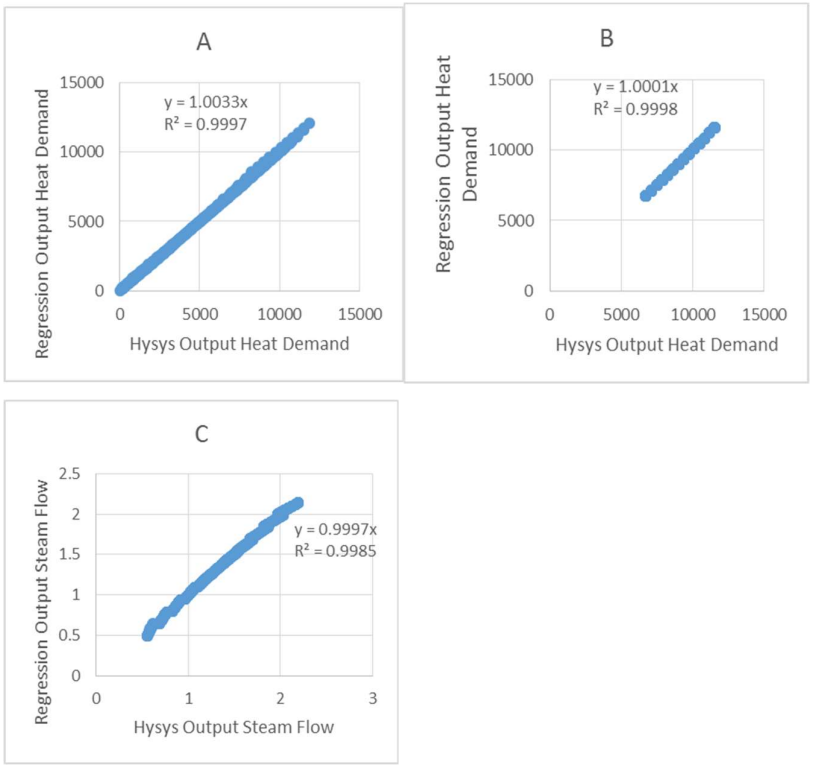


Figure A- 19 Regression fits vs Hysys Case study Modelling. A) High heat output model with low concentration CO and CH_4 gas B) High heat output model with high concentration CO and CH_4 gas and C) for Low grade steam model

Appendix 5. Further details for logistics study inputs

Cases		Biomass Properties					Biomass Cost	
Cases	Location	Biomass Type	Biomass Vols (wt.% Dry Basis)	Biomass Ash (wt.% Dry Basis)	Biomass FC	$kgCO_2$/tonBM	Biomass Cost	References
1	UK	Hardwood	84.7	0.4	14.9	0.041	150	Forest Fuels (2017)
2	UK	Miscanthus	69.9	8.4	21.7	0.059	60	s2biom (2017)
3	UK	Straw	75.1	6.8	18.1	0.049	50	see lit review
4	Spain	Olive Cake	66.3	6.75	26.95	0.074	100	see lit review
5	Spain	Grape Cake	60.8	6.7	32.5	0.089	40	see lit review
6	Spain	Eucalyptus Pellet	68	0.55	31.45	0.086	45	s2biom (2017)
7	Greece	Olive Cake	66.3	6.75	26.95	0.074	110	s2biom (2017)
8	Greece	Grape Cake	60.8	6.7	32.5	0.089	60	s2biom (2017)
9	Latvia (E. Europe)	Pinewood	81.9	0.6	17.5	0.048	35	s2biom (2017)
10	Austria (C. Europe)	Pinewood	81.9	0.6	17.5	0.048	45	s2biom (2017)
11	USA	Softwood Pellet	81.9	0.6	17.5	0.048	108	(Lamers *et al.*, 2015)
12	Australia	Eucalyptus Pellet	68	0.55	31.45	0.086	108	Lamers (2015)

Cases		Biomass or Charcoal Shipping										
Cases	Location	Shipping Method	Distance (km)	CO_2 Emm (kg CO_2/Ton BM)	Cost (£/ton)	Shipping Method	Distance (km)	CO_2 Emm (kg CO_2/Ton BM)	Cost (£/ton)	Total Distance (km)	Ship Cost (£/ton BM)	CO_2 Emissions kg CO_2/Ton BM
1	UK	Truck	90	-5310	9					90	9	-5.31
2	UK	Truck	90	-5310	9					90	9	-5.31
3	UK	Truck	90	-5310	9					90	9	-5.31
4	Spain	Truck	180	0	0	Boat - Europe	1000	-10000	12	1000	12	-10
5	Spain	Truck	180	0	0	Boat - Europe	1000	-10000	12	1000	12	-10
6	Spain	Truck	180	0	0	Boat - Europe	1000	-10000	12	1000	12	-10
7	Greece	Truck	50	0	0	Boat - Europe	1500	-15000	18	1500	18	-15
8	Greece	Truck	50	0	0	Boat - Europe	1500	-15000	18	1500	18	-15
9	Latvia (E. Europe)	Truck	50	0	0	Boat - Europe	2000	-20000	24	2000	24	-20
10	Austria (C. Europe)	Rail	50	0	0	Boat - Europe	2000	-20000	24	2000	24	-20
11	USA	Truck	200	0	0	Boat - World	3000	-30000	50	3000	50	-30
12	Australia	Truck	100	0	0	Boat - World	9000	-90000	50	9000	50	-90