DEGRADATION OF BIOMASS FUELS DURING LONG TERM STORAGE IN INDOOR AND OUTDOOR ENVIRONMENTS

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Abstract

This project has focused on the long term storage of different biomass fuels in outdoor and indoor stockpiles and was a joint study between the Efficient Fossil Energy Technologies Engineering Doctorate Training Centre at the University of Nottingham and E.ON Technologies at Ratcliffe.

Biomass has very different properties compared to coal and in order to increase the viability of larger cofiring ratios and dedicated biomass combustion, pre-treatment of biomass such as pelletisation and thermal treatment have been developed. This study compares the behaviour of freshly harvested Willow chips, thermally treated wood pellets and untreated white wood pellets in both indoor and outdoor piles. This is one of the few studies carried out on the storage of thermally treated wood pellets worldwide.

Novel research on biomass storage has been carried out, by combining a range of different fuels, a range of storage scenarios, a range of stockpile sizes and a range of weather/seasonal patterns. Also, a wide spectrum of tests was regularly performed on the stored fuel samples, to determine the extent of chemical, mechanical and biological degradation.

The storage trials have been divided into Phase 1 and Phase 2, with Phase 1 starting in April 2011 (spring) and Phase 2 in November 2011 (autumn). This enabled the fuels' degradation behaviour in the warmer summer months to be compared to that in the colder winter months. This also allowed the impacts of the weather parameters, especially ambient temperature, relative humidity and rainfall, on fuel degradation to be understood.

Both the chemical and mechanical degradation of the fuels were measured. The chemical properties included moisture, volatile, ash content as well as calorific value. The mechanical properties of the pellets were measured and included durability, axial and diametrical compression strength and inter laminar shear modulus. Photographs and SEM images of fresh and degraded fuels were also generated.

The environmental and occupational health implications of long term stockpile storage of biomass were also considered. The in-situ temperature was

continuously measured at multiple locations within the stockpiles in order to understand the potential of piles self-heating and self-combustion. And at regular intervals, samples were taken from both the surface and middle of each pile and analysed for the identification of fungal species and fungal count.

The results showed that the different fuels remain chemically stable with time in storage, as reflected by a lack of significant changes in the dry ash, dry ash free volatile content and calorific value. The main concern for the Willow chips storage was the high concentration of a range of fungi on the Willow chips after three and six months in storage. Two pathogenic fungi were identified. As expected, biological growth was faster and more widespread in the warmer summer months. In order to fully appreciate the inhalation and ingestion potential of fungal spores as well as their deposition onto the skin and eyes of workers, the release mechanism of the spores from the wood fuels into the air needs to be understood and the resulting concentration of airborne spores. This was not done in the scope of this study, but would be recommended as future work.

The indoor white wood pellet pile stored in an open barn suffered severe mechanical degradation, and significant disintegration of pellets into dust was observed, particularly on the surface of the pile. Therefore it would be advisable to store white wood pellets in a fully enclosed environment with no exposure to ambient temperature and humidity.

For the thermally treated pellets, the extent of degradation on the outdoor piles was far more significant than on the indoor one, despite the claims from the suppliers that the pellets are fully hydrophobic. Degradation on the surface of the outdoor pile was the main concern as pellets started to crack and break up. Changes in the durability, compression and shear tests reflected the degree of degradation. The amount of rainfall and level of humidity could be seen to have a large impact on the extent of degradation of the pellets stored outdoors. Therefore, while the long term storage of thermally treated wood pellets in an open barn with covered storage would be a viable option, pellets stored in outdoor stockpiles would still be vulnerable to mechanical degradation, especially on the surface of the piles.

Although the thermally treated wood pellets stored outdoors showed significant deterioration, the extent of mechanical degradation of the white wood pellets in the open barn was a lot higher. So outside storage of thermally treated pellets might be an option for short term strategic stocks, but in the majority of cases, covered storage would still be necessary (as for white wood pellet) therefore reducing the attractiveness of using thermally treated pellet.

List of conference presentations on research project

- 'Mechanical degradation of wood pellets during long term stockpile storage' at the European Conference on Coal Research and its Applications, University of Hull 2014
- 'Effects of storage methods on the properties of biomass fuels part 2' at the Materials Handling Engineers Association Bulk Solids Handling Conference Lincolnshire 2014
- 'Degradation of biomass fuels during indoor and outdoor storage' at the Midlands Energy Graduate School Conference Nottingham 2012
- 'Effects of storage methods on the properties of biomass fuels part 1' at the European biomass conference and exhibition Milan 2012
- 'Effect of storage methods on the physical and chemical properties of biomass fuels' at the Sustainable Energy Technologies Conference Istanbul 2011
- Research presentations at summer schools in China (2010) and India (2011)

List of conference proceedings

- Williams O, Eastwick C, **Graham S**, Cooper A. The Impact of Storage on the Optimisation of Milling of Biomasses used in Power Generation *In:* 3rd IEA CCC Workshop on Cofiring Biomass with Coal, 2013.
- **Graham S**, Eastwick C, Snape C. Effects of storage methods on the properties of biomass fuels. 20th European Biomass Conference and Exhibition, Milan 2012. DOI: 10.5071/20thEUBCE2012-3CO.5.4.
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Publication in peer reviewed journal

- **Graham S**, Eastwick C, Snape C, Quick W. Degradation of biomass fuels during artificial storage in a laboratory environment. Int. J. Low-Carbon Tech. (2012) 7(2): 113-119.doi: 10.1093/ijlct/cts029

Future publications in peer-reviewed journals

- **Graham S**, Eastwick C, Snape C, Quick W. 'Impacts of long term stockpile storage on the mechanical properties of woody biomass pellets' to be submitted to Fuel journal
- **Graham S**, Ogunfayo I, Eastwick C, Snape C, Quick W. 'Mechanical degradation of woody biomass pellets during artificial degradation in a laboratory environment' to be submitted to 'Bioresource technology' journal

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1 Introduction

A joint research project has been carried out between the University of Nottingham Efficient Fossil Energy Technologies (EFET) Engineering Doctorate Centre and E.ON Technologies (Ratcliffe) Ltd. The study has focused on the long term storage of different biomass fuels in indoor and outdoor stockpiles and the extent of fuel degradation during storage.

1.1 Project background

According to the UK Department of Energy and Climate change, (DECC, 2015), bioenergy will play a significant role in helping the UK meet its 2050 low carbon targets. Biomass has the potential of achieving a decarbonisation cost saving of £44 billion. Therefore there is likely to be an increase in the use of biomass fuels in decarbonising power generation around 31% of which currently uses coal as a feedstock.

Biomass is a renewable, low carbon fuel that is already widely available throughout the UK. Its production and use also brings additional environmental and social benefits. Correctly managed, biomass is a sustainable fuel that can deliver a significant reduction in net carbon emissions when compared with fossil fuels (Biomass Energy Centre, 2010).

The benefits of using biomass as a sustainable fuel are listed below:

•Biomass is a "carbon lean" fuel producing a fraction of the Carbon emissions of fossil fuels

•Biomass can be sourced locally, from within the UK, on an indefinite basis, contributing to security of supply

•UK sourced biomass can offer local business opportunities and support the

rural economy.

•The establishment of local networks of production and usage, allows financial and environmental costs of transport to be minimized. There is no region in the UK that cannot be a producer of biomass.

•The use of biomass fuel provides an economic incentive to manage woodland which improves biodiversity.

•The combustion of biomass fuels generates lower levels of such atmospheric pollutants (for example sulphur dioxide) which contribute to 'acid rain'. Modern biomass combustion systems are highly sophisticated, offering high combustion efficiency and emission levels comparable with the best fossil fuel boilers.

•Biomass residues, arisings, co-products and waste not used for energy, or some other application will usually rot. This will generate CO_2 in any case, and may also produce methane (CH_4), a greenhouse gas 21 times more potent that CO_2.

However, biomass has very different properties to coal, such as a higher moisture content, lower energy density and a higher tendency to degrade physically and biologically. These bring a number of challenges to the energy sector in areas of supply, transport, storage, handling and conveying, milling and combustion. This work relates to the issue of biomass storage. This study will focus on each of the chemical, mechanical and degradation of the different biomass fuels as a result of storage in indoor and outdoor stockpiles.

1.1.1 Impacts of chemical degradation during storage

The extent of chemical degradation can significantly impact the handling, milling and combustion of the fuel. The resulting impacts of changes in each of the moisture content, volatile matter content, calorific value and ash content are described below:

- A significant increase in the fuel moisture content can result in a wide range of issues such as:
    - Increased fungal and bacterial activity in the stockpiles which can in turn lead to heat generation and self- heating of piles (Jirjis, 1995) and occupational health concerns during fuel handling and conveying
    - Increased likelihood of lump formation and bridging which can lead to blockages during conveying and milling and reduced mill performance (Mattsson and Koffman, 2003)
    - A lowering of furnace temperature and increase in flame standoff (Shanmukharadhya and Sudhakar, 2006) and more importantly a reduced efficiency
- In terms of volatile matter, a significant decrease due to pile heating, will result in a reduced energy value and can also make ignition more difficult to achieve in the furnace (Jenkins et al., 1998)
- A decrease in the calorific (energy) value of the fuel has significant financial implications and would lead to power generators opting for a different fuel altogether
- The ash content of the fuel corresponds to the non-combustible constituents of the fuel and the higher the ash content, the lower the calorific value. Furthermore ash can contribute to slagging and fouling issues in burners, (Doosan and Babcock Energy, 2007).

1.1.2 Impacts of mechanical degradation during storage:

It is important for biomass fuels to retain mechanical integrity during storage as significant loss of mechanical strength can result in major issues. A few of these are listed below:

- High levels of dust which can in turn increase the risks of fires and explosions as well as present a serious health hazard to the workers

- Blockages in handling and conveying systems
- Heat generation in stockpiles caused by microbial attack (increased on dust and finer particles) and lack of aeration of piles (reduced if piles too dusty) (Lehtikangas, 2000)

Examples of incidents occurring at power plants operating on wood pellets include the fire in the conveyor belt and storage bunker at Tilbury power station in February 2012 (Essex County Fire and Rescue Service, 2012) and the fire at Ironbridge power station in the wood pellet store in October 2013 (BBC News, 2013).

1.1.3 Impacts of biological degradation during storage:

The presence and growth of micro-organisms on wood fuels can lead to the following issues (Noll and Jirjis, 2012):

- Reduction in fuel quality which can affect handling, milling and combustion
- Self-ignition of the stockpiles catalysed by the microbial activity
- Occupational health hazards to workers on site as they are exposed to the different fungi and bacteria

Fungi are superior to bacteria in metabolising the main compounds of wood (Noll and Jirjis, 2012) and so biomass piles act as reservoirs of fungal spores. Moving significant volumes of biomass fuel (chips/pellets) can result in the release of a large quantity of spores which can then be inhaled or ingested by workers or deposited on their skin (Grisoli et al., 2009).

1.2 Project aims and objectives

The aims of this study were to:

- Carry out novel research on biomass storage, by combining a range of different fuels, a range of storage environments, a range of stockpile sizes and a range of weather/seasonal patterns. Also to characterise the extent of chemical, mechanical and biological degradation of the various biomass fuels
- Determine the optimum storage scenario for the different fuels and provide a comparison of the fuels' resistance to degradation
- Present findings at conferences and in journal publications
- Produce a comprehensive thesis to report all findings

The objectives of the project were as follows:

- Investigate impact of indoor and outdoor stockpile storage on different biomass feedstocks
- Quantify mechanical, chemical and biological changes during storage
- Determine impact of weather on stockpile behaviour
- Determine impacts of degradation on handling and combustion
- Investigate the occupational health and environmental impacts of biomass storage
- Make recommendations on optimum storage practices for fuels investigated

1.3 Storage trials

The three fuels investigated in this project were: freshly harvested Willow chips, white wood pellets and thermally treated wood pellets. The fuel choice was carried out jointly with E.ON Technologies and the three above listed fuels were of highest interest to them when the project started in 2010. At E.ON's power stations where coal is used, for example Ratcliffe on Soar power station, the coal is stored outdoors in a stockpile in the yard. It was important for the company, through this long term research, to understand how Willow chips and thermally treated wood pellets would store and to what extent they would degrade in a similar environment. This explains why outdoor stockpiles of

Willow chips and thermally treated wood pellets were set up outdoors. Because the degradation outdoors would be caused by exposure to weather conditions, covered storage in an open barn was also carried out to help E.ON understand the benefits and advantages of indoor storage over outdoor storage. The choice of the storage site and pile sizes and features is explained in detail in Chapter 3.

In April 2011 (Phase 1), four stockpiles were set up consisting of two outdoor Willow chip piles of different sizes (3.8x3.8x2.5m and 2.4x2.4x1.7m) and two (2.4x2.4x1.5m) thermally treated wood pellet piles (one indoor and one outdoor). Thermocouples were positioned at multiple locations within each pile for continuous in situ temperature measurement. A weather station was also set up on the storage site consisting of an ambient temperature and relative humidity sensor, a rain gauge, an anemometer and a wind vane. Full experimental set up is explained in Section 3.2.

In November 2011 (Phase 2), three further stockpiles were set up consisting of one indoor and one outdoor Willow chip piles of the same size (3.8x3.8x2.5m) and one white wood pellet indoor pile (2.4x2.4x1.5m). In December 2011, an additional outdoor thermally treated pellet pile (2.4x2.4x1.5m) was also constructed. As for Phase 1, in situ monitoring of temperature at multiple locations within each pile and continuous weather data logging took place throughout the trials.

Throughout the storage trials a number of different tests were carried out at regular intervals on samples extracted from the piles. By also monitoring weather and pile temperatures continuously, the changes seen in the fuels could be linked back to both the storage methods (indoor/outdoor and pile size) and environmental conditions. This would allow the impact of storage for different fuels to be analysed and recommendations on the most appropriate storage approach given.

1.3.1 Characterising the extent of chemical degradation of the fuels during storage

The chemical properties were measured on monthly samples for the first six months of storage and included: total and free moisture content, volatile content, ash content and calorific value. After the first six months, the frequency of the tests was reduced to two or three monthly with all the tests carried out fully described in Section 3.7.

1.3.2 Characterising the extent of mechanical degradation of the woody biomass pellets during storage

In this study, the mechanical durability of the pellets from both the surface and middle of the different piles was measured at regular intervals. Axial and diametrical compression strengths and the inter-laminar shear modulus were also determined. Photographs and SEM images of the degraded pellets were also generated. All the tests carried out are fully described in Section 3.6.

1.3.3 Characterising the extent of biological activity on the fuels during storage

It was important in this long term biomass storage project to understand the potential and extent of the biological degradation of the Willow chips, thermally treated wood pellets and white wood pellets. Biological analysis was only a small part of the project and was contracted out to Mologic UK (Mologic UK, 2015). Fresh samples, as well as samples after three and six months in storage, were sent to Mologic without any drying or pre-treatment. They were analysed for fungal count and identification, see Section 3.5.

The detailed results from this work will be presented in Chapters 4 to 7, following the literature review and methodology chapters.

2 Literature review

2.1 Background

2.1.1 Tensions within the energy industry

The energy industry has reached a high level of complexity. Growing energy demand worldwide, along with an increasing awareness and concern about energy security as well as increasing levels of carbon dioxide and other greenhouse gas emissions, are giving rise to tensions within the industry on an international scale. The world population will continue to grow as will the hunger for more energy, resulting in about 1.6% rise in electrical consumption each year, so that it would have doubled by 2050 (Rebhan, 2009). The world's largest economies use coal for power generation; and even if coal burning is the main source of greenhouse gas emissions and is a key contributor to climate change, air pollution and acid rain formation; to date, no viable alternative exists (Breeze, 2008).

In the worldwide effort to reduce greenhouse gas emissions, nuclear energy evolved in the 1970s-1980s and could provide the potential to generate a lot of power efficiently, with minimal environmental impact. However, in recent years, there has been a drop in nuclear orders for the following reasons (Jamasb et al., 2006): economic concerns, public perceptions over waste management, safety, nuclear weapons and the development of alternative technologies. Nuclear power plants also require high capital costs. Growth in wind power capacity, perhaps the best option for the medium term, is already showing signs of being restricted by global manufacturing capacity (Breeze, 2008). Solar power, potentially the earth's long-term solution to electricity supply will probably take another generation before it can begin to provide the sort of capacity the world needs (Breeze, 2008). Hydropower might be able to provide significantly more output, particularly in Africa where the infrastructure

associated with increased hydro capacity can have other major benefits. But the availability of water and the high building and installation costs impose obvious constraints on hydro power (Breeze, 2008).

So in order to meet the increasing energy demand and at the same time contribute to climate change abatement, it seems obvious that improvements/changes to coal technologies need to be implemented in the short term. The main technologies currently being researched and developed include supercritical steam cycles, integrated gasification combined cycles (IGCC), carbon capture and storage (pre and post combustion capture, oxyfuel combustion, biomass co-firing and conversion from coal to biomass.

2.1.2 Biomass co-firing

Co-firing biomass with coal can reduce the net carbon dioxide and other greenhouse gases emissions in power generation (McIlveen-Wright et al., 2006). It is also a cheap and low risk approach to tackling climate change and can also provide local employment and a boost to the rural economy. Biomass co-firing with coal is now an established technology and all sixteen major UK power plants are now co-firing a proportion of biomass, at an average level of 3% (energy basis) making use of a range of fuels including wood (virgin and recycled), olive cake, palm kernel expeller, sewage sludge and energy crops (Biomass Energy Centre, 2015).)

2.1.3 Conversion from coal to biomass

An increasing number of power plants are now converting from coal to biomass. For example, Drax power station, the largest coal power plant in the UK, now has two units generating power (7.9 TWh) using sustainable biomass (Drax, 2015). The materials that Drax use include sustainable forestry and forestry residues, residual agricultural products, such as straw, sunflower seed husks and peanut husks, and purpose grown energy crops.

Examples of other large scale biomass power plants include (Power Technology, 2015):

Ironbridge, UK, 740 MW
Alholmens Kraft, Finland, 265 MW
Polaniec, Poland, 205 MW

2.1.4 Logistical challenges of using biomass

Biomass has different physical, mechanical and chemical properties to coal and hence stores, flows, mills and burns differently. Different issues are experienced in each of the areas of transport, storage, milling, conveying and combustion, and can limit the scale of co-firing and extent of coal to biomass conversion. This project will focus on the storage of biomass fuels and the fuel property changes which can occur and subsequent implications to handling, conveying, milling and combustion. There are a variety of potential challenges which could arise at a power plant from storing of biomass fuels. A few examples include:

- Degradation of the biomass which could lead to a decrease in calorific value and increase in ash
- Self-heating and spontaneous combustion of biomass piles
- Off gassing and emissions of harmful substances from biomass stockpiles
- Dust formation and spread on site
- Severe mechanical degradation which would result in chips/pellets breaking up and forming dust during handling and conveying
- Fungal and bacterial growth on fuels and harm to workers on site
- Stickiness of fuels and agglomeration, leading to handling difficulties such as blockages

- Run offs from biomass piles contaminating the ground in outdoor storage

2.2 Structure of this literature survey

This project is investigating the degradation of different types of biomass fuels in indoor and outdoor storage and the subsequent impacts on handling and combustion. The fuels investigated include Willow chips, white wood pellets and thermally treated wood pellets. The fuel selection was driven by the industrial sponsor as explained in Sections 1.2 and 3.1.

The purposes of carrying out this extensive literature review were as follows:

- Obtain background information on Willow chips, white wood pellets and thermally treated wood pellets to provide context to this work
- Research the various storage experiments carried out on Willow chips and wood pellets (biomass form, storage conditions, length of storage period)
- Research the properties of fuel which have been measured to determine the changes in the fuel and the extent of degradation during storag and the laboratory test methodologies which have been used
- Identify the gaps in the literature domain on the storage of Willow chips and wood pellets which could be addressed by this study

A sequential approach has been used in structuring this literature review. The focus will be on Willow chips and wood pellets, which are the fuels being investigated in this project and some background information on these fuels is provided before the studies by other researchers on the storage of Willow chips and wood pellets are listed out. The storage scenarios are described in detail, followed by the main findings. In the section on biomass property measurements related to storage losses, work on other fuels other than Willow and wood pellets has also been included. This is to ensure a wide range of tests are covered. The final section in this chapter discusses how the literature

survey has impacted the project scope and the gaps in the literature which this work is addressing.

2.3 Background information of fuels investigated

2.3.1 Willow Chips

Growing Willows as a short rotation crop has been investigated in Sweden since the mid 1960s-70s, following the oil crises (Mitchell et al., 1999). Short-rotation forestry, particularly coppice (SRC), is now seen in Europe as a means to produce a non-food crop on agricultural land which has to be taken out of food production and, hence, a means to provide a future livelihood for farmers. In the United Kingdom, incentives are being provided by the government to stimulate the deployment of short- rotation coppice crops and to establish a market for the product. Willow grows best in mildly acidic, well drained fertile soils and large flat sites improve the efficiency and flexibility of machinery operations (Mitchell et al., 1999). The planting rates for Willow are typically in the region of 5000-20000 plants/ha with corresponding rotation periods of 3 to 5 years. Upon harvest, the willow can be either cut and chipped or kept as whole stems. Cut chips can be collected in self trailed bins or tractor-trailer units. Whole stems are cut and retailed whole by self-propelled or trailed harvesters. In the UK, Willow crops are harvested in the period late November to mid March and so if SRC Willow is to provide fuel in the UK throughout the year, storage is needed (Mitchell et al., 1999).

A number of projects have been and are being carried out on the storage of Willow chips and they will be described in Section 2.4.1.

2.3.2 Wood pellets

White non-thermally treated wood pellets are made from dry sawdust compressed under high pressure and extruded through a die. They are currently regarded as the short term most reliable and available biomass fuel for co-firing and dedicated biomass combustion (Department of Energy and Climate Change, 2012). The market for such pellets is established and suppliers have manufactured and shipped a large quantity of the fuel around the world and so it is a proven technology. They provide a number of advantages over energy crops and agricultural based biomass fuels in terms of lower moisture content, lower ash content, higher calorific value, improved handleability and ease of milling. The pellets also have a more homogenous particle size distribution. The main raw materials for woody biomass pellets include wood residues from wood shavings, chips and sawdust (Stelte et al., 2011). Agricultural residues, food wastes and energy crops are gaining use as raw materials for pellets.

It would be, in the short term, the most practical fuel to be used in increasing cofiring ratios in existing coal fired plants. Therefore, in the last few years, there has been a lot of work carried out on the storage of white wood pellets.
Wood pellets are easier to store and handle than raw woody biomass. However, they still present a number of issues such as brittleness which is accompanied by dust formation during transport, handling and conveying. Also wood pellets have to be stored in a completely enclosed environment as any exposure to moisture and high humidity would result in severe degradation and disintegration as well as fungal growth. Furthermore because of the wood having retained much of its fibrous nature during the pelletisation process, co-firing wood pellets in existing coal plants would require potential changes in the types of milling and conveying equipment. Biomass also has a relatively lower calorific value compared to coal (Arias et al., 2008).

All the above challenges have given rise to a growing interest in pre-treating the biomass prior to pelletising. Thermal treatment of biomass can include

torrefaction and steam explosion. Each of the methods is described briefly below, along with the improvements which it brings to the fuel properties.

2.3.3 Torrefaction of biomass

Torrefaction is a mild pyrolysis process carried out within a temperature range of 225-300°C in an inert atmosphere (Prins et al., 2006a). The treatment involves dehydration and de-carboxylation reactions that result in a mass reduction in the wood due to the decomposition of the volatile hemicellulose components (Prins et al., 2006a). The output products of the torrefaction process include an aqueous phase acidic yellowish colour, CO and CO_2 gases, and a black-brown solid product (Prins et al., 2006b). Torrefaction reactions cause the biomass to become completely dried and to lose its tenacious and fibrous structure. Therefore the grindability of the biomass is improved significantly (Bergman and Kiel, 2005). In addition, the calorific value is increased and a hydrophobic nature acquired. For example, untreated willow has an energy density of 17.7MJ/kg compared to 20.7MJ/kg after being torrefied for 15 minutes at 270^0C (Prins et al., 2006a).

Depending on the applied torrefaction conditions, torrefied biomass is coloured brown to dark-brown and approaches the properties of coal. These changes make torrefied biomass very attractive for combustion and gasification applications. Logistic properties can be further improved by combining torrefaction with densification (pelletisation). By this combination highly energy dense fuel pellets are produced.

In the last ten years, there has been a lot of work carried out on fully understanding torrefaction and optimising the process to generate the best quality fuel. A few examples are provided below:

Chen and Kuo (2010) investigated the impact of torrefaction temperature on four different types of biomass fuels, namely bamboo, Willow, coconut shell and wood. All four fuels were torrefied at 240°C (light torrefaction) and 275°C

(severe torrefaction). The hemicellulose, lignin and cellulose content of each were determined after the thermal treatment. Results showed that light torrefaction leads to a complete destruction of the hemicellulose whereas the lignin and the cellulose are only slightly affected. Severe torrefaction, on the other hand, had a significant impact on the cellulose.

Arias et al. (2008) investigated the effect of torrefaction on the grindability and reactivity of eucalyptus. Ground eucalyptus (<5mm) was torrefied in a horizontal tubular reactor at three different temperatures, 240, 260 and 280°C and for different residence times ranging from 0 to 3 hours. The mass loss of the samples was measured after torrefaction. Proximate and ultimate analyses were performed, and the gross calorific value of the torrefied samples was also determined. The grindability properties of the torrefied biomass were evaluated using a cutting mill with a bottom sieve of 2 mm (Retsch SK100). After grinding, the samples were sieved to various size fractions in order to evaluate the changes in the grindability of torrefied samples.

The samples were examined using an optical microscope (Zeiss Axioplan). The thermal behaviour of the samples was studied by means of non-isothermal thermogravimetric analysis in a thermobalance (Setaram TAG 24). A sample mass of approximately 5 mg was heated at a constant rate of 15 °C min−1 under an air flow rate of 50 mL min−1. A mathematical model was applied to calculate the kinetic parameters of the thermal decomposition of the torrefied biomass in air. From the results of this work it can be concluded that the mildest operating conditions for the decomposition of hemicelluloses was 30 min of residence time at a temperature of 240 °C. At these conditions, the improvement in grindability and handleability characteristics of the torrefied biomass seemed to compensate the mass loss (20%) and the heating value yield (90%) attained after torrefaction.

Prins et al. (2006a) carried out an extensive research on the weight loss kinetics involved in the torrefaction of Willow using isothermal thermogravimetry. A two-step reaction in series model (Bridgeman et al., 2008) was found to give an

accurate description. The two steps, had activation energies of 76.0 and 151.7 kJ/mol, respectively. The first reaction step has a high solid yield (70–88 wt%, decreasing with temperature), whereas less mass is conserved in the second step (41 wt%). The faster initial step may be representative of hemicellulose decomposition, whereas the slower second reaction represents cellulose decomposition and secondary charring of hemicellulose fragments.

Bridgeman et al. (2007) torrefied two energy crops (reed canary grass and Willow) and an agricultural residue (wheat straw). Different torrefaction conditions were used and in-situ measurements were carried out to determine mass and energy losses during the process. Proximate and ultimate analyses were carried out on the products of torrefaction. Herbaceous biomass showed bigger changes in its properties during torrefaction than woody biomass, in terms of mass loss and atomic composition. The overall mass loss in both herbaceous species investigated was similar but wheat straw underwent greater changes in its elemental composition and increases in energy content: carbon content rose by a maximum of 14% to 51 wt%, oxygen content was reduced by 30% to 25% and the energy density rose by 20% to 22.6 MJ/kg. However, the overall energy yield was slightly lower for wheat straw. In contrast the mass and energy yields of Willow were noticeably higher than the two herbaceous species. For example, after treatment at 543 K the mass yield of Willow was 80%, whereas the figures for wheat straw and reed canary grass were 72% and 71%, respectively. The energy yields for these conditions were 77%, 78% and 86% for wheat straw, reed canary grass and willow respectively. However, Willow torrefied at 563 K only experienced an increase in its overall energy content of 9.5%. These differences appear to be mostly attributed to differences in the lignocelluloses composition of the fuels, specifically the higher hemicelluloses content of graminaceous crops. Observations of combustion behaviour revealed a number of differences between torrefied biomass and raw fuels. For all fuels, volatile combustion was modified and occurred over a shorter temperature range and the herbaceous crops produced heats of combustion that were between 10–65% higher, depending on the treatment temperature and crop. The higher fixed carbon content also meant that torrefied biomass produced greater heats of combustion during char burnout. All these

observed behavioural changes were more pronounced for the product of higher torrefaction temperatures.

2.3.4 Steam explosion of biomass

Steam explosion of woody biomass is more recent compared to torrefaction. Steam explosion was originally used in ethanol production and binderless panel production and in the last few years, it has been applied to improving wood fuel quality (Biswas et al., 2011). Woody biomass consists of cell wall mainly with polysaccharides (cellulose and hemicelluloses) and aromatic polymers named lignin. In steam explosion (SE) process, biomass is exposed to saturated steam at the temperatures range from 453 K to 513 K with a wide range of residence time, which results in both morphological and chemical changes in wood (Anahashi, 1990). SE pretreatment is known to bring adequate disruption of carbohydrate linkage by releasing hemicelluloses into solution (Negro et al., 2003). Additionally, both cellulose and lignin are also altered depending on the severity of the process (Ramos, 2003), (Stenberg et al., 1998). Biswas et al. (2011) investigated the effect of steam explosion conditions on the reactivity of Willow during the thermal process. Structural and thermal analyses were performed on raw and treated samples. Different steam explosion temperatures and sample residence times were used in the experiments. After the pretreatment, thermogravimetric analysis was carried out in a pure nitrogen atmosphere.

Implementation of steam explosion significantly altered the structure and pyrolysis characteristics of biomass. At pre-treatment temperature of 478 K, biomass became more resistant to thermal decomposition. While hemicellulose decomposition rate was increased, cellulose decomposition peak intensity was reduced significantly in pretreated residue in comparison with untreated biomass. Likewise, pre-treatment also enhanced thermal stability of lignin at this pre-treatment condition. Increase in pre-treatment temperature to 493 and 501 K resulted in the increase of cellulose decomposition peak intensity. On the other hand, lignin decomposition rate reduced at severe conditions due to

apparent increase of lignin. However, lignin content of pre-treated biomass under severe conditions decomposed earlier than that of pre-treated biomass under mild conditions. Hence, severe pre-treatment condition seems to produce more reactive biomass compared with mild pre-treatment conditions.

2.4 Storage of Willow and wood pellets

2.4.1 Storage of Willow

In this section, storage experiments on Willow will be described. The two sub categories below relate to the two types of storage methods investigated, namely outdoor (uncovered and covered) and indoor.

2.4.1.1 Outdoor uncovered and covered

'Outdoor uncovered' refers to the storage of biomass outside and exposed to the atmospheric conditions. In the 'outdoor uncovered' storage experiments, a range of variables have been considered such as climate, substrate, pile type, fuel type amongst others. Below are reviewed a number of studies on the 'outside uncovered' storage of Willow.

Gigler et al. (2000a) stored Willow stems in large piles outdoor in the Netherlands and studied the natural drying effects in order to generate a simple drying model. The 3-4 year old stems were piled up on the headland of the Willow fields immediately after harvest and the edge effects were eliminated by stacking the piles against each other and using foils where gaps were left. The spacial distribution of the moisture content of the stems within the piles was also determined by sampling a few stems from different rows within the piles on a regular basis for moisture content measurement using the oven drying weight method. From the results, the main conclusions were as follows:

- Diffusion of moisture within the stems, a slow process which is governed by relative humidity and ambient temperature
- Evaporation and rewetting on the surface of the stems, a relatively fast process. Rainfall, wind and global radiation govern this process
- A pile of Willow stems dries almost uniformly, except the top of pile which follows ambient conditions
- Within a single Willow stem, the moisture content is more or less uniform, which shows that water is distributed internally
- Dry matter (DM) loss was found to be low in the piles of Willow stems which were allowed to dry naturally in the wind for 4-9 months

Jirjis (2005) determined the effects of pile height and particle height on fuel quality changes which take place during storage due to degradation. Fresh Willow shoots were reduced in size to chips and chunks (22-45mm) and then stored in 3m and 6m high piles in Sweden for 2 and 3 months respectively. Each of the four piles was approximately 20m long. In-situ pile temperature measurements and weather monitoring were in place. Regular sampling and testing were also integral to the project.

In the 3m high chip pile, temperature followed ambient during the first two weeks of storage. Afterward, a sudden rise in temperature was measured in many regions inside the pile, reaching around 60°C. Temperature stayed high until the end of 2 months of storage. Although ambient temperature was very low at the start of this experiment, heat development in the 6m high chip pile was measured after few days of storage and temperature was around 40°C in many areas. A maximum temperature of 63°C was measured after 8 days of storage. The increase in temperature could be attributed to heat generated by the respiration of the living cells and also by the fungal activity within the piles. Most of the measured points remained at high temperature until the end of March. By the end of 2 months of storage, the temperature started to decline rapidly in most areas, as mesophilic (non-temperature resistant) fungi are eliminated. At the end of 3 months of storage trial, the temperature varied between 10 and 25°C. Changes in temperature in both the 3m and 6m high

chunk piles were minimal during the first month of storage, and mostly followed ambient temperatures. Heat started to develop slowly around the beginning of March but it did not exceed 10°C by the end of the storage trial. In the two chip piles, fungal growth was extensive and fast whereas in the chunk piles, the extent of fungal activity was generally lower. The ash content and calorific value before and after storage were not significantly different for both the chipped and chunked storage.

First Renewables Ltd. (2002) carried out an extensive research on the storage of wood chips. Willow chips were one of the fuels investigated. A Willow chip pile was constructed at a storage site in North Yorkshire. In-situ temperature measurements and regular sampling and testing were in place. Results showed that the pile's moisture content followed the average rainfall more or less, although natural drying did occur throughout the storage period taking the moisture content of the chips from 50% down to 30%. No clear trends were observed in both the ash content and calorific value of the chips with time in storage, reflecting no significant chemical degradation

A few storage experiments have also been carried out involving Willow being stored outdoor but in a covered environment. They were fewer in number compared to the outdoor uncovered ones described above.

In their work on the 'Influence of particle size and moisture content on tendency to bridge in biofuels made from Willow shoots', Mattsson and Kofman (2003) stored Willow in outdoor piles but covered with plastic. Gigler et al. (2000a) stored a large pile of Willow stems outdoor but covered the top with a thick impregnated cotton sheet.

Mattsson and Kofman (2003) investigated how particle size and moisture content impacts bridging in biofuels made from Willow shoots. The influence of cutting and storage method on the tendency to bridge was studied for chips and chunks made from 3 to 5 year old Willow shoots harvested in January and December. Shoots were cut with four different machines to produce five fuel

baskets with nominal particle length from 28 to 200mm, and stored outdoors, in central Jutland, Denmark, in 160 m^3 loose volume piles. Some piles were uncovered, some covered with plastic and two were sealed in an airtight silage plastic enclosure. The bridging tendency was measured at the end of May and September by determining the maximum width a "bridge" of fuel over a slot opening could be before collapsing. With a 500mm thick layer of fuel above the slot opening, the bridge width varied between 58mm for the small chips and 977 mm for the large chunks. Most of the variation was due to two fuel properties, the proportion of particles longer than 100mm and the moisture content of the fuel.

2.4.1.2 Indoor

The other storage environment considered in this report is indoor storage. In an effort to protect the biomass from the weather conditions, some power plants and other biomass end users often choose to store the fuel indoor. Indoor storage of Willow chips has been studied to a lesser extent than outdoor storage.

Gigler et al. (2000b) in their work entitled 'Forced convective drying of Willow chips', carried out both thin layer drying and deep bed drying as they stored the Willow in farm facilities for potato storage and drying. In thin layer drying, the Willow chips were stored in baskets with perforated bottoms, and dry air was blown up from the bottom at 20ºC and 60% humidity. In deep bed drying, the Willow was placed in potato boxes with perforated bottoms and ambient air was blown through the boxes from the bottom.

2.4.2 Storage of wood pellets

The majority of the work done on wood pellet storage has been on off gassing and emissions during pellet storage, with a lesser focus on changes in pellet properties as a result of storage.

Approximately 6 500 000 tonnes of wood pellets were consumed in Europe in 2007. 800 000 tonnes were shipped from Canada, mainly from British Columbia (BC). One of the issues related to the safe handling of wood pellets is excessive concentration of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and depletion of O_2 in storage tanks and shipping vessels. It is well known that all biomass gradually decomposes over time, both chemically and biologically, slowly releasing toxic and oxygen-depleting gases such as CO, CO_2 and CH_4 (Reuss and Pratt, 2000, Johansson et al., 2004, Arshadi and Gref, 2005). The off-gases from wood pellets have not been considered an issue until recently when incidents of injuries and even fatalities occurred among people who worked around large storage tanks and vessels. Gauthier et al. (2012) reports of two deaths that occurred within the space of about a year in wood pellet storerooms of private households in German-speaking countries and were investigated by forensic medical teams. Both victims died of carbon monoxide (CO) poisoning; one of the victims was a woman who was 4 months pregnant. Measurements at the scene detected life-threatening CO concentrations (7500 ppm, >500 ppm), which were not significantly reduced after ventilation of the storerooms as required by regulations

Kuang et al. (2008) investigated the concentration of CO_2, CO and CH_4 in sealed vessels containing wood pellets at different storage temperatures (range 20-55°C) and developed a kinetic model to link the emission rates to the temperatures. Five 45L metal vessels built with heating and temperature control equipment were used. The gas concentrations were measured using gas chromatography and were determined as a function of storage time and temperature. The temperature controlled tests were only carried out on wood pellets from British Columbia (BC). They were manufactured from fresh mill residues such as sawdust and shavings from pine trees. Furthermore a comparison between emissions from BC pellets and a European wood pellet was also performed in 2L aluminium containers. The European pellets were made from Scots Pine harvested in Europe.

The results from the temperature controlled tests showed that the rate of emission increased at first before reaching a plateau after a few days. As the storage temperature increased from 20°C to 55°C, the rate of emission increased rapidly. While the concentration of CO_2 remained highest throughout, CH_4 had the lowest concentration. A first order kinetic equation was developed to fit the dependence of emission rate on temperature, reflecting that chemical degradation is the main mechanism driving the emissions. An interesting finding was that the emission levels from the European pellets were significantly lower compared to those from the BC pellets.

Tumuluru et al. (2008) carried out a similar work in steel column reactors and thermocouples were positioned to monitor the pellet and headspace temperature during storage. The wood pellets were obtained from Fiberco Inc Vancouver. The range of temperatures studied was 30-50°C. Wood pellet properties were also determined before and after storage and the measurements included % fines, pellet density, bulk density and durability index. The emissions of CO (5000 ppm) and CO_2 (10000 ppm) were relatively high at room temperature, but these values increased exponentially when the storage temperature was >30°C. At a storage temperature of 50°C a maximum concentration of CO_2 of about 60000 ppm and CH_4 of 3000 ppm were observed, whereas in the case of CO the maximum concentration of 18000 ppm was observed at a storage temperature of 40°C. The formation of CO and CO_2 during storage at room and elevated temperatures can be due to auto-oxidation of unsaturated free fatty acids in the wood pellets initiated by temperature. The pellet % fines had significantly increased after storage at elevated temperature where a maximum of 0.96 % was observed. The bulk density and durability of the wood pellets decreased by about 60 kg/m^3 and 20% respectively when the storage temperature was increased to 50°C.

Tumuluru et al. (2007) investigated the off gassing of wood pellets at room temperature but at different pellet moisture contents. The wood pellet properties measured were pellet density, specific density, porosity, bulk & tapped density and durability. The reactors were filled with wood pellets and

were insulated to prevent any loss of heat. The gases were collected for every 15 days of storage using gas sampling bags with help of a vacuum pump. The gases were further analysed using Gas Chromatography. Results indicated the emission of CO was considerable and reached 800-900 ppm, CO_2 around 1800 ppm and CH_4 was around 25 ppm. The temperature of the pellets during the complete storage period was around 19±1°C. Increasing the moisture content of the wood pellets from 3.6 to 10% by adding water resulted in an increase in temperature of the wood pellets by 3-4°C. At the end of 150 days of storage the pellet was very soft and around 70% dissolved which can be mainly attributed due to change in the moisture content during storage.

An even more detailed study by (Kuang et al., 2009a) investigated the effects of temperature, moisture and headspace ratio on the emissions from wood pellets in an enclosed space. The wood pellets were supplied from a pellet mill in British Columbia and they were made from fresh pine sawdust and shavings from mountain pine. Twelve 10L plastic containers were used to study the effects of headspace ratio (25, 50, and 75% of container volume) and temperatures (10–50°C). Another eight containers were set in uncontrolled conditions of storage relative humidity (RH) and temperature. Concentrations of CO_2, CO, and CH_4 were measured by gas chromatography (GC). The results showed that storage temperature has a greater impact on the emissions of CO_2, CO, and CH_4 from stored wood pellets than relative humidity which in turn has a greater impact that relative volume of headspace. Higher peak emission factors are also associated with higher temperatures. Increased headspace volume ratio increases peak off-gas emissions because of the availability of oxygen associated with pellet decomposition. Increased RH in the enclosed container increases the rate of off-gas emissions of CO_2, CO, and CH_4 and oxygen depletion.

Kuang et al. (2009b) investigated how the storage characteristics can affect the off-gas emissions from wood pellets in storage. In their work, wood pellets were stored in metal containers with different headspace to container volume ratios and different initial oxygen levels. The results showed that higher

headspace ratios resulted in higher peak emissions and emission rates. Lower O_2 levels gave lower CO and CO_2 emissions at room temperature but methane emission was independent of O_2 levels. Replacing O_2 with inert gases was found to be an effective method to reduce biomass degradation and toxic off-gas emissions. Ventilation can also reduce the concentration of unwanted gases.

Yazdanpanah et al. (2013) investigated whether the concentration of these emitted gases and the available oxygen within enclosed wood pellet spaces can reach flammable levels. Glass jars filled to 75% volume with pellets were sealed and placed in controlled environments at 25, 40 and 60°C for a period of 9 weeks. Each batch of the stored pellet had a moisture content of 4%, 9%, 15%, 35% or 50% (wet mass basis). The concentrations of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), nitrogen (N_2) and hydrogen (H_2) were determined using gas chromatography. The flammability of the gas mixtures in the container headspace was calculated using ISO 10156 Standard 'Gases and gas mixtures—Determination of fire and oxidizing ability for selection of cylinder valve outlets.' It was concluded that the composition of the gas mixture does not reach flammable concentrations under all experimental conditions

The papers cited above focus on the emissions of CO_2, CO and CH_4 from wood pellet storage. However there are a number of other compounds which are released and the next two papers cover a few examples of that.

Granstrom (2010) measured the emission of monoterpenes and aldehydes during the storage of undried and dried sawdust from Pine and Pine pellets. The storage took place under controlled laboratory conditions and the volatile species identified using Gas Chromatography Mass Spectroscopy (GCMS). The concentration of terpenes in undried sawdust dropped significantly in the first days of storage, with only 10% of the original content present after 10 days. For the dried sawdust, two thirds of the terpenes which were present after drying were emitted in the first 10 days of storage. During the first 10 days, no

aldehyde emission was observed. As the terpenes emissions decrease after 10 days, the aldehyde (hexanal) emissions start to increase, reaching a maximum at 40-50 days. For pellets, the emission of hexanal was consistently higher than the emissions of terpenes and reached its maximum after about 1 month. The wood was low emitting regarding both terpenes and hexanal after 2 months for undried sawdust, 2.5 months for dried sawdust, and about 3 months for pellets.

The above mentioned papers mostly relate to small scale laboratory based tests. There has also been work carried out on a larger scale, as reported in the papers below:

Svedberg et al. (2004) studied the emissions of volatile compounds (hexanal and CO) from small and large scale wood pellets storage. Air sampling was carried out with FTIR and adsorbent sampling in a range of places at varying scales including pellet warehouses, domestic storage rooms, lumber kiln dryers and experimental set ups. The measurements showed that in the pellet warehouses, the dominant organic compounds were aldehydes (50-60 % by weight), acetone (30-40% by weight) and methanol (10% by weight). A maximum aldehyde reading of 457 mg/m^3 was recorded at the surface of a pellet pile. Hexanal (70–80% w/w) and pentanal (10–15% w/w) dominated, but acetone (~ 100 mg/m^3), methanol (~ 25 mg/m^3) and carbon monoxide (~60 mg/m^3) were also present.

The domestic storage facility was a closed and passively ventilated bin and emissions were shown to rise with increasing temperature, with similar compounds being identified. Aldehyde levels of ~ 100 mg/m^3 and carbon monoxide levels of ~ 130 mg/m^3 were recorded. Elevated levels of hexanal (0.084 mg/m^3) were recorded inside domestic houses and 6 mg/m^3 in a room next to an inadequately enclosed storage area. Experimental laboratory studies confirmed the findings of the field studies. A field study of the emissions from industrial lumber drying also showed the formation of aldehydes and carbon monoxide. From this study, it was concluded that high concentrations of hexanal and carbon monoxide could be associated with storage of wood pellets

and could constitute an occupational and domestic health hazard. The results from lumber drying showed that the emissions of hexanal and carbon monoxide were not limited to wood pellets but were caused by general degradation processes of wood, facilitated by drying at high temperature.

All the above references focus on the emissions from wood pellets storage. There has been, but to a much smaller extent, work done to measure the changes in the pellet properties as a result of storage. The next paper covers these a bit more.

The work carried out by (Lehtikangas, 2000) was by far the most comprehensive study done on the storage of wood pellets and the extent of degradation during storage. Nine different types of pellets made from fresh and stored sawdust, bark and logging residues were used in this study. The pellets were all made in the same press to 6mm diameter and produced without additives. Each pellet type was cooled and then placed in two large plastic bags which were manually tied at the top and placed on a pallet for storage. Storage took place in an unheated barn for 5 months from December to May. A very extensive range of tests were carried out including moisture content, ash content, heating value, hydrogen content, pellet length, bulk density, durability, temperature at the middle of bag, water absorption resistance and particle size distribution. The main trends observed in the results are summarized below:

- The different types of pellets all showed a tendency to equilibrate to a moisture content of about 11%
- No significant changes were observed in the bulk density, individual pellet density, ash content and calorific value of the different pellets. The differences observed could be attributed to sample variations.
- No temperature surges were observed in the middle of the bags with the average temperature being a few degrees C above ambient in most cases

- Storage resulted in breaking up of the pellets, as reflected in the reduced pellet length. Furthermore the pellet durability was reduced during storage

Other authors have researched how storage affects pellet properties but used raw materials other than wood in the pellets manufacture. For example, Fasina and Sokhansanj (1996) studied the storage and handling characteristics of Alfalfa pellets. The measured properties included moisture content, moisture absorption, angle of repose, bulk density, angle of internal friction and airflow resistance. The results showed that moisture content and fines concentration have significant impact (linear correlation) on the bulk storage and handling properties of alfalfa pellets. As the moisture content increased, the pellet bulk density decreased and the angle of repose increased. In addition, the moisture absorption by the pellets is dependent on the relative humidity but independent of temperature. In humid conditions, the pellets went through a 30% increase in volume.

The last paper in this section by (Larsson et al., 2012) investigated the temperature trends in large scale wood pellet silo storage. Over a period of 7 months, temperatures were monitored in six large scale silos (~ 4500 tonnes) and each silo had 124 temperature sensors mounted evenly throughout the storage space. The study took place in a harbour in North Vancouver. Throughout the trial, the silos were emptied and filled several times to create a variety of storage scenarios. The maximum measured pellet temperature was recorded as 69°C. When silo temperatures were rising continuously from lower to higher levels and a further temperature increase considered hazardous, the respective silo was discharged. The temperature patterns were influenced by the loading and unloading regimes, ambient conditions (temperature and relative humidity) and pellet characteristics. The main conclusions from this work were as follows:

- Pellet temperatures increased with time in storage and from the bottom of the silos to the top

- The maximum rate of temperature increase observed was 2.4°C/h near the top of a silo
- In some scenarios, the silo temperatures rose uncontrollably and the silos had to be emptied to eliminate the risks of fire

To reduce the risk for condensation of moisture from the ventilation air on the stored pellets, fan operation could be based on dew point calculations and pellet temperatures.

2.5 Biomass property changes during storage

In this section, the testing methodology to measure biomass degradation during storage is described. While storage of Willow chips and pellets are mentioned, they would not be the exclusive fuels focused on in this section. The main aim this section is to cover a comprehensive range of testing methods and therefore the range of fuels is wider. This part of the literature survey was carried out so that an informed decision on the selection of test methods for this work could be made. The section is divided into:

◊ Chemical property changes
◊ Biological property changes
◊ Mechanical property changes

2.5.1 Chemical property measurement related to storage losses

Below are listed the main chemical properties of biomass fuels which have been measured and considered important during biomass storage. Emphasis here will be on the experimental techniques and methods used to measure these properties. Therefore, only papers which detail out experiments will be discussed in detail.

2.5.1.1 Moisture

Moisture is considered an important property of biomass fuels as moisture can affect combustion, gasification and the higher the moisture, the lower the combustion efficiency and hence calorific value of the fuel. High moisture also promotes physical degradation and microbial growth, both of which are undesirable. Moisture measurement during storage experiments has been reported by many authors and a few examples are given here. After Gigler et al. (2000a) erected piles of Willow stems, samples were regularly taken from the top, middle and bottom rows at regular intervals for moisture determination by oven drying at 105°C for 72 hours. The moisture measurements taken over time, at different locations in the pile, showed that the piles dried uniformly throughout, except at the top.

Jirjis (2005) also measured moisture contents by oven drying his biomass samples at 105 ± 2°C, immediately after sampling. In his work entitled 'Storage effects on pelletised sawdust, logging residues and bark', Lehtikangas (2000) stored wood pellets in plastic bags. In order to measure the moisture content, eight 1 kg samples from two of the bags were oven-dried at 103°C to constant weight. Two samples representing the top surface area in the bags were also taken and tested. Nolan et al. (2009) also used an oven drying method when determining the moisture of Miscanthus. The oven drying method for moisture determination appears to be a well-established method. It was used by (Shinners et al., 2007) as well in their work with corn stover. Samples were placed in plastic bags, transported to a laboratory, size reduced in a laboratory chopper, and the entire subsample oven dried at 103°C for 24 h. Nixon and Bullard (2003) dried Miscanthus at a lower temperature of 80°C when determining the moisture content and the lower temperature was possibly chosen due to the high volatile content of Miscanthus.

Research experiments on moisture show that after the piles have been in storage for several months outdoor, their moisture levels drop. This reflects natural drying and was shown in the work of (Jirjis, 1995), (Lehtikangas,

2000), (Pettersson and Nordfjell). The amount of rainfall is a key factor in the extent of drying. Results from the work of work of (Jirjis, 1995) of freshly harvested summer dried logging residues with and without cover, show that the moisture reduction from 43% is higher in the covered bundles (26%) compared to the uncovered ones (30%). This trend was also demonstrated in the work of (Pettersson and Nordfjell) on compacted young birch trees and uncompacted and compacted logging residues

2.5.1.2 Weight/Density

The weight of the fuel, measured before, during and at the end of storage, can determine moisture level variation but on a dry basis, can be used to determine dry matter loss.

In their work on 'Natural wind drying of Willow stems', Gigler et al. (2000a) placed one of the piles on a frame with load sensors and the weight of the pile was recorded every hour. Load sensors were then used again by (Gigler et al., 2000b) when experimenting on Willow chips. Monti et al. (2009), when carrying out storage experiments on switchgrass bales, measured the weight of each bale weekly using an electronic load cell. Sanderson et al. (1997) also measured the weight of switchgrass bales using an electronic load cell and weighing was carried out after 3.25, 6.5, 13 and 26 weeks of storage.

2.5.1.3 Dry matter

It is important for biomass fuels to retain their dry matter during storage and handling. Any decrease in dry matter would result in a drop in calorific value and hence energy content of the fuel. Dry-matter loss, which is the degradation of lignin, cellulose, and hemicellulose, occurs when wet woody biomass, in any form, is not utilized immediately. The extent, to which dry-matter loss occurs, is largely dependent on the material moisture content. Woody biomass having higher moisture content is more susceptible to colonization by fungi and mould and at a faster rate. These microorganisms, via metabolic activity,

generate heat which in turn accelerates oxidation, moisture adsorption, hydrolysis, pyrolysis and other chemical processes resulting in dry-matter loss. Dry matter loss turns out to cause a reduction of overall energy content as well as leading to an increase fuel's ash content (Lopez et al.).

Dry matter and moisture measurements were very similar and closely linked together in a lot of papers. A few people, in their work on biomass storage, have measured dry matter or dry matter loss specifically and separately from moisture content. A few of these experiments are described below.

In their work on 'Biomass losses during harvest and storage of switchgrass', Sanderson et al., (1997) determined dry matter by removing 50 to 75 cm from the end of each bale to expose the unweathered layer and the visibly weathered layer. A 300 to 500g subsample from each of the layers was dried at 55°C over 48 hours to determine dry matter.

In section 2.5.1.1 above, the oven drying method was described for moisture content determination. Dry matter loss can also be determined using the oven drying method. Biomass samples are taken at different times and dried thoroughly to remove all the moisture and then the dry weight is measured. From the difference in dry weight of biomass samples taken at different times, the dry matter loss can be calculated. This was done by (Shinners et al., 2007).

2.5.1.4 Heating value

The heating or calorific value of a fuel is also an important chemical property which should be retained during storage. A rise in moisture content, microbial activity and chemical fuel degradation can all decrease the calorific value of a biomass fuel. Below are a few techniques which have been used in previous work to measure heating value:

Heating value was determined using a bomb calorimeter in the work of (Jirjis, 2005)

In the work of (Lehtikangas, 2000), the gross calorific heating value (HHV) in MJ/kg was also determined by using a bomb calorimeter (LecoAC-300). The effective heating value (LHV) (net calorific value) was calculated by correcting HHV (gross calorific value) by the heat energy required to vaporise water due to hydrogen released during combustion:

$$LHV = HHV - (2.45 \times 9 \times H \times 0.01) \qquad [Equation\ 1]$$

The hydrogen content values (H) used in calculations are based on the literature data: sawdust assortments: 6.38% dry weight bark assortments: 5.72%; fresh logging residues: 6.11%, and stored logging residues: 6.14%

Pettersson and Nordfjell also used a bomb calorimeter to determine the gross calorific value of the biomass samples and from it, all the other calorific values were determined

More recently, Nolan et al. (2009) in their work on storing Miscanthus bales, also used a bomb calorimeter set up in the lab to determine the higher heating value (gross calorific value) (HHV) of the samples. The values were then adjusted to take into account the moisture content (MC) of the bales at sampling and hence the lower heating values (net calorific value) (LHV) were determined as shown below:

$$LHV\ (MJ/\text{kg}) = HHV \times \left(1 - \frac{MC}{100}\right) - \left(\frac{4.18 \times MC}{100}\right) \qquad [Equation\ 2]$$

The Miscanthus bales were stored in three storage environments as follows: outside uncovered, outside covered with heavy duty poly-urethane caps and inside an open sided barn. From the change in properties of the Miscanthus in storage over time, it was concluded that the natural ventilation with ambient air is enough for the drying of bales. It was also concluded that while covered storage with tarpaulin is cheaper than roofed structures, it is equally as effective for storage and drying. However, it was recommended that covered

storage is essential to guarantee a year round supply of dry, high quality Miscanthus

A number of calculation methods have been developed to determine the calorific value of biomass and other solid fuels. The following papers describe a few of the most widely used ones:

Parikh et al. (2005) described how proximate analysis was used to determine the higher heating value of solid fuels

Sheng and Azevedo (2005), in their work entitled 'Estimating the higher heating value of biomass fuels from basic analysis data, also describe how correlations could be determined for the heating value of biomass using the proximate, ultimate and chemical analysis data. They discussed in their work how ultimate analysis provides higher accuracy than proximate analysis when determining HHV for solid fuels, but how ultimate analysis also uses a lot more expensive and advanced equipment and requires higher a level of training. They proposed two equations for calculation of HHV from proximate and ultimate analyses respectively and they are shown below:

$$HHV\ (MJ/kg) = 19.914 - (0.2324 \times Ash) \qquad [Equation\ 3]$$

$$HHV\ (MJ/\text{kg}) = -1.3675 + 0.3137\text{C} + 0.7009\text{H} + 0.0318\text{O} \qquad [Equation\ 4]$$

C, H and O are the content of carbon, hydrogen and oxygen in weight %

2.5.1.5 Ash content

Biomass ash has the potential of causing a number of issues such as (Doosan Babcock Energy, 2007):

- ◊ Slag deposits in furnaces

- ◊ The formation of bonded ash deposits and accumulations of ash materials at lower temperatures on surfaces in the convective sections of boilers
- ◊ Increased metal corrosion and erosion
- ◊ Formation and emission of aerosols and fumes
- ◊ Drop in performance and efficiency of flue gas treatment process
- ◊ Handling and disposal of ash residues

Therefore there have been a few studies carried out to monitor the variation in ash content with storage conditions. Jirjis, (2005) determined the ash content of Willow samples using the SS 18 71 71 standard (Svensk Standard. Biobranslen-Bestamning av askhalt (Biofuels-Determination of ash content)). This seems to be a well known and used method for determining ash content in solid fuels. It is a standard European method whereby the fuel is combusted at 550°C until loss of ignition and the unburned ash quantity determined. Obernberger and Thek (2004) andLehtikangas (2000) used the same method when calculating the ash content in samples of sawdust, logging residues and bark.

In his work on storing pelletised sawdust, logging residues and bark, Lehtikangas (2000) concluded that ash content did not change significantly over the 5 months of storage. Pettersson and Nordfjell measured the ash contents of young compacted birch trees and logging residues and as would be expected, the ash content was higher in the logging residues (1.6-2.2%) than young trees (1-2%).

2.5.1.6 Thermogravimetric analysis (TGA)

TGA has been used to measure chemical properties of coal and understand the combustion mechanisms and characteristics. It is now being used for biomass analysis as well. One application of the two technique from available literature is described briefly below:

Biagini et al. (2006) studied the devolatilisation of biomass fuels and identified the components using thermogravimetric analysis followed by Fourier transformed infra-red spectroscopy (FTIR). TGA accurately measures weight change and can be used to study the devolatilisation of biomass fuels and biomass components and to investigate the kinetics of the thermal decomposition of biomass and combustion of the resultant chars.

The determination of moisture, volatile and ash content constitutes the proximate analysis of the fuel. Proximate analysis has routinely been carried out by the determination of each of the moisture, volatile and ash content of the biomass separately using the following standard methods (Table 2-1):

Table 2-1. British standard methods for fuel characterisation

BS EN 14774-1:2009	Solid biofuels - Determination of moisture content - Oven dry method. Total moisture: Reference method
BS EN 14774-2:2009	Solid biofuels - Determination of moisture content - Oven dry method. Total moisture: Simplified method
BS EN 15148:2009	Solid biofuels. Determination of the content of volatile matter
BS EN 14775:2009	Solid biofuels. Method for the determination of ash content

However, TGA can also be used to determine the moisture, volatile and ash contents in a single multi step test. The test is described for coal by (Thermal analysis instruments, 2012). The temperature is increased in stages followed by an isothermal stage during which each of drying, devolatilisation and combustion take place. The gas is changed from nitrogen to air/oxygen for the final stage which is combustion.

2.5.2 Biological property measurement related to storage losses

Microbial growth in piles of biomass fuels needs to be monitored and controlled for several key reasons. Microbial activity results in decay and loss of combustible matter. Also, high level of spores can be a health and safety

hazard and could cause respiratory and skin issues. Jirjis (1995), in his work on 'Storage and drying of wood fuel' using Birch and Willow chips, explains how fungal growth in wood chips is the major cause of initial heat development in the pile, which can then promote more fungal growth and lead to higher temperatures in the pile, which could in turn give rise to self ignition of the pile. In order to promote heat dissipation and eliminate the risk of self-ignition, a ventilated tunnel was placed underneath the 7 metre high pile. This pile was then compared with a similar one, but without the ventilated tunnel. The results showed that the ventilated tunnel did promote heat dissipation as the pile temperatures were lower and the moisture level was also reduced. However, the cooler temperatures were ideal for the establishment and the growth of various species of microfungi, which are not thermally resistant. In the same work by (Jirjis, 1995), fungal activity is higher in small Birch chips than in larger ones, because of larger area of exposure and contact. Similarly, when Willow chips was compared with Willow chunks, the former showed larger number of fungal spores than the latter.

There are a few methods detailed out in literature on how to assess the extent of microbial growth on biomass in storage. A few papers mention monitoring the number of spores of the different types of fungi/bacteria/microbes, so counting the spores had to take place. In the work of (Monti et al., 2009) on sheltered bales of switchgrass, the count of spores showed that as the moisture content decreased, the microbial activity also decreased. This showed that moisture is necessary for microbial growth.

First renewables Ltd. (2002) in their work on Willow chip and forestry residue storage on a large scale measured the spore levels in the air around the piles. Emphasis was on the thermophilic actinomycetes and Aspergillus Fumigatus. Furthermore the piles were disturbed at the end of the storage trial to simulate handling operations. Throughout the experiments, the levels (194 colony forming units/m3) were within the Health and Safety guidelines.

There has also been work carried out on the changes to wood after biological activity. Gelbrich et al. (2008) studied the chemical changes in wood degraded by bacteria and fungi. The wood investigated was from foundation piles and archaeological wood from 21 sites. The wood samples were ground through a cutting mill Retsch SM 2000 to obtain a uniform particle size distribution and then the following tests were carried out: C/N analyses, FTIR spectroscopy, determination of ash and elemental content. It was found that with increasing decay (observed under microscopy), the lignin concentration increases, along with the nitrogen and phosphorus contents. Due to the ability of the microorganisms to degrade mainly polysaccharides, the hemicellulose and cellulose content decrease with increasing decay. The amount of phenolic compounds in waterlogged wood was considerably lowered, whereas the ash content increased due to the very long water storage conditions.

Vane et al. (2005) researched the decay of cultivated apricot wood by the ascomycete Hypocrea sulphurea, using solid state 13C NMR and off-line TMAH thermochemolysis with GC–MS. Samples of fresh and decayed apricot wood were cut from the branch of a living tree near Cranberra, Australia. The bark was removed by scalpel, and native sapwood from an uninfected section of the branch and a block of decayed sapwood from underneath the fruit body was extracted, freeze-dried and then pulverised using a ball mill. The fungus was identified on the basis of morphology of the ascocarp; the size, shape and colour, as well as ostioles bearing a striking similarity to photographs in a field identification guide. ^{13}C NMR was also performed on fresh and degraded wood samples. Results showed that the fungus H. sulphurea did not decompose appreciable amounts of polysaccharides. The tannins observed in the native wood may have inhibited other parasitic fungi of the Basidomycota and enabled the H. sulphurea to colonise the apricot wood. The aromatic sub-structures of tannins were decayed by the fungus. Lignin decomposition occurred. The decay patterns observed in this work suggest that H. sulphurea is not as an aggressive decomposer as white-rot fungi.

Vane et al. (2006) then studied the decay of bark by the white rot fungus Lentinula edodes. The work followed a very similar sample preparation and testing methodology as above. The NMR analysis showed that the cellulose and xylans were the main structural components of fresh bark but that L. edodes caused a 46% decrease in polysaccharide content and that loss of crystalline and non-crystalline cellulose regions occurred in parallel. The bark lignin, on the other hand, showed resistance to the fungus.

The occurrence of fungal activity during the storage of biomass can have occupational health implications. Schlunssen et al. (2010) studied the effects of biofuels on the respiratory health of energy plant workers in Denmark. Respiratory symptoms in 138 woodchip workers, 94 straw workers and 107 control workers from 85 heating or combined heating and power plants were gathered by questionnaire. Spirometry, metacholine provocation tests and skin prick tests were performed on 310 workers. The work area concentrations of 'total dust', airborne endotoxin, cultivable Aspergillus fumigatus and cultivable fungi were measured at each site. Personal exposure was calculated from the time spent on different tasks and average work area exposures. Results showed that working with biofuel at an energy plant does not generally enhance the prevalence of respiratory symptoms. However, the exposure level to micro-organisms has an impact on the occurrence of respiratory symptoms among biofuel workers.

2.5.3 Mechanical property measurement related to storage losses

Most of the available papers relate to the pellet quality tests and pellets comparison after manufacture. They are not directly focused on mechanical property changes as a result of storage. The common mechanical property measurements reported in existing literature are: durability, dust concentration, fines content, compression strength, bulk and pellet density, particle size distribution. One paper mentioned impact resistance and another milling energy requirement. There is one paper (Wu et al.) which also describes the

large scale annular shear test, the linear wall friction test, angle of repose test and attrition test.

Each of the most commonly used above mentioned tests will be briefly described below:

2.5.3.1 Pellet durability

This section will demonstrate that a wide range of methods have been used for durability testing.

Temmerman et al. (2006) carried out a comparative study on different test methods to measure the durability of pellets and briquettes. 5 briquettes and 26 pellets were used in the experiments. For briquettes, different rotation numbers of a prototype tumbler and a calculated durability index were compared. For the pellets, a tumbling device according to ASAE S 269.4, the Lignotester according to O¨ NORM M 7135 and a second tumbling method with a prototype tumbler were compared. The results showed for both pellets and briquettes, the durability values and their variability were influenced by the testing method. Moreover, the variability of the results depended on the biofuel itself.

Samuelsson et al. (2009) in their work on how the biomaterial affects the pellet quality, determined durability using a LignoTester (LignoTech Sweden AB). Tumbling was induced by air pressure and tumbling time was two cycles of 30 s each. The percentage of oversize to total sample weight when sieved through a 3.15mm sieve was the pellet durability.

Kaliyan and Vance Morey (2009) used the tumbling can method, the Holmen tester and the LignoTester. Tumbling can method is used to estimate the pellet quality in terms of pellet durability index (PDI), or, simply percent durability. This test mimics the mechanical handling of pellets and estimates the possible fines produced due to mechanical handling. During tumbling, pellets abrade and produce fines due to impact, and shearing of pellets over each other and

over the wall of the tumbling can. After tumbling 500 g of pellets for 10 min at 50 rpm, the pellets are sieved using a sieve size of about 0.8 times the pellet diameter. The PDI or durability is calculated as the ratio of weight after tumbling over the weight before tumbling, multiplied by 100. A detailed procedure can be found at ASABE Standards. Other authors who used the ASABE standard include (Sultana and Kumar, 2012).

The Holmen durability tester simulates pneumatic handling of pellets. The Holmen pellet durability tester pneumatically circulates a sample of pellets through a square conduit of pipe or tubing with right-angled bends, and the pellets are impacted repeatedly on hard surfaces. When pellets strike the right angle corners of the tester, they fracture. The sample circulation time is in the range 30–120 s. The remaining pellets are collected, sieved with sieve size of about 80% of the pellet diameter, weighed, and the PDI is calculated. The Holmen tester only requires 100g of sample.

The Ligno tester uses air to rapidly circulate 100 g of pellets around a perforated chamber for 30 s. The chamber is an inverted square pyramid with perforated sides. Forced air is the destructive force. The chamber is set at 60 mbar pressure. Fines are removed continuously during the test and there is no need to screen the pellet. Based on this standard, 100 g of pellets are exposed to an air stream of 70 mbar for 60 s, and the percentage of fines that pass through a 3.15-mm sieve is taken as the measure of durability.

Carone et al. (2011) used the method in the technical specification UNI CEN/TS 15210-1:2006 for testing the mechanical durability of pellets. The method exposes a 500 g pellet sample to controlled shocks by collision of pellets against each other and against the walls of a defined rotating chamber. The rotation speed is fixed to (~50) rpm for 500 rotations. The durability is calculated from the mass of sample remaining after separation of abraded and fine broken particles.

Gil et al. (2010), in determining pellet durability, placed samples of 40 pellets in a rotating drum with an internal diameter of 130 mm and a depth of 110 mm. The drum was equipped with two opposite inner baffles arranged perpendicular to the cylinder wall. The rotation speed was set at 35 rpm. Each pellet sample was analysed after 3000 revolutions. The sample material was then screened using a 2 mm sieve. Particles smaller than 2 mm were then weighed. The abrasion index was calculated as the mass percentage of pellets below 2 mm relative to the total initial sample mass after 3000 revolutions in the rotary drum.

Samuelsson et al. (2012) used a pellet tester (Q-tester, Simon Heesen BV, Netherlands) according to the CEN standard 15210. Filbakk et al. (2011) and Carroll and Finnan (2012) used the same method in their studies.

Theerarattananoon et al. (2011) determined pellet durability according to ASABE Standard S269.4 (2007). A sample of pellets was sieved at 3.36mm to remove fines. A 100-g sample of sieved pellets was tumbled at 50rpm for 10 min in a dust-tight enclosure. After tumbling, the sample was removed and sieved, and the percentage of whole pellets was calculated using the following formula:

$$Durability = \frac{Mass\ of\ pellets\ after\ tumbling}{Mass\ of\ pellets\ before\ tumbling} \times 100 \qquad [Equation\ 5]$$

2.5.3.2 Compression strength

There are an increasing number of papers in which the internal strength testing of pellets is mentioned.

Kaliyan and Vance Morey (2009) defined compressive resistance (or hardness or crushing resistance) as ‘the maximum crushing load a pellet/briquette can withstand before cracking or breaking’. The compressive resistance test is described by placing a single pellet between two flat, parallel surfaces which

have facial areas greater than the projected area of the pellet/briquette. An increasing load is applied at a constant rate, until the test specimen fails by cracking or breaking. The load at fracture is read off a recorded stress–strain curve, which is the compressive strength and reported as force or stress. Compressive resistance test simulates the compressive stress due to weight of the top pellets on the lower pellets during storage in bins or silos, crushing of pellets in a screw conveyor, and crushing. The Kahl tester, Stokes tester, Schleuniger tester, tablet hardness tester, universal testing machine (Instron), and Kramer shear strength tester have been used to measure the compressive strength of the densified products (Benke, 1994), (Franke and Rey 2006), (Thomas and Van der Poel, 1996) and (Tabil, 1996).

Stelte et al. (2011) determined the internal strength of a number of different biomass pellets by compression testing and measuring the force at break according to the method by (Nielsen et al., 2009). The pellets were placed horizontally in a compression tester (TT-CM, Instron, USA) using a disc shaped metal probe, 50mmin diameter, attached to a 50 kN load cell. The test was performed at a compression rate of 20 mm/min, and stopped after pellet failure. The average force at break and its standard deviation were calculated based on at least 5 tests per sample.

2.5.3.3 Particle size analysis

In the work of (Mani et al., 2004) on the grinding performance and physical properties of wheat and barley straws, corn stover and siwtchgrass, particle size analysis was carried out by placing a sample grind of 100 g was in a stack of sieves arranged from the largest to the smallest opening. The sieve series selected were based on the range of particles in the sample. The set of sieves was placed on the Ro-Tap sieve shaker (Tyler Industrial Products, OH). The sieving was carried out for 10 min. After sieving, the mass retained on each sieve was weighed. A similar method was used by (Mani et al., 2006).

Wu et al. (2011), in their work on the 'Physical properties of solid biomass' used the method described below for the particle sizing test. For all the test materials, ten 1L samples of materials were used. Sieving was carried out using 9 different sizes of sieves (ranging from 6.3 to 50 mm). The results were classified into sieve fractions (oversize), and the weight of each group was determined.

2.5.3.4 Bulk, pellet density and particle density

Temmerman et al. (2006) defines particle density as 'the ratio of the sample mass and its volume including pore volume'. The volume of the pellet is determined using the buoyancy method in liquid. The buoyancy method, along with the hydrostatic and paraffin coating methods, constitute the liquid displacement methods for the determination of particle density. In the buoyancy method, the apparent weight of the sample during submergence is determined; the buoyancy is the difference between the sample's weight in air and its apparent weight in liquid. The sample volume was determined by the difference between the mass of a sample in air and the mass of the same sample submerged in the liquid. The particle density (ρu) of the sample is calculated according to the equation below:

$$\rho u = \frac{(mu - ms)}{(mu - \rho w)} \qquad [Equation\ 6]$$

where ρw is the density of liquid at a given temperature, mu is the weight of the test sample in air and ms is the weight of the sample in liquid.

The SIS-CEN/TS 15103:2006 was used by (Samuelsson et al.) to determine the bulk densities (mass per unit volume) of biomass pellets. Mani et al. (2006) determined the bulk density of ground biomass samples using the grain bulk density apparatus. The sample was placed on the funnel and dropped at the centre of a 0.5 L steel cup continuously. The cup was levelled gently by a rubber-coated steel rod and weighed. Mass per unit volume gave the bulk

density of the biomass in kgm^{-3}. Theerarattananoon et al. determined the bulk density of pellets according to the ASABE standard S269.4 (2007). Pellets were poured into a cylindrical container from a certain height until the container overflowed. Net weight of the pellets was obtained by subtracting the weight of the empty container from the combined weight of the pellets and container. Bulk density was calculated by dividing the mass by the container volume. Reported values are the average of three measurements for each type of pellet. A similar method was used by (Wu et al., 2011). The determination of bulk density using the CEN 15103 was also mentioned by (Filbakk et al., 2011). Arshadi et al. (2008) used the Swedish standard method SS 187120.

Pellet unit density can be simply calculated from the pellet weight and dimensions (Stelte et al.).

2.6 How literature review impacted project scope and gaps which this thesis is addressing

The literature review provided a better understanding on the work which has been carried out on the degradation of Willow chips and wood pellets during storage. Furthermore, in the detailed literature survey, the range of measurement techniques and testing methods to characterise biomass degradation has been reviewed. This has enabled an informed assessment to be made on the methodology to be used in this project to measure chemical, mechanical and biological degradation of the different fuels during storage. The rationale for the chosen testing methodology is described in Section 3.1.
The literature survey also highlighted a number of gaps. For example, it showed that most of the previous studies on Willow chips and pellet storage have been focused on either one type of fuel or one storage environment or one type of degradation, for example chemical, mechanical or biological. The main gaps which were identified in the literature domain were as follows:

- Comparison between indoor and outdoor storage of Willow chips
- Studies on the degradation of thermally treated wood pellets during storage
- Studies on the degradation of white wood pellets during storage
- Comparison between more than one fuel type when stored in the same environments
- Studies where more than one type of degradation has been measured, for example chemical, mechanical, biological
- Comparison between summer and winter storage and thorough evaluation of weather effects on extent and type of biomass degradation during storage

The aim of this four year research project is to fill the above gaps through a fully encompassing storage project which would include more than one type of fuel, more than one type of storage environment, seasonal weather effects; and which would involve a very wide range of tests to investigate all of chemical, biological and mechanical degradation, as well as occupational health and environmental implications. This study should enable power generators to make an informed decision on the optimum storage scenario for each of the fuels investigated.

The fuel selection and experimental design and rationale are fully explained in Section 3.1

3 Methodology

This document covers the methodology of each of the experimental techniques used in the project investigating the effects of storage methods on the degradation of biomass fuels. A range of biomass fuels were stored in both indoor and outdoor stockpiles and monthly sampling and testing were carried out to measure the extent of degradation, characterised by changes in both mechanical and chemical properties. The first section in this chapter focuses on the experimental design and rationale which were based on the industrial relevance of this work.

3.1 Detailed experimental design

At power stations which use coal as a fuel, the coal is usually stored outdoor in stockpiles in the power station yard, prior to milling and combustion. It is therefore important to understand how biomass would store long term in an outdoor environment when continuously exposed to weather conditions. The extent of degradation (chemical, mechanical and biological) needs to be measured for biomass fuels of interest to energy users. In this study, the fuel choice was carried out in partnership with E.ON. Willow chips and thermally treated wood pellets were selected for outdoor storage. In order to understand the benefits of covered storage for these two fuels, Willow chips and thermally treated pellets were also stored in an open barn. But in 2010 when the project experimental was being out together, there was a lot of focus on white wood pellets as the most likely to be used biomass in co-firing with coal and dedicated biomass plants. Therefore a white wood pellet pile was also investigated in indoor storage in the barn.

At an early stage of the project, Coppice Resources Ltd were identified and approached as the supplier of the Willow chips for this work. They also supply Drax Power station and E.ON's Steven Croft. Their farms in Retford were visited as potential locations for the storage trials to be carried out. Other options were explored, for e.g. a few university owned sites. The Coppice Resources farm in Retford was chosen because of their staff's experience with fuel supply, delivery and handling. Also the Willow chips used in this project were grown and harvested at fields local to the farm. The farm staff assisted with the piles set up and deconstruction as well as with monthly sampling.

All the piles in this study were built on a concrete substrate. This was to match the outdoor environment in a coal stock yard. For the outdoor piles, slabs of concrete were joined together to provide the required area and for the indoor piles, the open barn had a concrete floor.

The main factor in choosing the sizes of the different piles at the start of Phase 1 was the quantity of thermally treated wood pellets shipped to E.ON from the American supplier. Based on the pellet availability, two 2.4x2.4x1.5m pellet piles were constructed in phase 1. In order to appreciate the differences in the extent of degradation between the surface and middle of the piles, it was desirable to have a minimum of 1m between the surface and middle of the piles. This led to the 2.4x2.4m base choice. And because of the angle of repose of the pellets, a 1.5m piles height was achieved. The same 2.4x2.4m base was chosen for the small Willow pile. But a height of 1.7m was achieved. The base size (3.8x3.8m) of the big Willow pile in Phase 1 was determined by the space available at the farm.

In phase 2, the same pile size was chosen for the outdoor thermally treated pellet pile and the white wood pellet pile as the phase 1 thermally treated pellet piles. For the Willow chips, the industrial partner decided to opt for the larger size.

In order to maintain the shape and size of the different piles, suitable enclosures were used. Metal gridded frames were used to enclose the Willow

chip piles. For the wood pellet piles, a permeable porous membrane enclosure was used to avoid pellets flowing through the holes in the metal grids.

As discussed in Sections 1.1.1 to 1.1.3, the chemical, biological and mechanical degradation of biomass fuels during storage can significantly affect the handling and combustion of the fuels. A comprehensive matrix of laboratory tests was put together in partnership with E.ON in order to characterise the chemical, biological and mechanical degradation. The test choices were influenced by equipment availability and experience and the feasibility of the tests within the time frame allowed for this work.

Figure 3-1 below shows all the different tests in sequential order and also the links between some of them. Each of the tests is described in sections 3.2 to 3.7. The frequency of the different tests listed in Figure 3-1 was driven by equipment availability and time constraints,

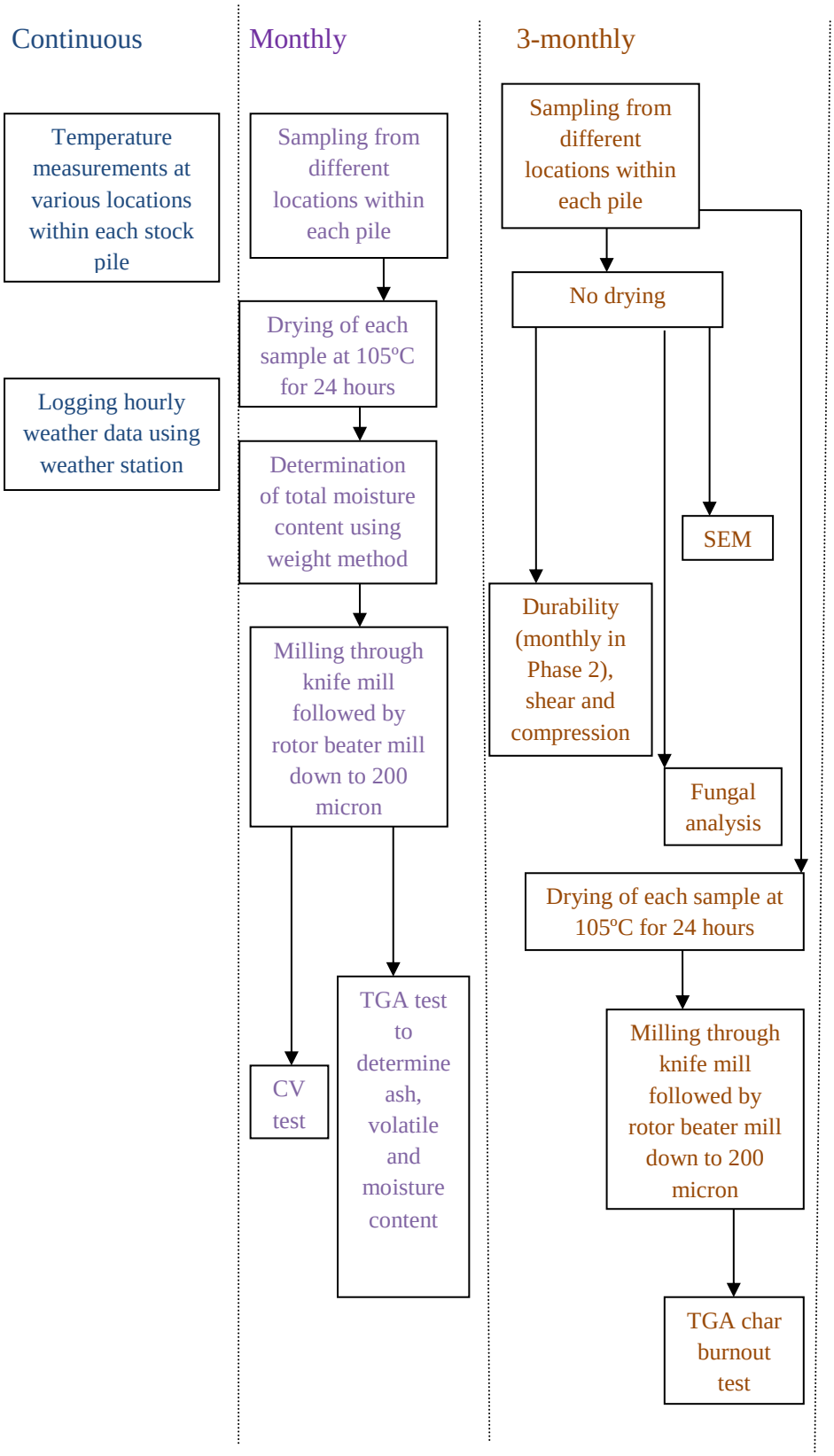

Figure 3-1. Flowchart of sequence of tests carried out on samples

3.2 Setting up storage piles

The stockpiles were all set up at the Coppice Resources farm in Retford [Coppice Resources Ltd]. The Willow chips were freshly harvested from the Coppice Resources Willow plantations. The white wood pellets were provided by E.ON and sourced from a storage facility at Ironbridge power station and the thermally treated wood pellets were sourced from an American supplier.

Table 3-1 below summarizes the piles of Phases 1 and 2 of the storage trials.

Table 3-1. Pile information

Period of storage	Fuel	Pile dimension	Pile location	Pile label
April to November 2011	Willow chip	3.8 x 3.8 x 2.5m	Outdoor	Big Willow
April to November 2011	Willow chip	2.4 x 2.4 x 1.7m	Outdoor	Small Willow
April 2011 to December 2012	Thermally treated wood pellet	2.4 x 2.4 x 1.5m	Outdoor	Outdoor pellet
April 2011 to December 2012	Thermally treated wood pellet	2.4 x 2.4 x 1.5m	Indoor	Indoor pellet
December 2011 to December 2012	Thermally treated wood pellet	2.4 x 2.4 x 1.5m	Outdoor	Outdoor pellet Phase 2
November 2011 to September 2012	Willow chip	3.8 x 3.8 x 2.5m	Outdoor	Outdoor Willow
November 2011 to September 2012	Willow chip	3.8 x 3.8 x 2.5m	Indoor	Indoor Willow
November 2011 to September 2012	White wood pellet	2.4 x 2.4 x 1.5m	Indoor	White wood pellet

The piles were set up on concrete slabs and while the Willow chip piles were enclosed by metal mesh frames, the pellet piles were enclosed by a permeable porous membrane (see explanation in Section 3.1 above. Before each pile was constructed, a thermocouple assembly was positioned at the centre of the frame/enclosure (more details on the assembly in section 3.2.1 below). The wood chips/pellets were delivered in bulk bags and then emptied out using a forklift to fill the frame/enclosure up to the desired height. The farm staff assisted with the construction of the piles. The wood pellet/chip flow out of the base of the bulk bag was controlled to ensure the thermocouple assembly stayed in place and no damage to equipment was incurred. Figure 3-2 to Figure 3-5 show each of the first four piles which constituted Phase 1 of the trial. The indoor pile was constructed in an open barn. The barn has three walls and one open side.

Figure 3-2. 3.8 x 3.8 x 2.5m Willow chip pile outdoor (Big Willow)

Figure 3-3. 2.4 x 2.4 x 1.7m Willow chip pile outdoor (Small Willow)

Figure 3-4. 2.4 x 2.4 x 1.5m thermally treated wood pellet pile outdoor

Figure 3-5. 2.4 x 2.4 x 1.5m thermally treated wood pellet pile indoor

3.2.1 In-situ temperature measurement and logging

Four locations within each biomass pile were selected for temperature measurement and logging throughout the storage period. Pile temperature was measured and logged at four locations within the pile. The four locations are shown in Table 3-2. Thermocouple locations within piles and Figure 3-6 below:

Table 3-2. Thermocouple locations within piles

Thermocouple	Position within pile
T1	10cm below pile peak
T2	Half way up centre of pile
T2	20cm up from base of pile, at centre
T4	20 cm up from base of pile, 20cm from edge

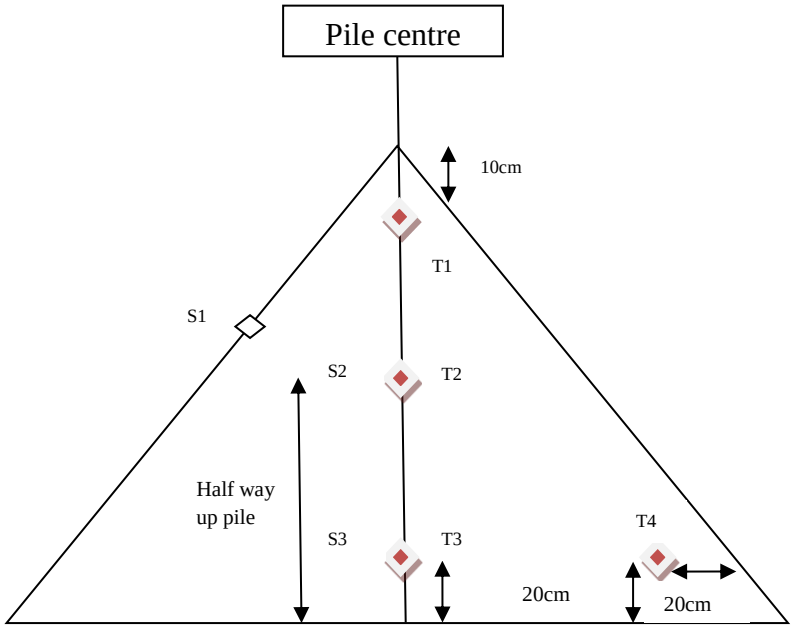

Figure 3-6. Thermocouple positioning (not drawn to scale)

However during pile construction, the planned pile height could not be achieved due to angle of repose and flowability of the different fuels. Due to the lower actual pile peaks, T1 was 10cm above the pile peak.

The thermocouples were all T type stainless steel mineral insulated sensors with pot seal, PVC insulated extension cables and miniature plugs. The sheath diameter was 6mm. T type (Copper vs. Constantan) operate within a temperature range of -185 to 400ºC

Each thermocouple assembly consisted of the four thermocouples threaded through plastic drain pipes and secured at the desired location using heavy duty tape. Figure 3-7 below shows one of the thermocouples secured in location, prior to being buried in the stockpile.

Figure 3-7

Cable exposure was kept to a minimum to ensure protection from wear. From the bottom of each pile, the cables were then run through flexible plastic pipes to the weather proof box where the data loggers were kept. In order to ensure that sampling did not interfere and cause damage to the thermocouple cables, these were run through one half of the pile only.

Figure 3-8 and Figure 3-9 below show the arrangements:

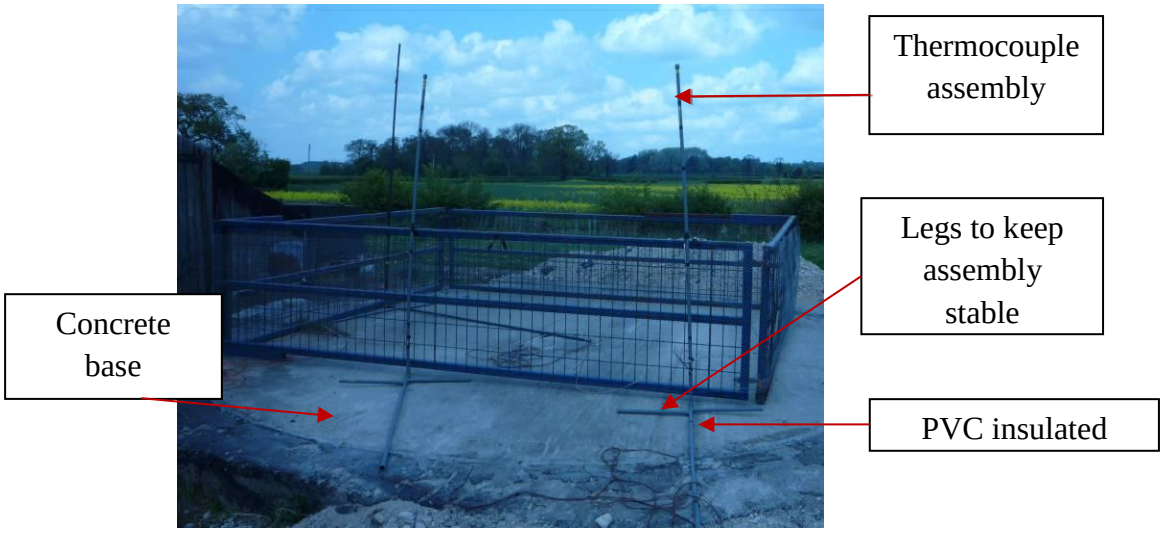

Figure 3-8. Frame and drain pipe assembly

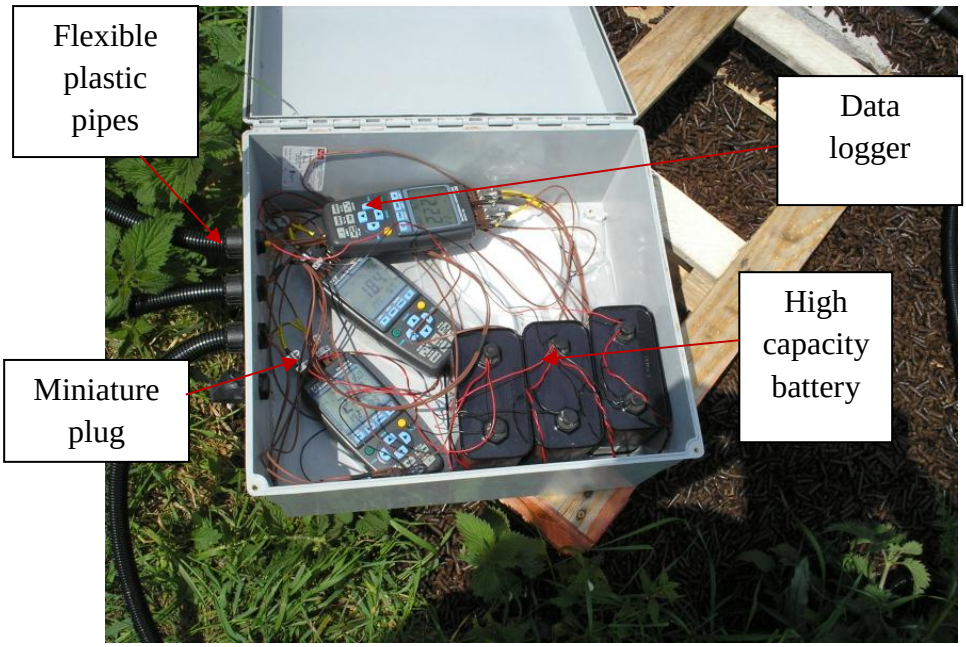

Figure 3-9. Plastic flexible pipes, protecting thermocouple cables and junctions with data loggers in weather proof box

The in-situ temperature data from the 4 thermocouples in each stockpile was logged on an hourly basis. Figure 3-9 above shows the weather proof box where the three data loggers attached to the thermocouples in the three outdoor piles were stored. Each logger was connected to a high capacity battery as shown in the picture. The data logger connected to the thermocouples in the indoor pile was stored in a plastic box in close proximity to the pile, with the same configuration as the outdoor piles.

Hand held YCT YC-747UD four channel data loggers with moulded rubber holster from TC Direct Ltd. (TC Direct Ltd) were used, with an accuracy of 0.1 ºC within a temperature range of -100 to 1300ºC. The sampling rate was set to hourly on each of the loggers. The time and date were set on the logger prior to starting the logging and the device logged hourly, the first date point being when the 'Rec' button was pressed. Hourly data included the temperature at the time it recorded and also the time and date at which the log took place. Data was downloaded by connecting the logger to a laptop/PC via a USB connector. The software 'Temp_Monitor S2', supplied with the logger, was used for downloading data

3.3 Weather monitoring

In order to fully investigate biomass degradation in storage, the impact of the weather had to be considered, especially in the outdoor storage scenarios. A weather station was therefore set up to monitor and log weather data throughout the duration of each storage trial. Figure 3-10 below shows the arrangement which consisted of a temperature and humidity probe enclosed in a radiation shield, wind speed and direction sensors mounted on a stand and a tipping bucket rain gauge which was placed on the ground. These were all set up outdoors. In the barn where the indoor pile was constructed, the base concrete floor temperature was also measured and logged hourly using a thermocouple. This was to investigate potential heat transfer between the concrete floor and the pellet pile.

Below is some information on each of the different sensors:

An MP100A temperature and relative humidity probe from Campbell Scientific (Campbell Scientific Ltd) was used to measure the ambient temperature and relative humidity. It was installed inside a shield for protection against radiation but also adverse weather for example hail and driving rain. The operating temperature range was -40 to 60°C and the operating relative humidity range was 0 to 100%. The accuracy for the humidity measurement was ± 1% within a range of 5-95% relative humidity, with a reproducibility of 0.5%. In terms of temperature, the accuracy was 0.5°C for the range of -40 to 60°C with a reproducibility of 0.1°C

A Didcot Instrument Ltd. tipping bucket rain gauge (DRC5 054) was used for rainfall measurement. Calibration was carried out on a laboratory scale by pouring a known volume of water slowly and carefully down the bucket and measuring the voltage and counting the number of pulses. This enabled a measured voltage to be converted to a number of pulses which is turn was converted to a volume of water. The mm per unit area was then determined by dividing the volume by the bucket's cross sectional area.

The wind vane was also from Didcot Instrument Ltd

The anemometer was an ELE International Ltd. product (DWR-205) with further information available at (DWR-205 ELE Environmental Ltd.). Accuracy was 2% and resolution 0.1 m/s.

The weather station is shown in Figure 3-10 below.

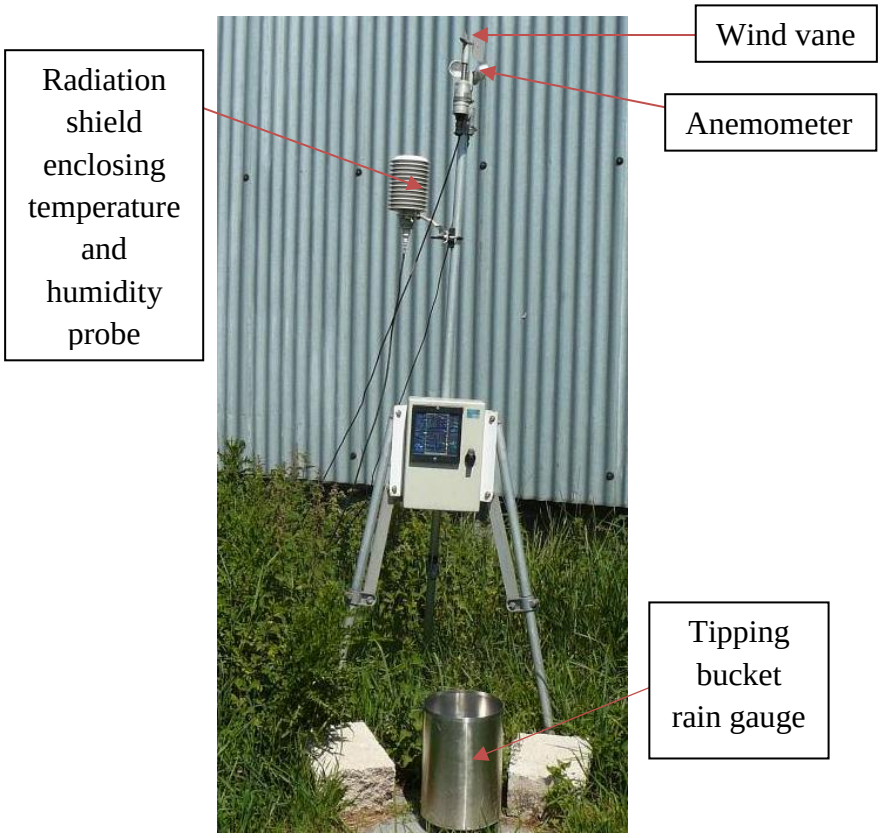

Figure 3-10. Weather station

The data measuring and recording was carried out by connecting each of the sensors to a CR10X Campbell Scientific data logger (Campbell Scientific CR10X). The logger measured the temperature, humidity, wind speed and direction every few seconds and generated a minutely and an hourly means. For the rainfall, the cumulative minutely and hourly values were calculated. Data was downloaded through the software 'PC 208W'. The logger is highly sensitive with an accuracy of 0.1% in a temperature range of -25 to 50°C and 0.05% in a temperature range of 0 to 40°C.

3.4 Monthly sampling

In weeks 1 and 2 of the trial, samples were taken only from the middle (half way up at the centre) of each pile for analysis. From the end of the first month onwards, sampling was carried out monthly but from 3 locations in each pile. Each sample consisted of approximately 500-600g of chips/pellets.

The 3 locations were:

- Surface of pile (S1)
- Middle of pile (half way up and at the centre) (S2)
- Bottom of pile at the centre (S3)

These locations were in the half of the pile opposite to the half where the thermocouple cables were threaded, to prevent damage to thermocouple cables during sampling (see Figure 3-6).

Sampling was carried out using a sampling probe which was designed and manufactured especially for this project. The probe was made of a polycarbonate material and 2m in length with internal and external diameters of 9.4cm and 10cm respectively. As shown in Figure 3-11, the sampling section only constituted a small part of the probe and was designed as a fully enclosed section with a trap door. It had an aperture of 6cm wide and 14cm long. A stainless steel rod and handle were connected to the sampling section. After the probe had been inserted to the right location inside the pile where sampling could take place, the handle was turned to open the trap door and allow sample to fall into the sampling section. The trap door was then closed again prior to the sampling probe being extracted out of the pile. The probe was also graded so that the depth reached within the pile could be monitored.

The sampling probe is shown in Figure 3-11 to Figure 3-14 below.

Figure 3-11. Probe full length

Figure 3-12. Grading on sampling probe

Figure 3-13. Aperture on probe and sampling section

Figure 3-14. Tip of probe

During sampling, high quality photographs of the piles and fuels were taken so as to enable visible changes in appearance in situ with time, for example change in colour, shape, form, texture, any mould formation, dust formation, presence of cracks

3.5 Biological characterisation (fungal analysis)

This part of the work was carried by Mologic UK Ltd (Mologic UK). Fresh samples and samples after 3 and 6 months in storage respectively, were analysed by Mologic for fungal count and identification. The samples were sent to Mologic UK without any drying or pre-treatment. Two samples from each pile were analysed, namely one from the surface, and one from the middle of the pile, halfway up the centre.

Mologic used the following procedure for analysis. Two to three grammes of each sample was ground and 10ml of 0.1% (w/v) Tween 80 was added to 1g of the fine material and the mixture was then vortexed for 2 minutes. The liquid extract was serially diluted in 0.1% Tween 80 and 100-200µl samples were plated out onto Oxytetracycline (100ppm) malt extract agar (OMEA). Plates were incubated at 25ºC and inspected daily for 7 days. After counting, moulds were picked off and re-streaked onto OMEA to ensure purity. Moulds were identified by D1/D2 rDNA sequencing. The results were presented as a list of all the identified species and the individual counts (number of colony forming units) per gram of wood.

3.6 Mechanical Characterisation

3.6.1 Scanning Electron Microscopy (SEM)

SEM analysis was carried out on fresh Willow chip and pellet samples and on degraded samples taken from the surface and middle of each pile after three and six months of storage.

For the Willow chips, SEM allowed changes in plant cell geometry and alignment to be observed. For the thermally treated and white wood pellets, bigger changes in the pellets as a result of degradation could be observed. SEM

analysis carried out on the circular cross section of the pellets showed cracks and crack propagation as well as changes in shape.

Before SEM could be carried out, epoxy setting of the sample, followed by and grinding and polishing were carried out. The different steps are described in full in Appendix A. The microscope used was a Quanta 600 by FEI (Quanta 600, FEI). The model has now been replaced but detailed information on the equipment is available on the Texas A&M University website (Quanta 600 SEM, TAMU). Genesis EDX software from EDAX was used for the analysis.

Sample preparation prior to SEM was a time consuming process and there was a cost associated with every sample, therefore only one chip/pellet per sample was studied in SEM analysis.

3.6.2 Durability test

This test was carried out only on the pellet samples. This test was conducted to quantify the tendency of pellets to break during handling. The durability of biomass pellets is a common property used to compare the handleability of different pellets. The samples were not dried prior to this test. Figure 3-15 below shows the Dural II pellet tester, which was used in these experiments. The equipment was designed by the Agricultural Process Engineering Laboratory at the University of Saskatchewan and manufactured by McEwan Machining Ltd. Other types of equipment can be used to determine durability and a range of them are listed and described in Section 2.5.3.1

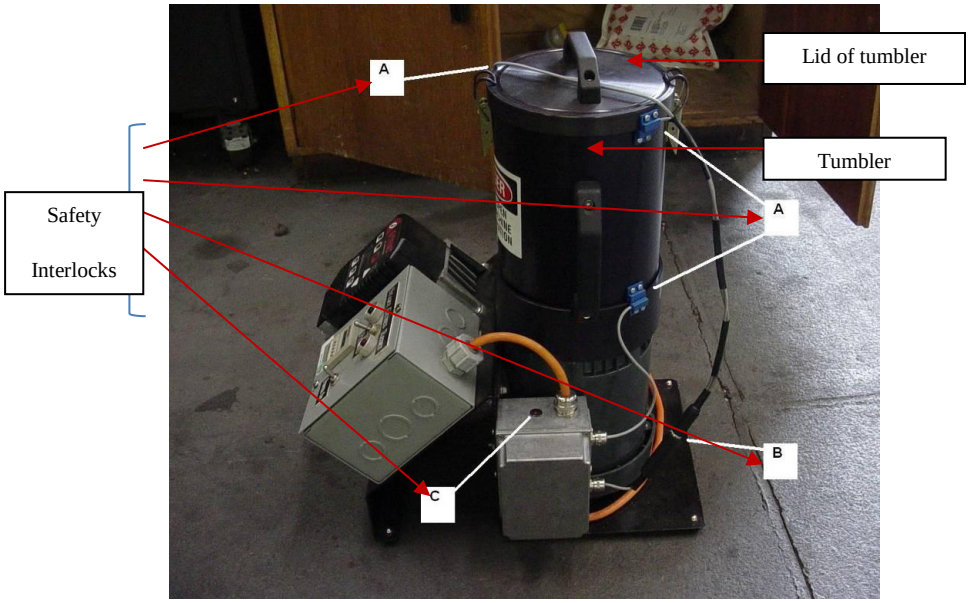

Figure 3-15. Dural II tester

A, B and C are safety interlocks.

Figure 3-16 shows the operating panel for the Dural II tester.

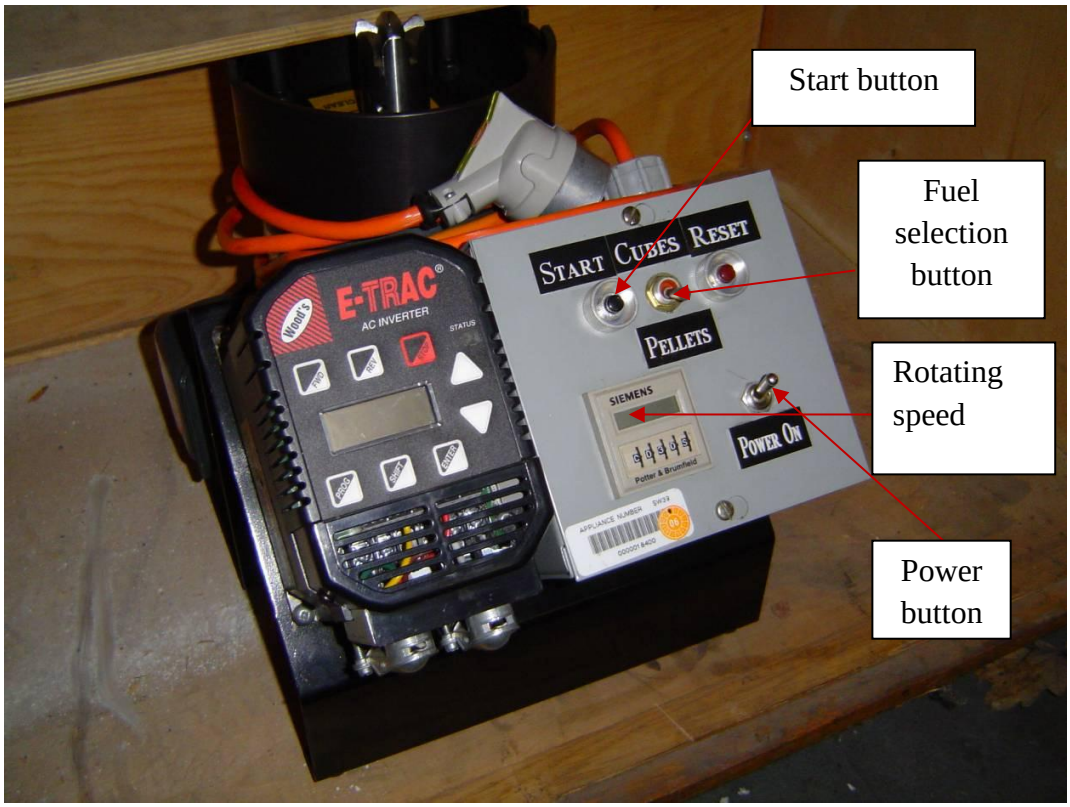

Figure 3-16

The procedure used for the test is described briefly below:

- Weigh out approximately 100g of sample
- Place in tumbler
- Close tumbler and secure lid
- Turn on tester
- Set speed to 1600rpm and time to 30s
- Start tester
- Wait until the tester has completed
- Isolate tester from mains
- Remove the chamber lid and recover the resulting product
- Sieve the resulting product at 4.75mm, recover and weigh the oversize and undersize fractions. The sieve size to be used was determined by the pellet diameter as shown in Table 3-3 below

Table 3-3. Choosing sieve size

Pellet diameter [mm]	Nominal sieve size [mm]
1 to 2	0.84
2 to 3	1.68
3 to 5	2.83
5 to 7	4.75
7 to 10	6.73

Durability is reported as a percentage. It is measured as the percentage of the sample which, after tumbling, remains in the oversize fraction when sieved at 4.75mm.

$$Durability\ (\%) = 100 \times \frac{oversize\ mass\ after\ test\ g}{original\ mass\ g} \qquad [Equation\ 7]$$

In this study, because of time constraints (linked to breadth of project scope and experimental work) and also the amount of pellets available in the monthly samples (500-600g), the durability test was only carried out once on 100g of pellets. But at the start and at the end of the storage trials, the test was done in triplicates and yielded a sample variation of 1-4%. More detail on this test is available in the appendix.

The durability test method used in this project is different from the EN 15210-1 method for the determination of mechanical durability of pellets and briquettes. The standard tester was purchased only at the end of the storage trials.

The method used in this study is a faster method of testing when compared to the standardised methodology, involving a small sample size (100 ± 10) g. This Dural (II) tester induces shocks to the pellets using a rotating drive operating at 1600 rpm for 30 seconds. This is a forceful method of testing simulating a larger impact on the pellets. The samples are then sieved through a sieve with 4.75mm holes using the vibrating screen method for 10 minutes.

The EN standard method uses a Bioenergy TUMBLER 3000 which has three rectangular chambers allowing for three tests to be carried out simultaneously allowing for an average of results. Each chamber has a large capacity of which a sample size of 500 ± 10 g is used. The tumbler subjects the test pellets to controlled shocks against the chamber walls and the other pellets, rotating at 50 ±2 rpm for a duration of 10 minutes. After the tumbling procedure, samples are sieved using a 40cm diameter sieve with round screen holes of 3.15 mm, which is manually shaken in a circular motion five to ten times. The durability can then be calculated from the percentage of pellets which remained in the sieve in relation to the total sample size.

It was considered important to determine the differences, if any, between the two test methods, in terms of the results they yield. Therefore fresh and degraded pellets from the Phase 1 and Phase 2 storage trials were tested in both testers and the results compared. The new tester, i.e. the one conforming to EN standard allowed the test to be carried out in triplicates for each sample, hence yielding the sample variation. When carrying out repeats, the sample was

carefully mixed and divided using riffle splitters to ensure the sub-samples were as similar as possible.

Table 3-4 below shows the results.

Table 3-4. Comparison of durability using non-standard and standard tests.

Pellet Samples	Durability %			
	1st run		2nd run	
	Non-Standard Test	Standard Test	Non-Standard Test	Standard Test
Fresh Phase 2 pellets	89.69	99.17	90.33	98.27
Month 13 Outdoor surface pellets (Phase 2)	71.6	97.73	72.64	95.89
Fresh Phase 1 pellets	95.2	99.6	95.16	99.14
Month 21 Outdoor surface pellets (Phase 1)	37.47	78.93	30.41	81.64

The following observations can be made about the two test methods:

- The EN standard test yields a higher value of durability (it is a less forceful method) than the non standard test
- For the fresh Phase 1 pellets, the difference in durability between the two tests is 4% and for the Phase 2 pellets, it is up to 10%
- For the degraded pellets after 13 months of outdoor storage (Phase 2), the EN standard method still results in an unexpectedly high durability of 96-98%. The non standard test yields a durability of 72%, which appears more realistic considering the appearance of the pellets and the compression and shear test results.

- For the very degraded pellets after 21 months of outdoor storage (Phase 1), the EN standard method gives a durability of about 80%. The non standard test yields an average durability of 34%, which again appears more realistic considering the appearance of the pellets and the compression and shear test results.

- For fresh pellets, the difference in the two durability results is up to 10%. But as the extent of mechanical degradation of the pellets increases, so does the difference between the two test results.

3.6.3 Mechanical tests on pellets using Instron machine

Shear and compression tests were introduced at a later stage in the project, after the ninth month of Phase 1. For Phase 2 of the project, compression and shear tests were carried out monthly on the pellets.

3.6.3.1 Compression tests

In determining the strength of biomass pellet samples, an INSTRON dual column table top universal testing system (model 5969) was used to compress the pellets both axially and diametrically. The strength was determined as the minimum force at which the pellet cracks, similar to the approach used in (Stelte et al., 2011), (Rose et al., 2012) and ASTM Standard D143-09 (ASTM Org). The INSTRON mechanical tester was operated at a load cell capacity of 5kN at a ramp rate of 1mm per minute.

For the axial compression testing (Figure 3-17 a and b), five pellets were ground at the end surfaces to 20 mm (±2 mm) in length. The grinding ensured that pellets could stand cylindrically with maximum stability on the 50mm metal base of the compression equipment. The opposing surface for compression tests was provided by a 50 mm diameter plate attached to the load cell. In the diametrical compression testing (Figure 3-18 and b), the pellets were positioned horizontally.

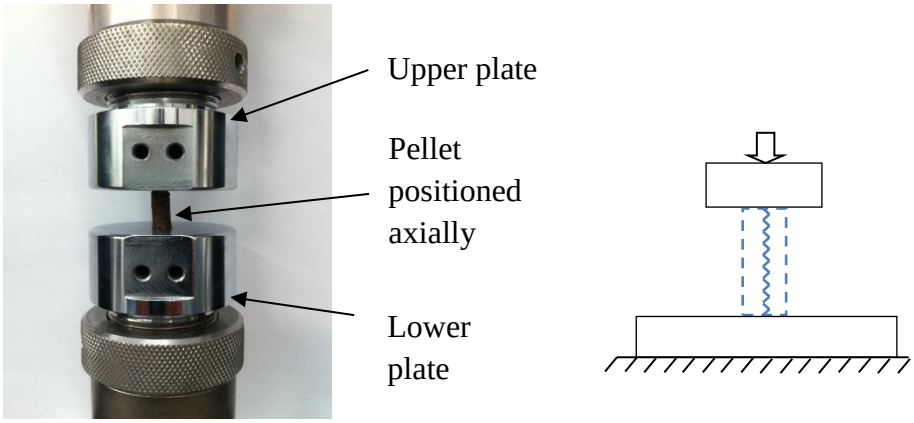

Figure 3-17 a and b. Axial compression test

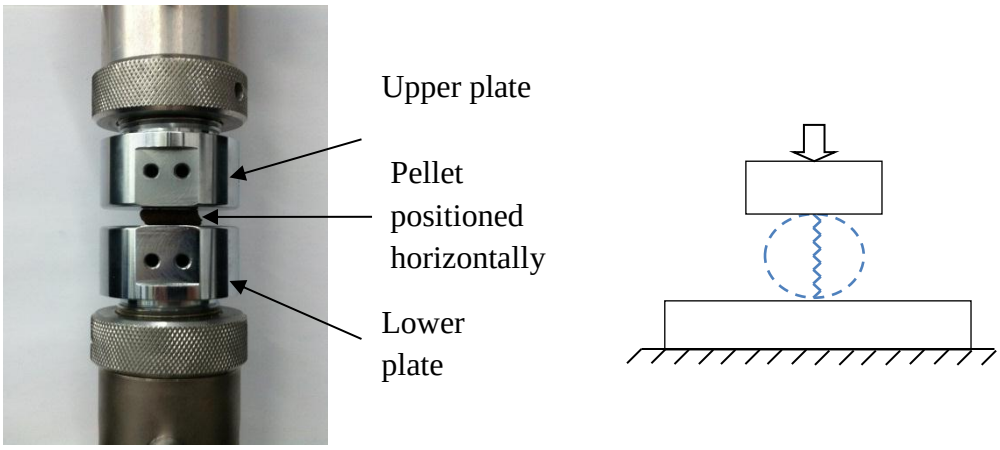

Figure 3-18 a and b. Diametrical compression test

In the axial and diametrical compression tests, the load was applied at a constant ramp rate and aborted after pellet failure (mostly caused by 'barrelling'), with a plot of the compressive extension against compressive load being generated automatically.

The pellet's mean average compressive strength and maximum load at failure, including standard deviation of measured values, were calculated using five pellets per test per biomass type, in order to accommodate any variation in the pellet samples. The range yielded by each of the tests on five pellets is shown in the results chapter 6

3.6.3.2 Inter laminar shear/flexural test

A shear test was also conducted on the pellet samples to determine and compare the shear modulus. The shear modulus is a measure of the pellet's resistance to crack deformation or stiffness. This inter-laminar shear test was performed based on a 3-point flexural test setup similar to ASTM D143-09, which are standard test methods for small clear specimens of timber (ASTM Standard D143-09, ASTM org). For this test, pellets were picked with a length of 18 mm (±1 mm) to achieve a geometry specification of L/D<2.5 in order to prevent possible errors during shearing and to maintain a level of uniformity in the shear pattern. By placing the pellets on the metal contact probes after measuring the diameter, the shear tests were executed on the same INSTRON mechanical tester used for the compression tests with the contact probes changed as shown in Figure 3-19 a and b. The lower contact probe on which the pellets are placed has two circular contact points (5mm diameter) with a span of 10.2 mm between the centres of the two contact base. The force is applied from another probe attached to the load cell of 5kN, and with an extension ramp rate of 1mm/min. For each pellet type, ten tests were carried out and standard deviation and range calculated (again expanded in results chapter 6). Flexural load-extension profile plots were generated for each repeat and the shear modulus calculated automatically.

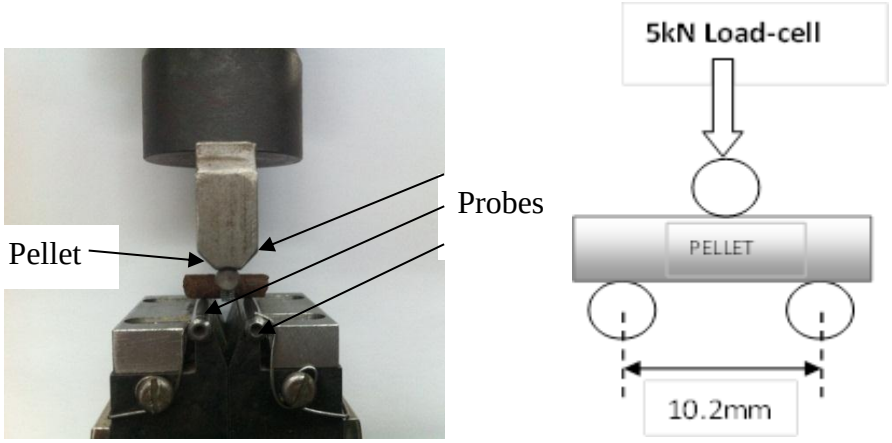

Figure 3-19 a and b. Shear test set up

3.7 Chemical characterisation (including sample preparation)

3.7.1 Sample drying and moisture determination

TGA analysis and bomb calorimetry required sample pre-treatment. The first step in sample preparation before chemical analysis was drying. 300g of the sample was placed in an oven at 105ºC for 24 hours according to [British Standard DD CEN/TS 15414-2:2010]. This ensured the total moisture of the sample was driven off. The sample was weighed before and after drying to determine the total moisture content. Because of the high moisture content of the samples from the farm (especially from the outdoor piles), drying had to take place within 1-2 days at the most after sampling. This was to minimise microbial activity. Drying at 105°C was only carried out on 300g of each monthly sample once. This was due to time constraints but also the weight of each sample taken from the piles was kept at around 500-600g to try and avoid too much material being removed from the piles, potentially causing movement of material within the piles. However sample variation for the moisture test was determined at the start and end of the storage period and the maximum sample variation range was 1%.

3.7.2 Sample milling

The next stage was milling. The biomass had to be reduced to powder form (200 micron) prior to thermogravimetric analysis and bomb calorimetry. Because of the fibrous nature of biomass, the range of mills which can be used for size reduction differs from mills used in coal applications. The two mills used in this project are described below.

3.7.2.1 Cutting mill Retsch SM-2000

The dried samples were first milled through a cutting mill (Figure 3-20) where size reduction occurred by cutting and shearing forces. The sample came into contact with the rotor (Figure 3-20), which is suspended in bearings on both sides, and was comminuted between the blades and the stationary cutting bars inserted in the housing. The knives of the parallel section rotor carry out comminution with a powerful cutting action. Information on this type of mill can be found at (Retsch milling, cutting mills). The SM-2000 mill has now been replaced by SM-100, SM-200 and SM-300 but the milling mechanism is very much the same.

Figure 3-20. SM 2000

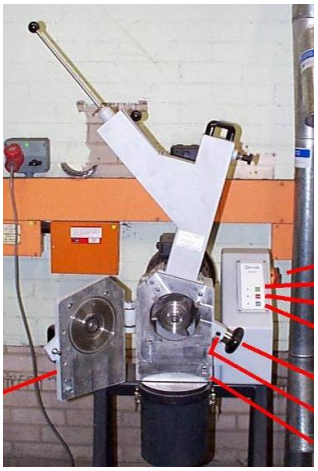

Figure 3-21. Mill internals

At the base of a mill a mesh allows the sample to fall into the collection chamber. Each sample was processed through the mill twice, firstly using a 4mm mesh followed by a 1.5mm mesh.

3.7.2.2 Rotor beater mill Retsch SR-200

In order to further reduce the sample to a uniform 200 micron particle size powder, the samples from the cutting mill were then milled in a rotor beater mill (Retsch milling, Rotor beater mills).

Figure 3-22 and Figure 3-22below show the mill.

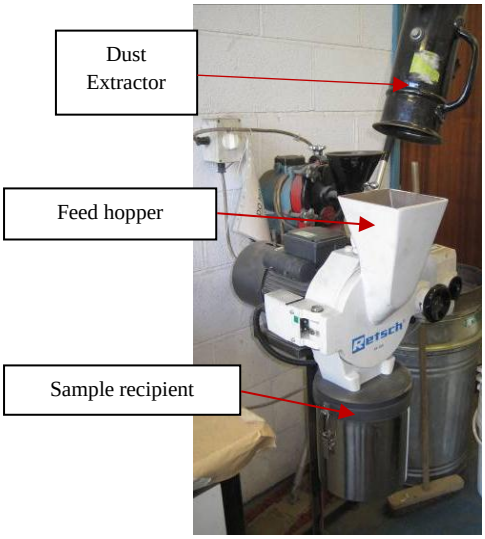

Figure 3-22

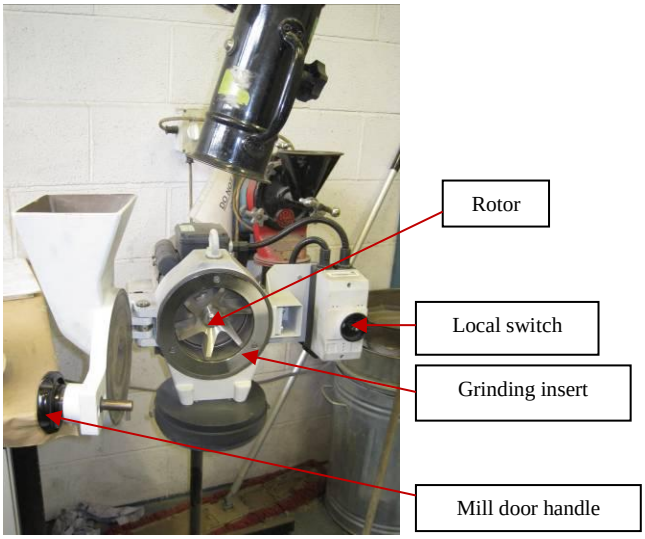

Figure 3-23

Size reduction and de-agglomeration take place by impact and shear effects. The feed material passes from the hopper to the centre of the grinding chamber where it is crushed between the rotor, sieve and grinding inserts. The mill is fed slowly with the pre-ground sample so as not to result in overheating. A 200um grinding insert was used and the resulting powder is stored in air-tight bottles and used for thermogravimetric analysis and bomb calorimetry.

3.7.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a well established technique in coal analysis and is now also being used to analyse biomass fuels. The technique accurately measures the weight change in the fuel sample as different processes (drying, devolatilisation, combustion) are carried out. A Thermal Analysis (TA) SDT Q600, with a balance sensitivity of 0.1µg and a differential thermal analysis of 0.001°C was used in this work and Figure 3-24 below shows a photograph of the equipment. More information on this equipment can be found at (SDT Q600 TGA)

Figure 3-24. SDT Q-600 TGA

The two tests carried out on samples in this project are described below.

3.7.3.1 Determination of moisture, volatile and ash content

The test consisted of four continuous stages which are run sequentially on a 10-15mg sample and constitute a single test. Figure 3-25 below illustrates the different stages of the test procedure used to determine the moisture, volatile, fixed carbon and ash content of the fuel. Similar continuous tests have been used by others (Stenseng et al., 2001) and (Lester et al., 2007).

The first step of the test consists of heating the sample at 50°C/min in nitrogen up to 110°C and then holding the temperature at 110°C for 5 min. This first step drives off any remaining moisture present in the sample. The second step involves further heating to 700°C at a rate of 100°C/min followed by an isothermal stage for 10 min. This step provides the volatile mass content of the sample. The choice of 700°C as a temperature for this stage was determined after extensive testing to determine sensitivity across a range of temperatures with further details available in (Graham et al., 2012). The third step consists of further ramping up the temperature to 850°C at 50°C/min and then holding isothermally for a further 10 min. The fourth and final step involves changing the gas to air and allowing combustion of the char to take place at 850°C for a period of 20 min. The timings of each of the four steps are explained by

(Graham et al., 2012). The residual weight of sample after step four is the ash content of the sample.

This technique is used to determine the moisture, volatile, fixed carbon and ash content of the sample. The different contents are usually expressed as a percentage weight of the whole sample. The detailed method used for the fuel characterisation is described below:

- Select nitrogen gas (gas 1 in programme) (100ml/min)
- Purge with nitrogen for 10 min at ambient temperature to eliminate any residual air out of the system
- Switch data storage on
- Increase temperature to 110ºC at 50ºC/min
- Hold temperature at 110ºC for 5 minutes
- Increase sample temperature from 110 to 700ºC at 100 ºC/min
- Hold temperature at 700 ºC for 10 min
- Then increase temperature to 850ºC at 50ºC/min
- Hold temperature at 850 ºC for 10 min
- Then change gas from nitrogen to air (100 ml/min)
- Allow sample to burn at this temperature for a period of 20 minutes
- Cool sample back down to 25ºC
- Run is completed and equipment is ready for next sample

The different processes in the TGA test are as follows:

- During the first heating step to 110ºC the moisture in the sample is driven off, as shown by a drop in sample weight

- The weight curve then stays flat during the period of 5 min where the temperature is kept constant at 110ºC
- During the second heating step from 110 to 700ºC, the volatiles are driven off and exit the TGA chamber. Because biomass contains a large amount of volatiles, the volatile loss corresponds to the largest weight drop on the weight loss curve
- The weight % stays mostly constant during the isothermal phase at 700ºC
- The temperature is then increased to 850ºC, prior to introducing the air for combustion of the char after moisture and volatiles have been driven off
- Combustion then takes place at fixed conditions for 20 min

The three weight drops on a proximate analysis weight % against time curve correspond to percentages of moisture, volatiles and fixed carbon in the sample. The % ash can also be obtained, as it is the value after combustion, and below which the curve drops no further.

Figure 3-25 below shows a typical proximate analysis curve:

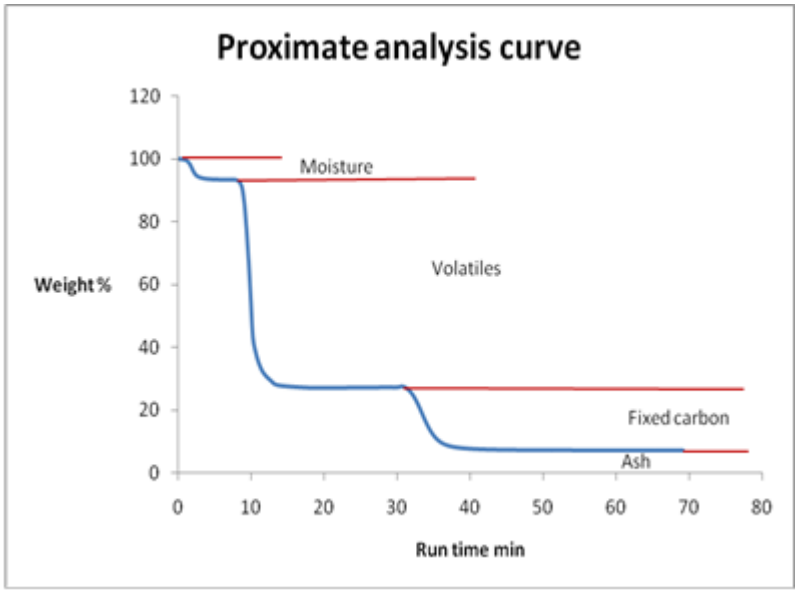

Figure 3-25. Proximate analysis curve

Biomass fuels tend to be less homogenous than coal and the variation in the fuel needs to be factored in when analysing data. This applies particularly to the TGA analysis as the sample size is very small (up to 15mg). The sample variation in the TGA analysis was determined by carrying out a minimum of three TGA runs on the same sample and then working out the standard deviation and range. The repeats were not carried out on every monthly sample due to time constraints and equipment availability but at least twice throughout each storage trial, usually planned in at the start and end of each trial. The range is shown as error bars in the respective graphs in Chapter 5.

3.7.3.2 Char burn off test

The char burn off test follows a fairly similar procedure to the proximate analysis. The sample is heated in nitrogen in two heating stages (drying and devolatilisation) but prior to combustion starting, the temperature is dropped from 700ºC down to 450ºC before the gas is changed from nitrogen to air. This lower combustion temperature (compared to 550°C in the standard method for ash determination) is chosen so as to ensure combustion takes place smoothly and at a slower rate in order to yield a reasonable burn off time. Figure 3-26 shows a typical char burn off curve:

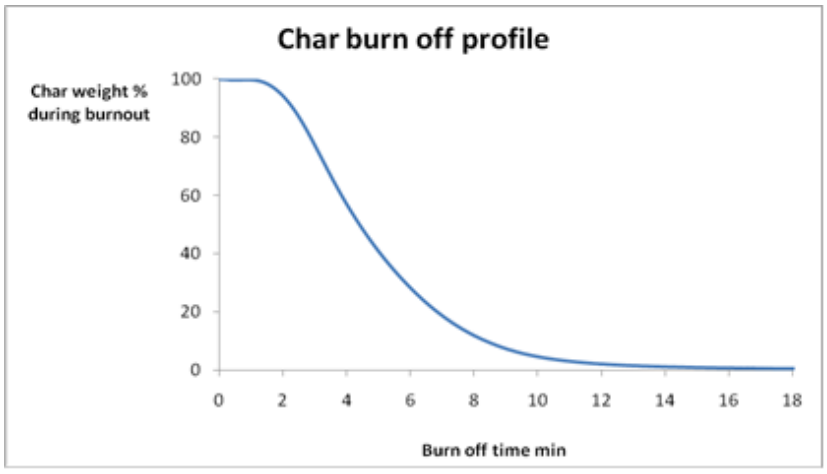

Figure 3-26. Char burn off curve

This test allows the burn off rate of different samples to be compared and the equation used to calculate the weight % of the remaining char is shown below:

$$Weight\ (\%) = 100 - \left(\frac{m0 - m}{m0 - mf}\right) \times 100 \quad [Equation\ 8]$$

m_0 = mass of sample at start of combustion, when air is introduced

m = mass of sample at time t

m_f = mass of sample at the end of combustion

t_0 = time at which char burn off starts = t_f – 30 (where t_f is the time at the end of combustion) and 30 is the time in minutes over which combustion is allowed to take place

Therefore t for char burn off time is the sample time minus t_0

3.7.4 Calorific value determination

Bomb calorimetry was carried out on each sample at E.ON Technologies (Ratcliffe) Ltd. to determine the energy value of the biomass. Training was provided by E.ON lab staff prior to using the equipment.

A Parr 1266 isoperibol bomb calorimeter was used. This model has now been replaced by the Parr 6100 compensated jacket calorimeter. Information can be found at (Bomb Calorimeter, Parr Instruments)

Prior to bomb calorimetry, the ground sample had to be pelletised. 2g of each sample was weighed and then manually pressed to form a pellet. The pellet was then broken into two halves and the test was carried in duplicates on 1g of pellet and the average value for gross CV was calculated. The pellet was first weighed and the weight recorded on the test sheet before 5ml of oil was added to ensure complete combustion. The weight of the oil was also recorded on the test sheet. The crucible containing the pellet piece and oil were then secured in a bomb, filled with oxygen and pressurized to 450 psi. It was then placed in a

container containing a fixed volume of distilled water (1994ml) and placed in the calorimeter for CV determination. The water jacket was kept at a constant temperature of about 28.5ºC.

The biomass sample was ignited and combustion took place inside the bomb. The resulting heat was transferred to the water jacket. The small heat flow that occurred between the jacket and its surroundings was monitored by a microprocessor and in case of any heat leak, a correction was applied automatically to the water temperature rise in the jacket.

At the end of each run, the water temperature rise displayed on the machine was recorded. The sample weight, oil weight, temperature rise were then all entered in a database where the gross CV was calculated, using the equation provided in the equipment manual (Bomb Calorimeter, Parr Instruments)

In Chapters 4 to 7 which follow, the results of the long term project are presented and discussed. The continuous weather and in-situ pile temperature data is presented in Chapter 4. Chapter 5 focuses on the chemical degradation of the different fuels throughout storage, while Chapter 6 and 7 concentrate on mechanical degradation and biological degradation respectively.

4 Continuous weather data and in situ pile temperature

4.1 Introduction

Throughout this project, weather data and temperatures at multiple locations within the different biomass piles were measured continuously on an hourly basis. The first half of this chapter discusses the weather trends and seasonal effects observed during both Phase 1 and Phase 2 of the project. This analysis of weather data is then used in the following chapters to set in context the extent of chemical, biological and mechanical degradation of the different fuels. The second half of the chapter focuses on the temperature profile seen in each of the Willow, thermally treated pellet and white wood pellet piles. Again links to weather behaviour will be drawn out.

4.2 Weather measurements at storage site

The hourly relative humidity, ambient temperature and rainfall were measured at the storage site in Retford and averaged into daily, weekly and monthly trends. The weather pattern during this long term storage project is also compared to the weather patterns measured in the last ten years at a local weather station in Waddington. This section contains the weekly relative humidity, ambient temperature and rainfall data measured at the farm in Retford where the stockpiles were stored. The data presented below is from 19 May 2011 to 30 January 2013. Unfortunately a few teething issues were experienced with the weather data logger in the first four weeks of the storage trials which resulted in data not logging properly. However a local weather station at Waddington was able to provide data for this period, the correlation between the site and local weather station being the subject of Section 4.3.

While the wind speed and direction were also measured, a few issues were encountered with the anemometer and particularly the wind vane, which resulted in loss of data. Furthermore, the biomass stockpiles and the weather station were set up close to the open barn at the storage site and the building would have had an impact on the measured wind speed and direction. Therefore the impacts of wind speed and direction on changes in fuel properties will not be explored to the same extent as relative humidity, ambient temperature and rainfall in the chemical, biological and mechanical degradation chapters. However, the next chapter which discusses the ten year weather trends will include wind speed and direction.

4.2.1 Weekly relative humidity

Figure 4-1 below shows the weekly average relative humidity measured at the storage site from May 2011 to January 2013. Phase 1 started in April 2011 with two Willow chip piles and two thermally treated wood pellet piles and in November 2011, the two Willow chip piles were deconstructed and removed. The two thermally treated wood pellet piles stayed and tests continued until December 2012. In November 2011, Phase 2 began with two new Willow chip piles and a white wood pellet pile. In December 2011, an outdoor thermally treated wood pellet pile was also constructed. In September 2012, the Phase 2 Willow chip piles and the white wood pellet piles were removed. The outdoor thermally treated wood pellet pile stayed, along with the Phase 1 thermally treated wood pellet piles, and sampling and testing continued regularly until December 2012.

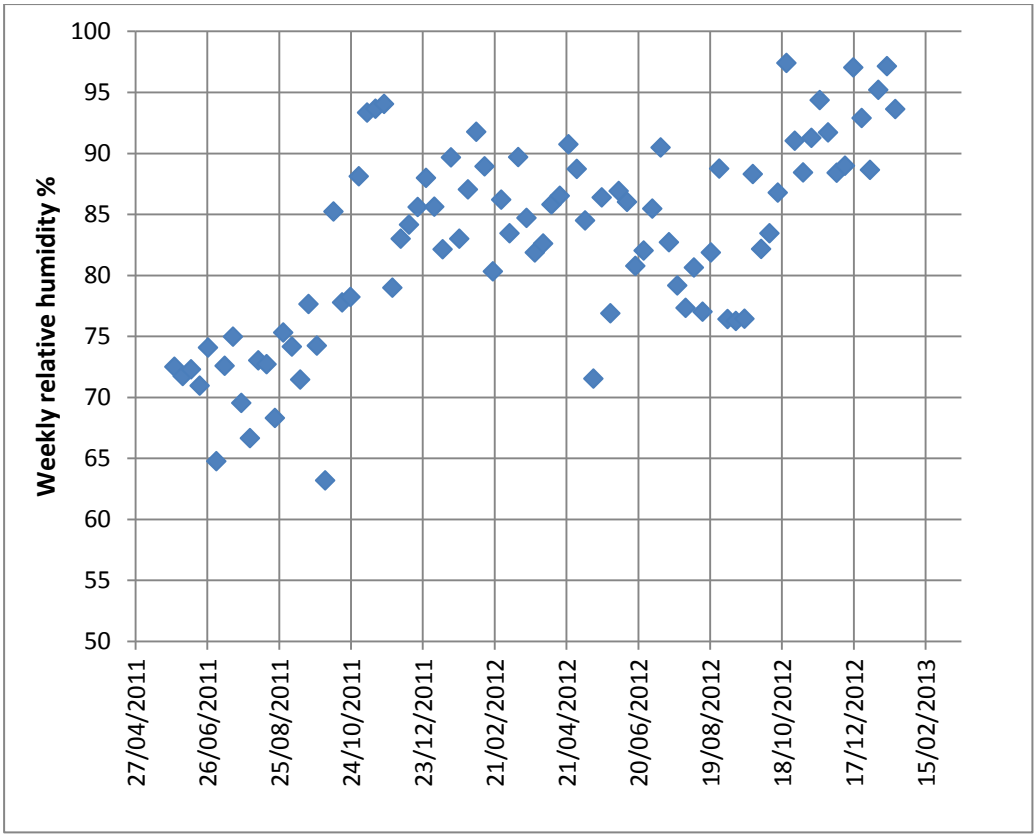

Figure 4-1. Weekly average relative humidity at storage site

The first six months of Phase 1 saw a lower weekly average relative humidity with a range of 65-75% when compared to the rest of the storage period where the humidity levels ranged from 75 to 95%. Humidity increased consistently as the project progressed. This increase in humidity can be explained by the much higher levels of rainfall in 2012 compared to 2011, see Section 4.2.3 below. Figure 4-1 also shows that relative humidity is higher in the winter months than in the warmer summer months and consistently higher in Phase 2 compared to Phase 1.

4.2.2 Weekly ambient temperature

Figure 4-2 shows the weekly average ambient temperature for the same time period as Figure 4-1.

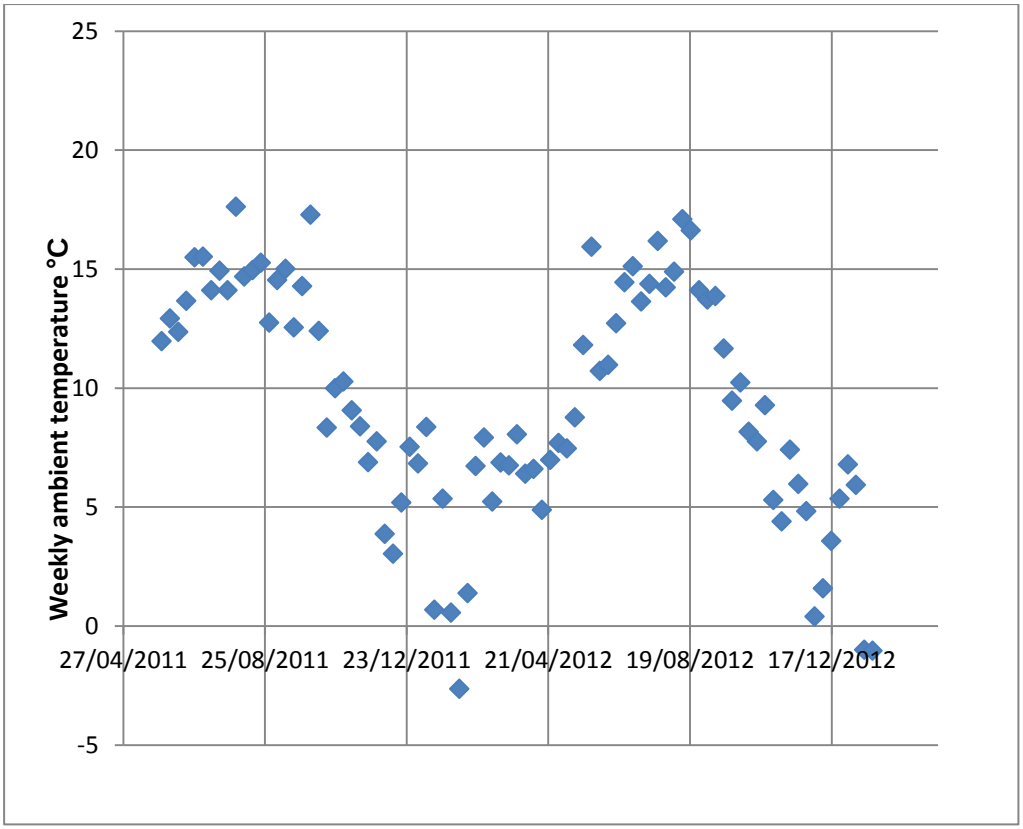

Figure 4-2. Weekly average ambient temperature at storage site

The summer-winter cycling can be observed with the two peaks and two troughs. The two summer-winter cycles in the above graph do not appear very dissimilar. The few differences which can be observed are as follows:

- Autumn 2011 was generally warmer than autumn 2012
- The lowest temperature was in winter 2011
- It stayed warmer for a longer period in summer 2011 compared to summer 2012

4.2.3 Weekly total rainfall

For rainfall, unlike relative humidity and ambient temperature, the hourly data was processed into daily, weekly and monthly total rainfall as this showed the maximum amount of precipitation/water the different fuels were subjected to.

Figure 4-3 below shows the weekly total rainfall measured at the storage site from 19 May 2011 to 30 January 2013.

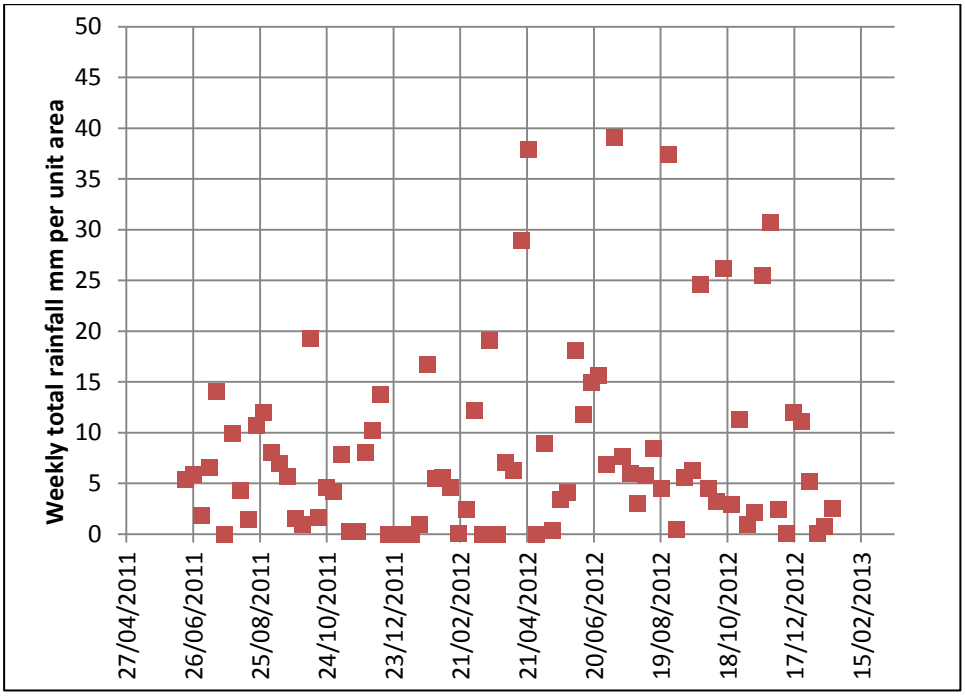

Figure 4-3. Weekly total rainfall at storage site

Figure 4-3 clearly shows that Phase 2 saw much higher rainfall levels than Phase 1, especially between March and November 2012. The highest weekly total rainfall was in July 2012 at 39.1mm, followed by 37.9mm in April 2012 and 37.4mm in August 2012. The winter in 2012 was also wetter than the winter in 2011. The overall higher rainfall in 2012 compared to 2011 explains the upward shift in the relative humidity level which was highlighted in Figure 4-1.

4.3 Ten year average weather data

In this section, the weather data recorded at Waddington for the last ten years will be discussed. The data from the Waddington weather station (latitude 53.167, longitude -0.517) is used by Ratcliffe on Soar, Cottam and West Burton power stations with approval from the Environmental Agency. The weather station is approved and recognised and used by the (UK Met Office).

The main reason for looking at this ten year weather pattern was to determine whether the weather behaviour observed during the storage project was typical of yearly regional averages. The processed set of data includes wind speed, relative humidity, ambient temperature and rainfall, all averaged out on a monthly basis except for rainfall which was processed as a monthly sum. The Waddington weather trend is shown by the blue trace on each of the graphs. The red trace shows the collected data at the storage farm over the time period when the stockpiles were stored**.**

4.3.1 Wind speed

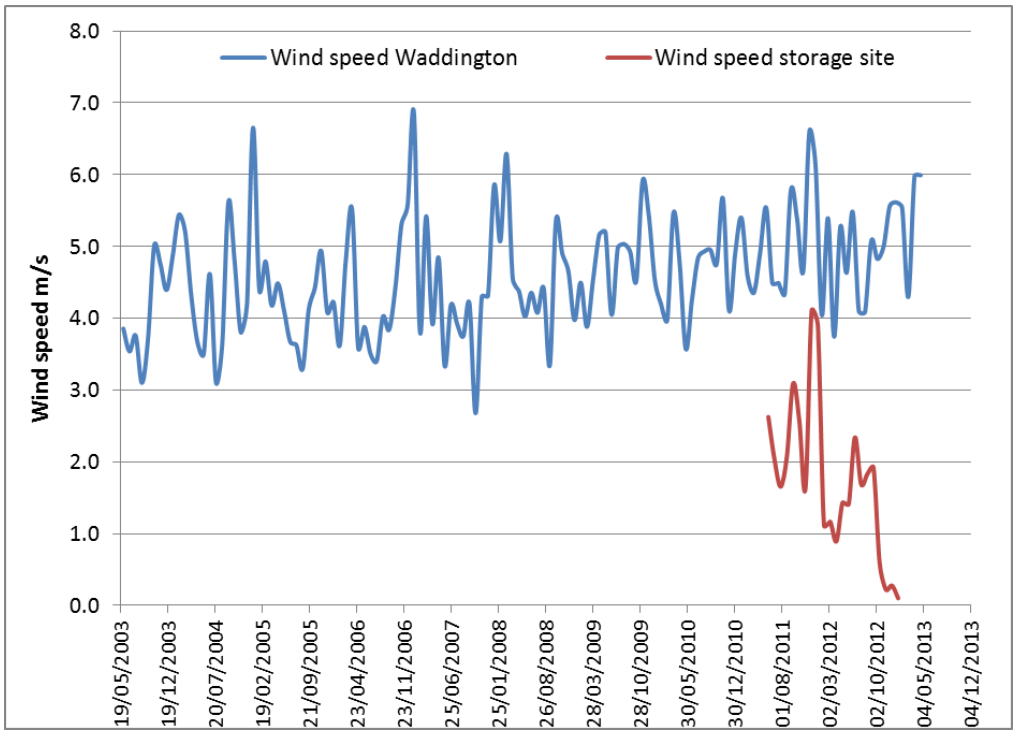

Figure 4-4. Ten year wind speed data from Waddington station

As shown in Figure 4-4, the wind speed at the stockpiles storage site was consistently lower than that at Waddington station. The weather station at the storage site had to be positioned next to an open barn as power from the mains was required for the data logger. So the lower wind speed was probably due to the barn providing shelter to the anemometer. In terms of the difference in wind speed between Phases 1 and 2 of the project, the start of Phase 1 saw an

increase in wind speed which lasted for a few weeks whereas the start of Phase 2 saw a drop in wind speed.

Looking at the wind speed trend at Waddington station, the wind speed during the period May 2011 to January 2013 (storage period) looks similar to the patterns observed in the three year period preceding it. If anything, the wind speed is slightly higher from April 2011 to January 2013 compared to previous three years. The wind speed in the years 2008-2013 shows an overall consistent behaviour of increasing in the spring months (March to May), then decreasing in the summer months (June to August), increasing again in the autumn months (September to November) and decreasing in the winter months (December to February). From 2003 to 2008, the seasonal cycling was different, with periods of high wind speed and low wind speed tending to last longer.

4.3.2 Relative humidity

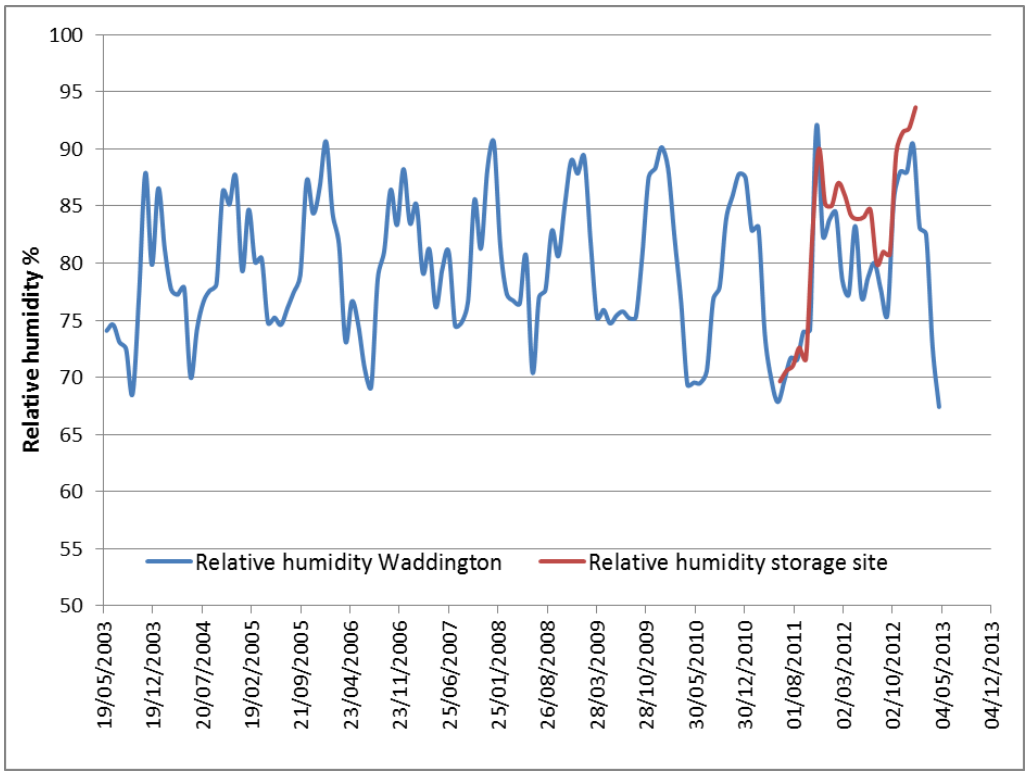

Figure 4-5. Ten year relative humidity data Waddington station

In terms of general behaviour in relative humidity during the period 2003 to 2013, the transition from summer into autumn sees a rise in relative humidity whereas from autumn through to winter, relative humidity decreases. The spring months see a small increase in relative humidity which then decreases in the summer. So the spring and autumn are more humid than the summer and winter.

The relative humidity trend over the storage period (May 2011 to December 2012) shows higher levels of humidity for sustained periods compared to most years. However there are similarities with the year 2006-7 and this may indicate that this can be something that is possible/probable over a 5-10 year period.

The relative humidity profile at the stockpiles storage site follows the same trend as the relative humidity at Waddington station. For the period February to December 2012, the relative humidity at the storage site stayed higher than at Waddington station.

4.3.3 Ambient temperature

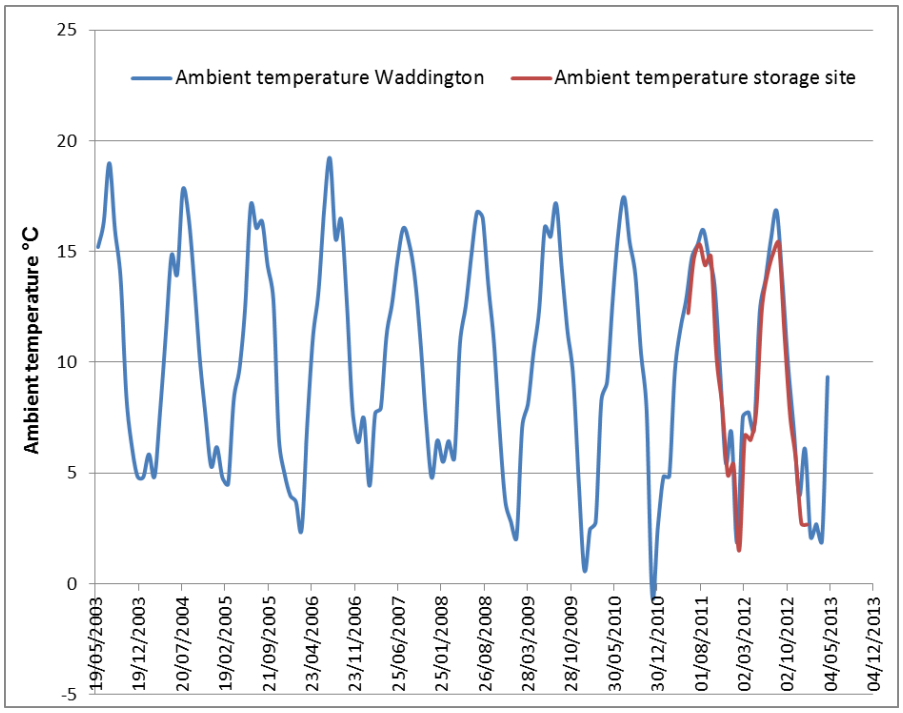

Figure 4-6. Ten year ambient temperature data Waddington station

Looking at the ten year ambient temperature data, it can be concluded that the overall ambient temperature behaviour during the storage trials was within the norms of the ten year behaviour and that 2011 and 2012 were fairly moderate years. Also there was a close match between the temperature behaviours at Waddington station and at the storage site.

4.3.4 Rainfall

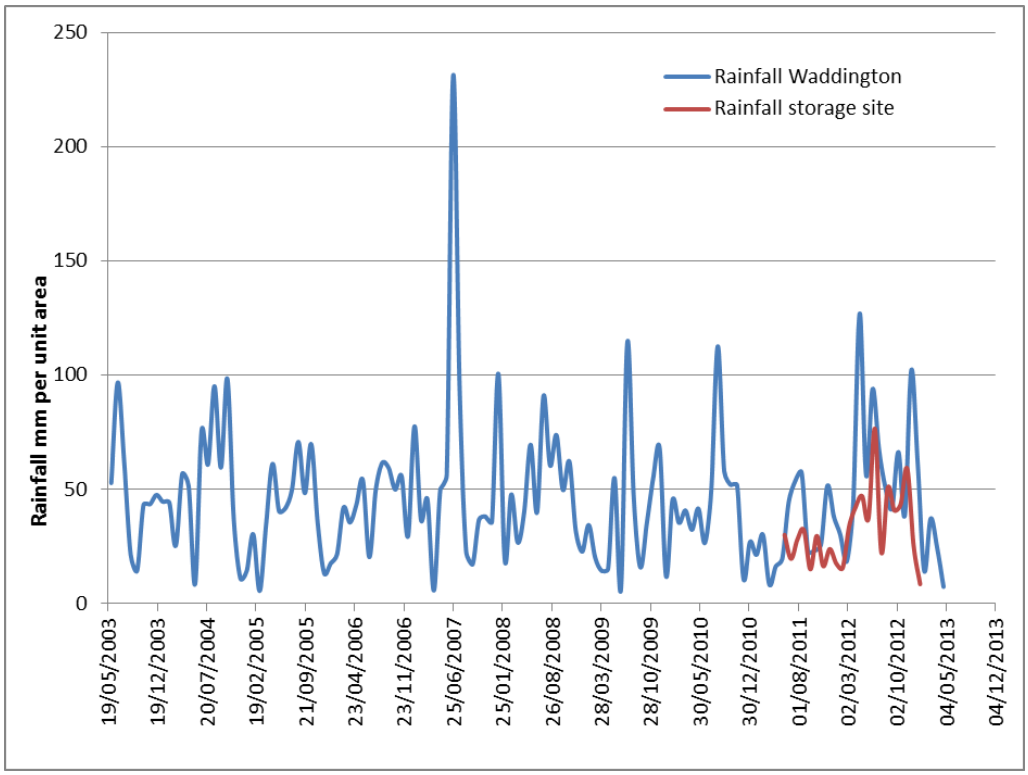

Figure 4-7. Ten year rainfall data Waddington station

From the above graph, it is clear than 2007 was an unusually wet year and many people will remember the severe floods which resulted in many part of the UK after very high levels of rainfall in the summer of that year. Compared to wind speed, ambient temperature and relative humidity, rainfall follows less of a seasonal pattern but in general, the warmer summer months tend to be wetter than the colder winter months. As far as the piles storage period is concerned, it is obvious from the above graph that Phase 2 saw much higher levels of rainfall than Phase 1. Rainfall in Phase 1 (April – October 2011) was

relatively low. For most of 2012, the monthly total rainfall exceeded 15mm. As will be discussed in Chapter 6, the very high level of rainfall seen in 2012 had a significant impact on the outdoor fuel moisture content and subsequently on its extent of mechanical degradation.

4.4 Pile temperatures measured inside piles

In this section, the temperature profiles seen at the centre and on the surface of each of the biomass piles in both Phases 1 and 2 of the project are discussed. The Willow chip piles will be discussed first followed by the thermally treated pellet piles and finally the white wood pellet piles.

4.4.1 Willow piles

Figure 4-8 to Figure 4-11 to below show the surface and middle temperature pattern in the Phase 1 and Phase 2 Willow chip piles, alongside ambient temperature which is shown as a solid green trace The hourly pile temperature and ambient temperature data is shown here, exactly as recorded by the thermocouple data loggers and weather data logger respectively. Section 3.2.1 of the methodology chapter contains full detail on the measurement and data logging system.

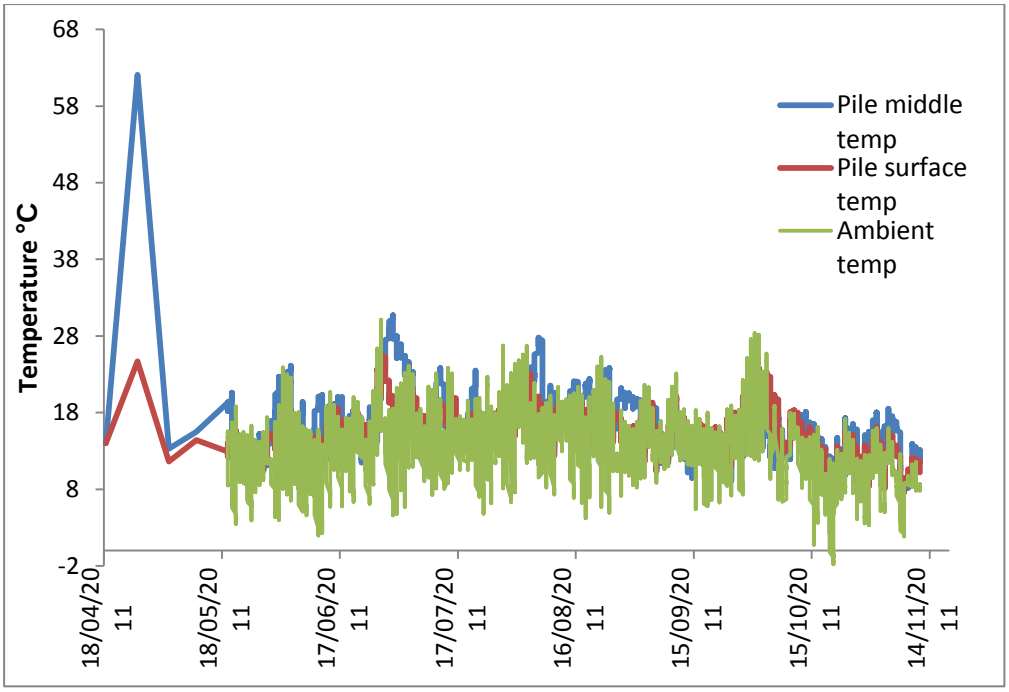

Figure 4-8. Phase 1 outdoor Willow chip pile (2.4x2.4x1.7m) temperature

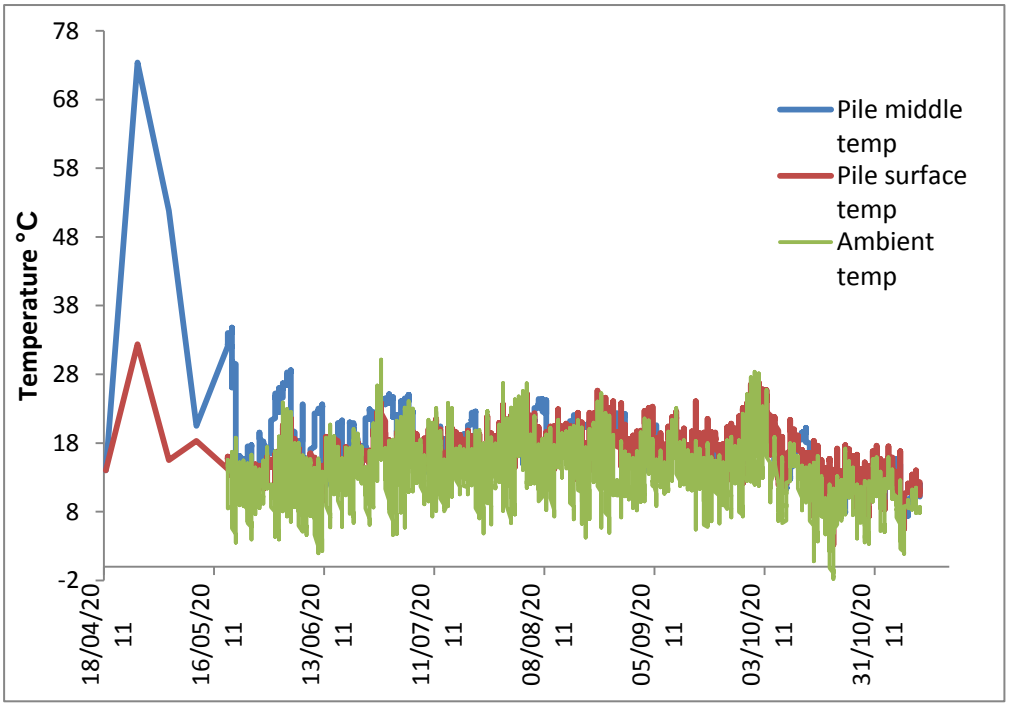

Figure 4-9. Phase 1 outdoor Willow chip pile (3.8x3.8x2.5m) temperature

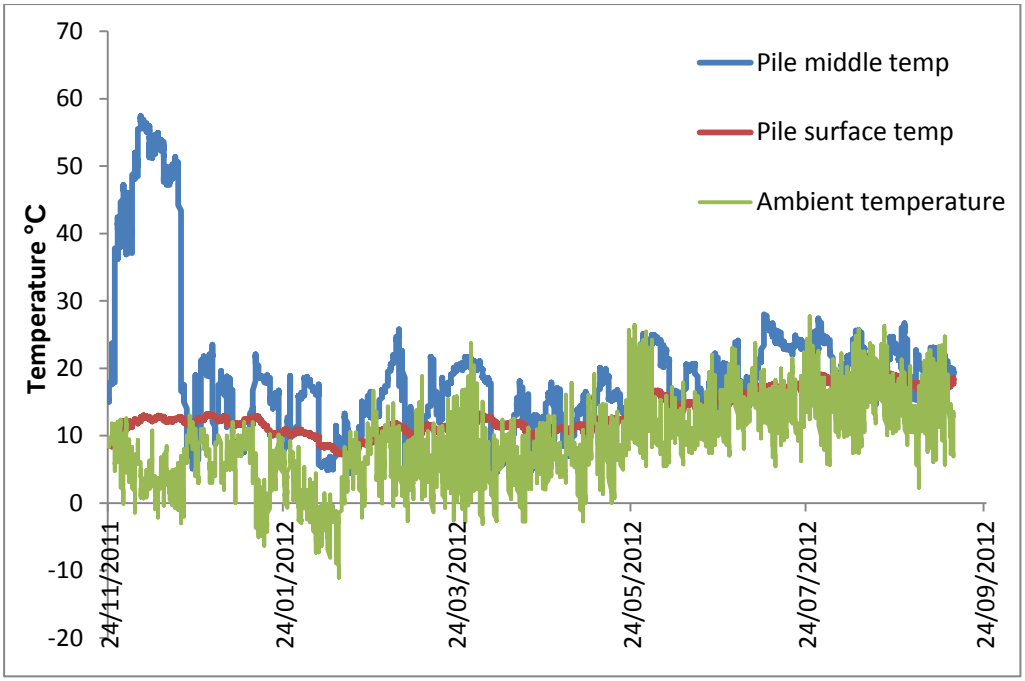

Figure 4-10. Phase 2 outdoor Willow chip pile (3.8x3.8x2.5m) temperature

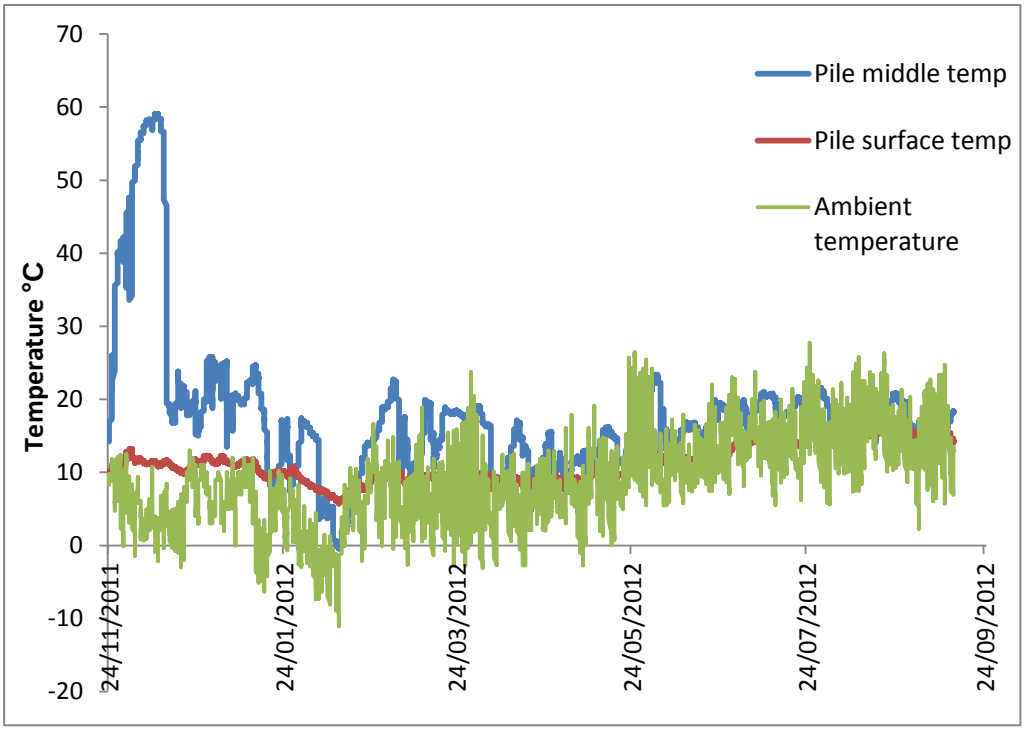

Figure 4-11. Phase 2 indoor Willow chip pile (3.8x3.8x2.5m) temperature

For both Phases 1 and 2 of the project, the Willow chips were harvested only a few hours before the stockpiles were constructed. In both Phases 1 and 2, the middle of the Willow piles heated rapidly to a high temperature in the first

week of storage before dropping again by the fourth week and reaching and staying at a few degrees above ambient temperature for the rest of the storage period. In Phase 1 of the project which started in April 2011, the surface temperature of both the small and big Willow piles also spiked in the first two weeks of storage before dropping by week four, with ambient temperature averaging at 11°C during this period. In Phase 2 which started in November 2011, the surface temperature of the indoor and outdoor Willow chip piles did not increase due to the cooling effect brought about by a much colder ambient temperature ranging from 2 to 10°C in the first four weeks of storage.

The larger Willow pile in Phase 1 got as warm as 73°C in the middle and 32°C on the surface, while the smaller Willow pile reached a peak temperature of 62°C in the middle and 25°C on the surface. Both the middle and surface temperatures then rapidly decreased in week two and stabilized to a few degrees above ambient temperature from week three onwards. The smaller pile cooled down more rapidly, reaching ambient temperature a week earlier than the bigger pile. The smaller Willow pile contained a lower volume of Willow chips with a shorter distance from the centre of the pile to the surface, hence resulting in a faster heat dissipation rate compared to the larger pile. After the temperature surge and drop had taken place, the surface and middle temperatures then lagged the ambient temperature by a short period ranging between one and three days. Again because of heat dissipation being faster through the small pile, it was more sensitive to ambient temperature changes, especially in the middle. However for most of the storage period, the surface and middle temperatures in the small and big piles were close to each other.

A similar behaviour in pile temperatures was observed by (First Renewables Ltd., 2002) in their work on Willow chip storage. They investigated a much larger Willow pile in outdoor storage and reported that the core temperature rose to 60°C in the first week in storage and then decreased to 25°C in the next 6 weeks. Because of the larger size of the pile, heat dissipation might have taken place more slowly than in the piles studied in this work, hence the slower drop in temperature at the core of the pile.

The rapid surge in temperature in week one could be explained by respiration of the living cells in the fresh chips generating heat and then the humid warm environment in the pile encouraging rapid fungal and bacterial growth which in turn generates more heat (Fuller, 1985). However, biological organisms have low resistance to high temperatures which would explain why the high temperatures did not persist, reflecting a decrease in the number of fungi and bacteria. Furthermore, the first heat surge would have resulted in partial drying of the chips, hence providing a less favourable environment for the organisms. In addition the plant cells died and ceased to respire. This hypothesis is supported by the fungal analysis presented in Section 7.3, where preferential growth for selected high temperature resistant fungi is observed.

There were a few differences between the Willow piles behaviour in Phase 1 compared to Phase 2. While the middle of both the indoor and outdoor piles saw a rapid rise in temperature at the start of the storage period, the maximum temperature was reached in the second week as opposed to the first week in Phase 1. The rate of respiration of the plant cells as well as the rate of biological growth could have been inhibited by the colder ambient temperature. The biological analysis of Phase 2 Willow chips (see Section 7.4) shows that fewer species populated the Willow piles in Phase 2 compared to Phase 1 and the count was also lower. The maximum temperature reached in the middle outdoor pile was 57°C (73°C in Phase 1). The middle of the indoor pile heated to a slightly higher temperature of 60°C as the pile was more sheltered from ambient conditions. In Phase 2, unlike Phase 1, the pile surface temperature behave differently to the middle temperature, showing a much flatter trend and staying mostly constant at about 10°C. The temperature at the middle of the piles followed the ambient temperature but because of the insulation provided by the wood chips, it stayed about 10°C warmer than ambient temperature.

4.4.2 Thermally treated pellet piles

Figure 4-12 to Figure 4-14 show the temperature profiles of the three thermally treated pellet piles.

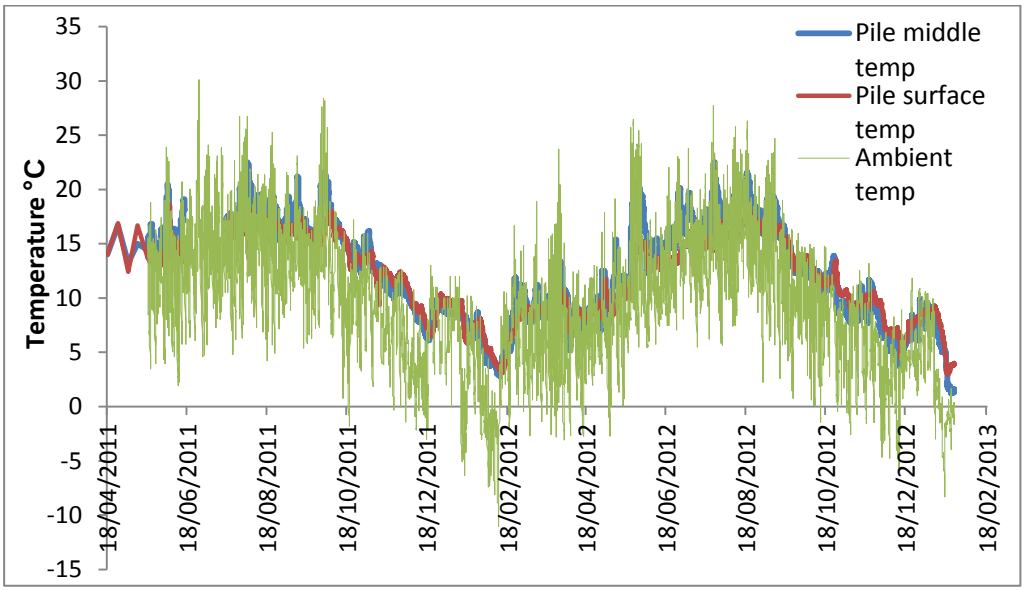

Figure 4-12. Phase 1 indoor thermally treated pellet pile (2.4x2.4x1.5m) temperature

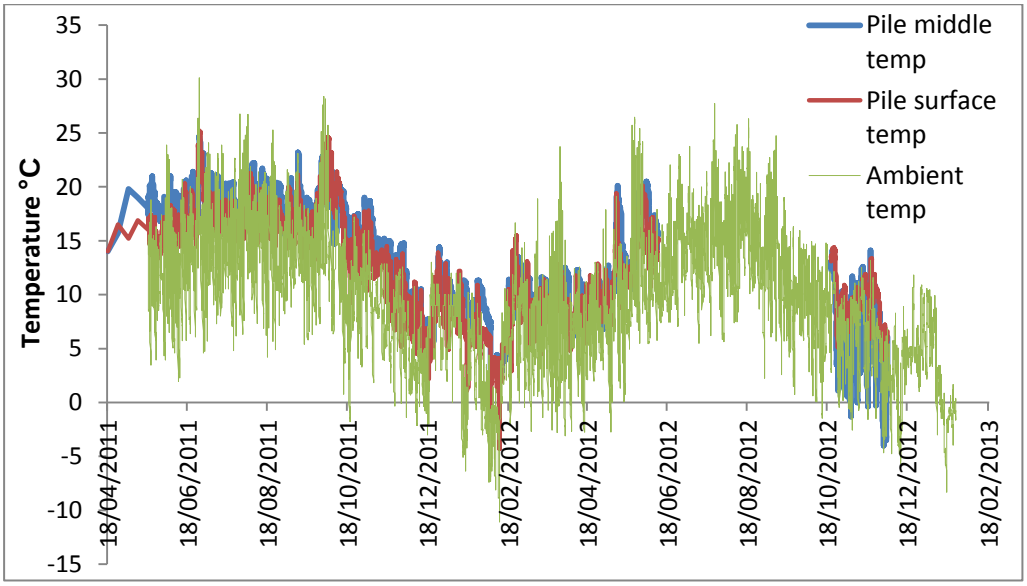

Figure 4-13. Phase 1 outdoor thermally treated pellet pile (2.4x2.4x1.5m) temperature

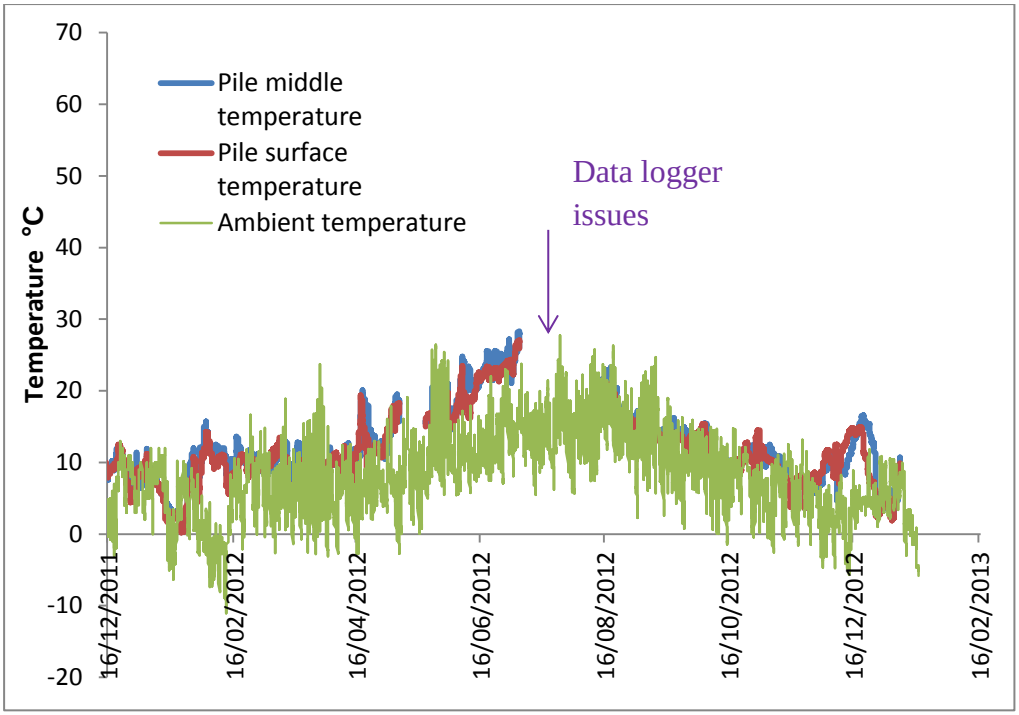

Figure 4-14. Phase 2 outdoor thermally treated pellet pile (2.4x2.4x1.5m) temperature

In both Phases 1 and 2 of the project, the temperature in the thermally treated pellet piles showed a stable behaviour and the trend followed the ambient temperature trend. In Phase 1, the middle of the indoor pile was warmer than the surface and the temperatures then switched over in the winter months. The Phase 1 outdoor pile responded to ambient changes to a larger extent than the indoor pile due to greater exposure and was generally cooler throughout. The middle and surface temperatures were also closer than those in the indoor pile. The Phase 2 outdoor thermally treated pellet pile had a very similar behaviour to the Phase 1 equivalent outdoor pile.

4.4.3 White wood pellet piles

The white wood pellet pile, stored indoor, responded less to ambient temperature compared to the indoor thermally treated pellet pile, .potentially due to lower thermal conductivity, as shown in Figure 4-15

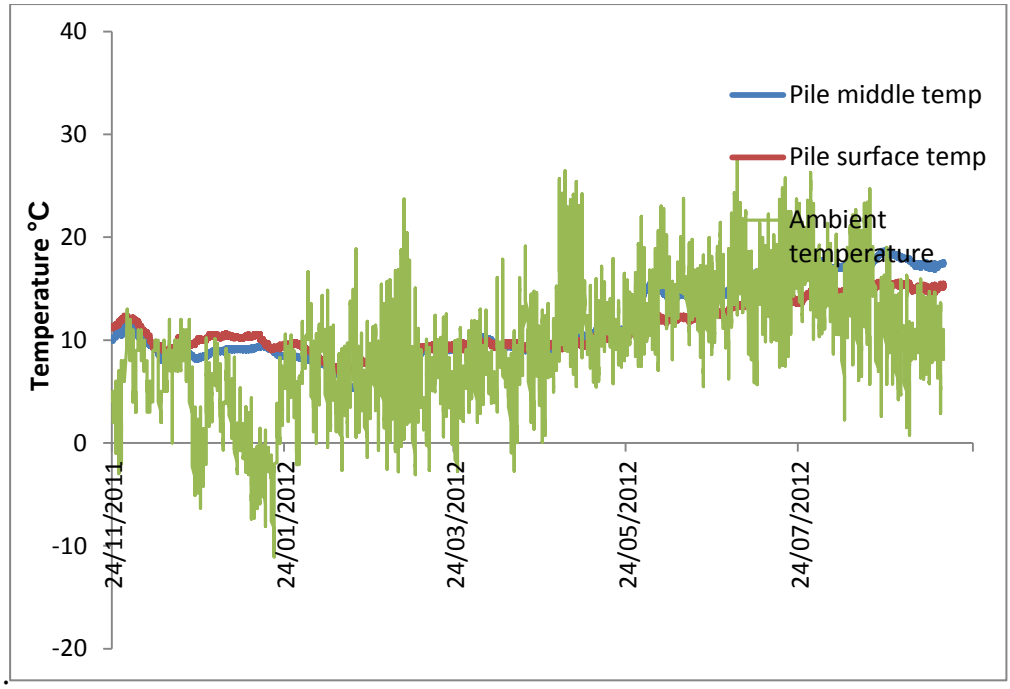

Figure 4-15. Phase 2 indoor white wood pellet pile (2.4x2.4x1.5m) temperature

5 Chemical degradation of biomass fuels during storage

5.1 Introduction

This chapter focuses on the extent of chemical degradation of the different fuels as a result of storage. The changes in chemical properties of the different fuels and the moisture variations with time in storage are discussed. Where appropriate, the impacts of the weather trends on the changes seen are explained.

Section 3.7 of the methodology chapter contains detailed information on the chemical analysis; including equipment used, test methods and calculations performed. Thermogravimetric analysis (TGA) yielded the ash and volatile content of each sample while the total moisture was determined using the oven drying and weight method. Although TGA is not the most accurate method for the determination of volatile and ash content (very small sample size), in this project, the main focus was a comparison between the changes in properties of the different fuels when stored in different conditions. The trend in ash and volatile content was more important than the exact property measurement. The very broad scope of the project also meant that there were time constraints. Therefore a single TGA test which would yield both the volatile and ash content was chosen over two separate oven tests.

Bomb calorimetry was carried out to determine the calorific value of the different fuels. Part of the raw data processing involved converting the ash to a dry basis and the volatile content and calorific value to a dry ash free (DAF) basis. Table 5-1 below shows the list of all the chemical terms used in this chapter along with their definitions.

Table 5-1. Definition of chemical terms

Term	Definition
Total moisture content	Amount of moisture driven off as sample is dried at 105°C for 24 hours. Expressed as a % weight of total sample weight
TGA moisture content	Amount of moisture given off by sample during TGA run, corresponds to first weight drop when sample is heated to 110°C
TGA volatile content	Amount of volatile matter released by sample during TGA run, corresponds to second weight loss when sample is heated to 700°C in nitrogen
TGA ash content	Amount of unburnt material left in crucible at the end of the TGA test after final combustion in air
Calorific value (gross)	Amount of energy released during combustion in bomb calorimeter including the recovered heat when the water of combustion is totally condensed
Calorific value (net)	Energy released during combustion but the heat in the water vapour is not recovered as combustion products include water vapour
Dry ash	Ash content of fuel normalised for moisture content
Dry ash free (DAF) volatile content	Volatile content of fuel normalised for moisture and ash contents
Dry ash free (DAF) calorific value (gross)	Gross calorific value of fuel normalised for moisture and ash contents

The trends in dry ash, dry ash free (DAF) volatile content and DAF gross calorific value will be presented first. The changes in moisture content of the

different fuels and the effects of the weather on this property are then discussed. The final section of this chapter shows the impact of moisture on the fuels' net calorific value.

5.2 TGA Results

For each of the stockpiles under investigation (eight in total), the dry ash, dry ash free volatile content and dry ash free (gross) calorific value have been plotted against time in storage. Table 3-1 in Section 3.2 of the methodology chapter contains a list of all the biomass stockpiles investigated in this project.

Not all the graphs will be shown in this chapter but only a selection for each of the three chemical properties. In order to best draw out the differences in fuel degradation brought about by indoor and outdoor storage, the results of four piles will be presented in this section, namely the Phase 1 indoor and outdoor thermally treated wood pellet piles and the Phase 2 indoor and outdoor Willow chip piles. The graphs for the other stockpiles can be found in Appendix B. In the first six months of Phase 1, samples were taken from the surface, middle and bottom centre of each of the stockpiles and analysed for changes in chemical properties. However, from the seventh month of Phase 1 onwards and for the entire duration of Phase 2, only two sample locations were used (surface and middle). This was due to time constraints and equipment availability as six stockpiles were being investigated as opposed to four in Phase 1. Also, extracting the samples from the bottom of the piles proved difficult as it involved inserting the sampling probe vertically down the pile from the top surface and it was difficult to ensure the same location was reached at each sampling. As discussed in Section 3.7 of the methodology chapter, sample variation was determined for each of the different fuels at least twice during each of Phases 1 and 2 of the project,.. Error bars were generated in the months when TGA repeats were carried out to determine the sample variation. Because of a small population consisting of five tests, the error bars represent the range (minimum and maximum values).

5.2.1 Dry ash

Figure 5-1 shows the dry ash content of the Phase 1 indoor and outdoor thermally treated wood pellets

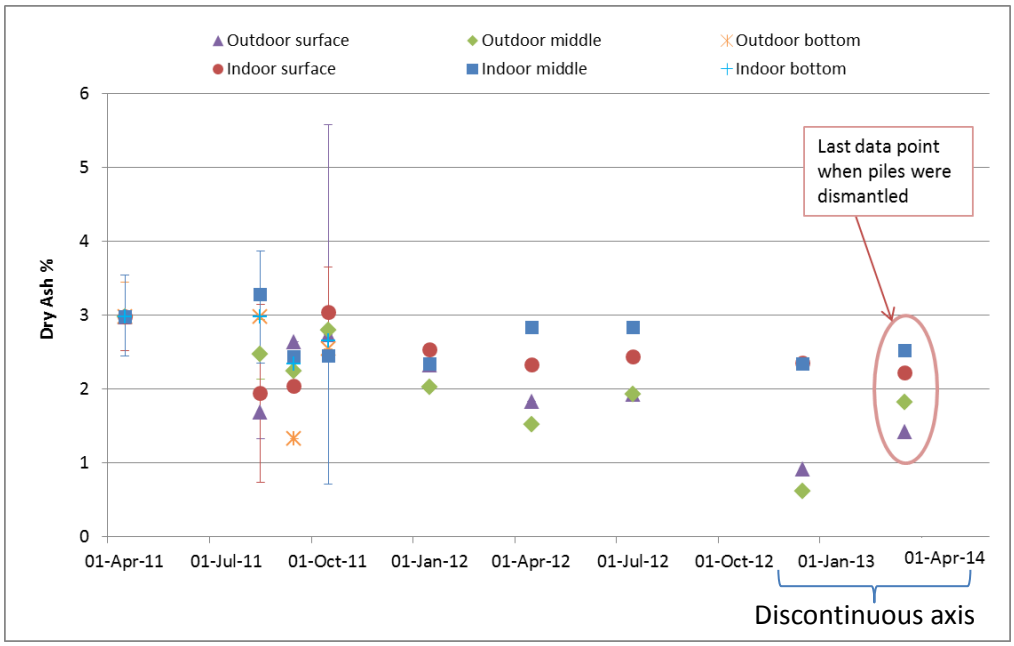

Figure 5-1. Dry ash Content of samples from Phase 1 thermally treated wood pellet piles

Figure 5-1 shows the dry ash content of the indoor and outdoor thermally treated wood pellets taken from both the surface and middle of each of the piles against time in storage. The April 2011 data point corresponds to the fresh sample when storage started. For the first six months, samples from the surface, middle and bottom of each pile were taken and analysed. But after October 2011, only the middle and surface samples were analysed. The last data points on the graph correspond to the final samples taken on 11 March 2014 when the piles were dismantled and removed. As storage progressed, no clear trends in dry ash content could be seen. Any changes were within the sample to sample variation. The sample variation in the dry ash content was in the range 0.8 to 2.5%.

Figure 5-2 shows the dry ash content of the Phase 2 indoor and outdoor Willow chips.

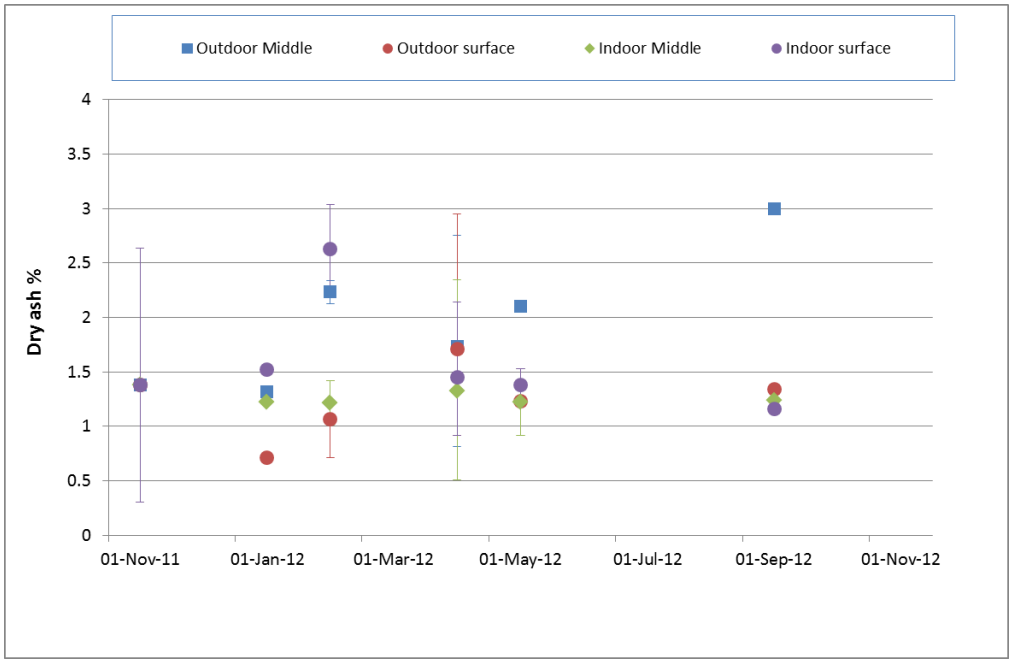

Figure 5-2. Dry ash Content of samples from Phase 2 indoor and outdoor Willow chips piles

Figure 5-2 shows the dry ash content of the indoor and outdoor Willow chips taken from both the surface and middle of each of the piles against time in storage. The November 2011 data point corresponds to the fresh sample when storage started. The piles were dismantled and removed in September 2012. Again, no significant changes in the dry ash content of the Willow chips could be seen. The same observations were made by (Jirjis, 2005), and (First Renewables Ltd., 2002) in their work on the storage of Willow chips. The sample variation in the dry ash content of the Willow had a range of 0.25 to 2.5%.

The graphs showing the dry ash content of the Phase 1 Willow chips, Phase 2 thermally treated wood pellets and Phase 2 white wood pellets are included in Appendix B. As for the Phase 1 thermally treated wood pellets and Phase 2 Willow chips, no clear trend in dry ash content could be found with time in storage.

5.2.2 Dry ash free volatile (DAF) content

Figure 5-3 shows the DAF volatile content of the Phase 1 indoor and outdoor thermally treated wood pellets with time in storage.

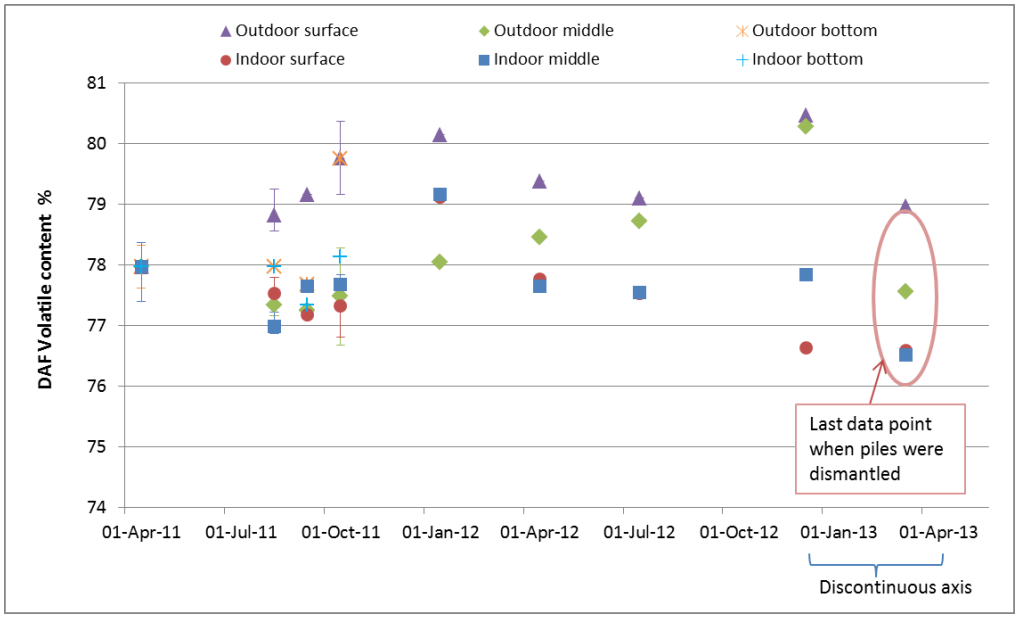

Figure 5-3. DAF volatile content of samples from Phase 1 thermally treated wood pellet piles

Figure 5-3 shows the DAF volatile content of the Phase 1 indoor and outdoor thermally treated wood pellets taken from both the surface and middle of each of the piles against time in storage. The April 2011 data point corresponds to the fresh sample when storage started. As noted above, after October 2011, only the middle and surface samples were analysed. The last data points on the graph correspond to the final samples taken on 11 March 2014 when the piles were dismantled and removed.

As storage progressed, no clear trends in dry ash free volatile content could be seen. Any changes were within the expected sample to sample variation. The sample variation in the dry ash free volatile content was in the range 1 to 2%.

Figure 5-4 shows the DAF volatile content of the Phase 2 indoor and outdoor Willow chips.

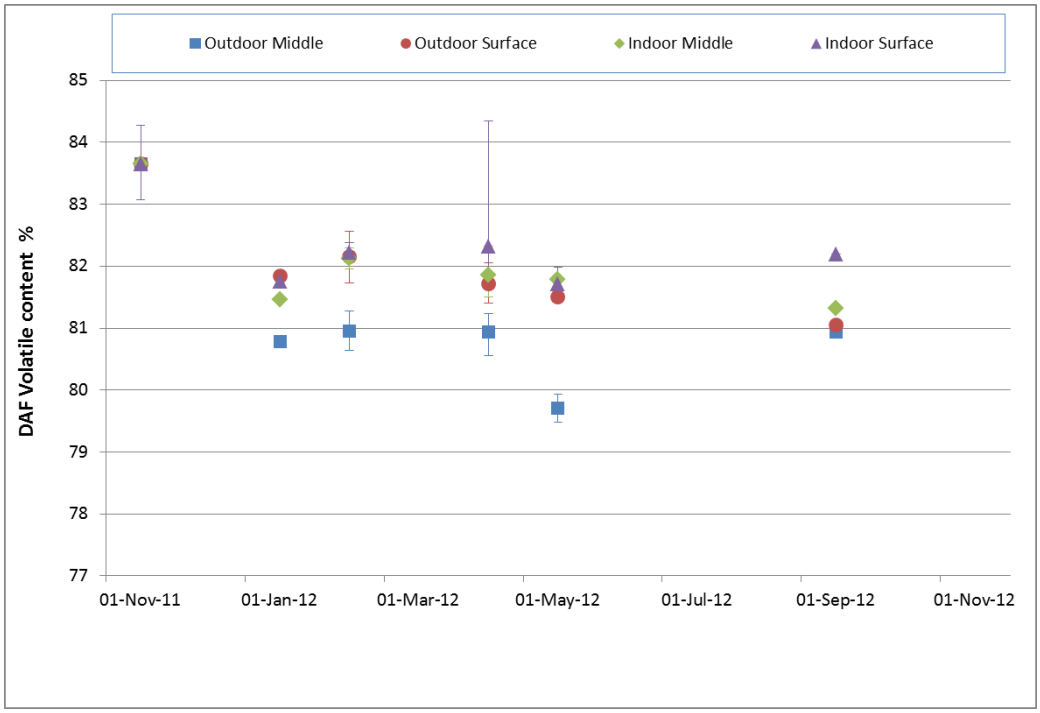

Figure 5-4. DAF volatile content of samples from Phase 2 indoor and outdoor Willow chips piles

Figure 5-4 shows the DAF volatile content of the Phase 2 indoor and outdoor Willow chips taken from both the surface and middle of each of the piles against time in storage. The November 2011 data point corresponds to the fresh sample when storage started. The piles were removed and dismantled in September 2012.

As storage progressed, no clear trends in dry ash free volatile content could be seen. From Figure 5-4, the DAF volatile content appeared to have dropped by about 2% in the first two months of storage, from November 2011 to January 2012. However because the normal sample to sample variation in DAF volatile content was in the range 1 to 4%, this decrease in DAF volatile content could be attributed to normal sample variability. The lack of trend in DAF volatile content during storage of Willow chips was also concluded by (Jirjis, 2005) and (First Renewables Ltd., 2002).

The graphs showing the DAF volatile content of the Phase 1 Willow chips, Phase 2 thermally treated wood pellets and Phase 2 white wood pellets are

included in Appendix B. As for the Phase 1 thermally treated wood pellets and Phase 2 Willow chips, no clear trends in DAF volatile content could be found with time in storage.

5.2.3 Dry ash free (DAF) calorific value

Figure 5-5 shows the DAF calorific value of the Phase 1 indoor and outdoor thermally treated wood pellets with time in storage.

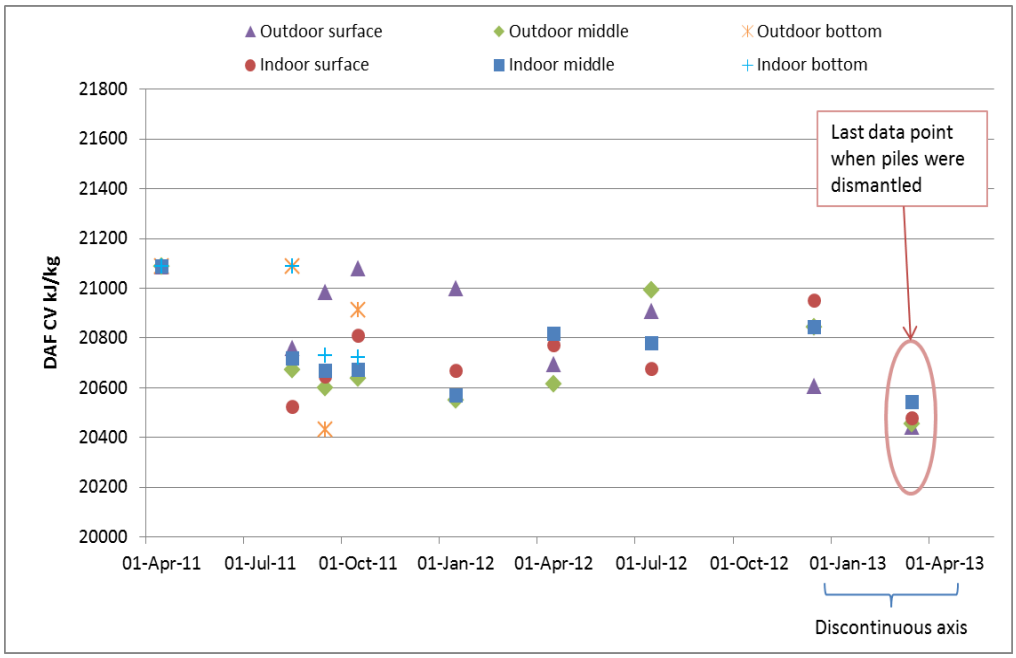

Figure 5-5. DAF calorific value of samples from Phase 1 thermally treated wood pellet piles

The April 2011 data point corresponds to the fresh sample when storage started. Once again, after October 2011, only the middle and surface samples were analysed. The last data points on the graph correspond to the final samples taken on 11 March 2014 when the piles were dismantled and removed.

The calorific value determination was always carried out in duplicate and the average value calculated. Multiple repeats were not carried out.

As storage progressed, no clear trends in DAF calorific value could be seen.

Figure 5-6 shows the DAF calorific value of the Phase 2 indoor and outdoor Willow chips taken from both the surface and middle of each of the piles against time in storage.

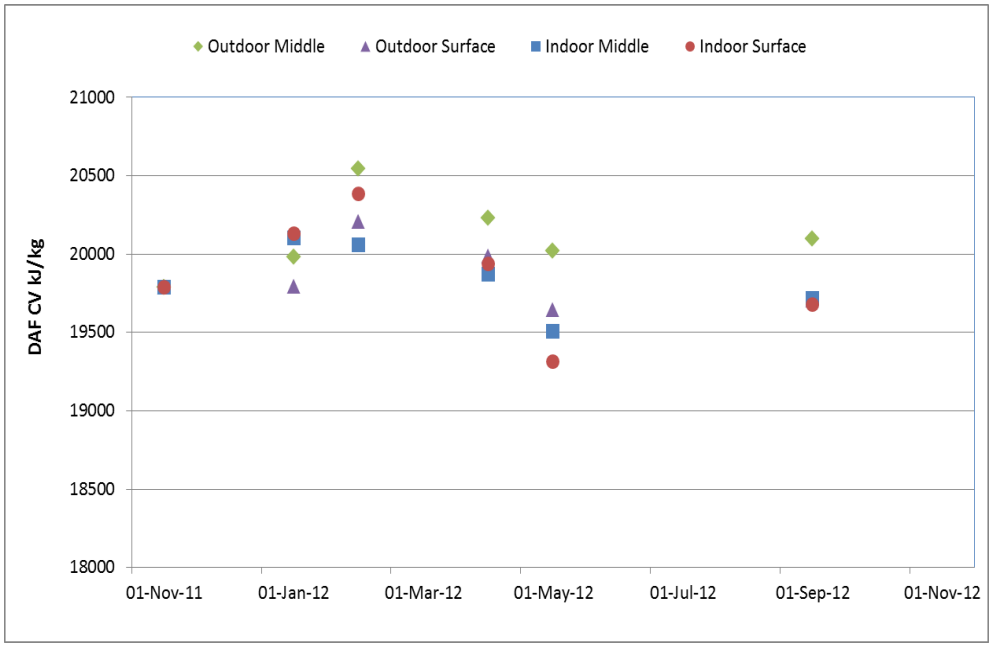

Figure 5-6. DAF calorific value of samples from Phase 2 indoor and outdoor Willow chip piles

The November 2011 data point corresponds to the fresh sample when storage started. The piles were dismantled and removed in September 2012.

As storage progressed, no clear trends in DAF calorific value could be seen.

The above graphs demonstrate that for the Phase 1 thermally treated wood pellets and Phase 2 Willow chips, there was no significant chemical degradation during storage. The dry ash content, DAF volatile content and DAF calorific value graphs showed no clear trends with time in storage. Any changes were found to lie within the normal range of fuel variability. The same observations were made by (Jirjis 2005) and (First Renewables Ltd., 2002) in their work on the storage of Willow chips. Similar trends were observed for the Phase 1 Willow chips, Phase 2 white wood pellets and Phase 2 outdoor thermally treated wood pellets. The graphs showing the trend in DAF calorific value of the Phase 1 Willow chips, Phase 2 thermally treated wood pellets and Phase 2 white wood pellets are included in Appendix B.

5.3 Moisture content of fuel

This section focuses on the total moisture content of the different fuels obtained at different periods throughout the storage trials. The moisture content data is presented alongside each of the weekly average humidity, weekly average ambient temperature and weekly total rainfall data. The total moisture content was obtained by the weight method after oven drying a fuel sample at 105°C for 24 hours according to [British Standard DD CEN/TS 15414-2:2010].

The free moisture content was also calculated as shown below:

$$Free\ moisture\ content = Total\ moisture\ content - Inherent\ fuel\ moisture\ content \quad [Equation\ 9]$$

Total moisture content is weight loss of sample after oven drying at 105°C for 24 hours

Inherent fuel moisture content is moisture content given by TGA test (moisture content that oven dried fuel sample would equilibrate to during milling and handling prior to TGA testing)

The total moisture content shown on all the graphs in this section is a single value (no repeats), see explanation in Section 3.7.1 for explanation.

The free moisture content follows the same trend as total moisture content and the graphs for free moisture content are shown in the appendix. The Willow chip piles total moisture content is shown first followed by the thermally treated pellet piles data followed by the white wood pellet pile data.

In the following graphs which show the trends in fuel moisture content, error bars are present on the relative humidity, ambient temperature and rainfall data points. They represent the range for the particular week (minimum and maximum values). This helped the average weekly value to be interpreted in context of the range for the week.

5.3.1 Phase 1 Willow Chip piles

Figure 5-7 to Figure 5-9 to below show the total moisture content of the Phase 1 Willow chip piles against each of the weekly average humidity, weekly average ambient temperature and weekly total rainfall.

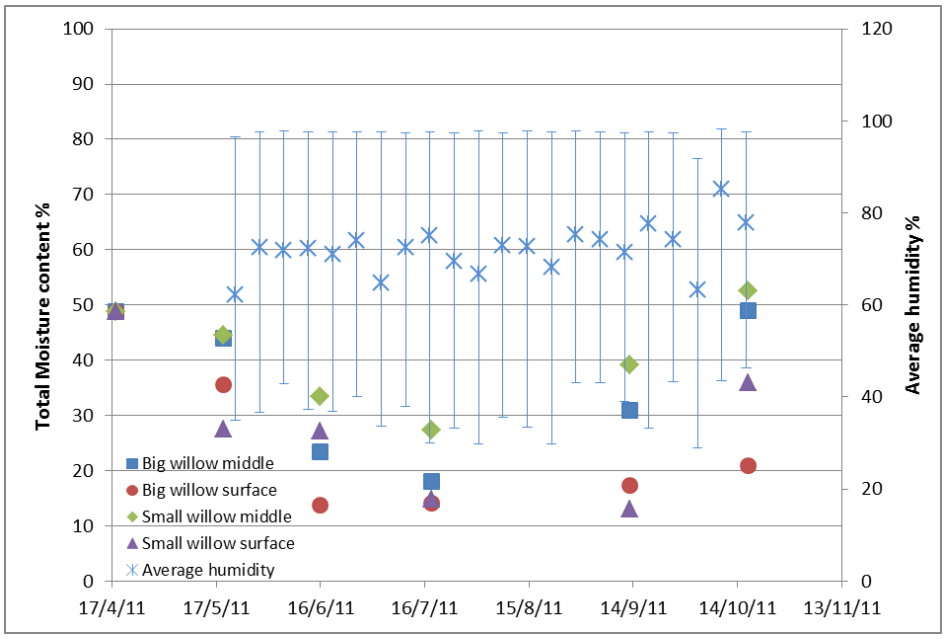

Figure 5-7. Total moisture content of Phase 1 Willow chips and weekly average humidity

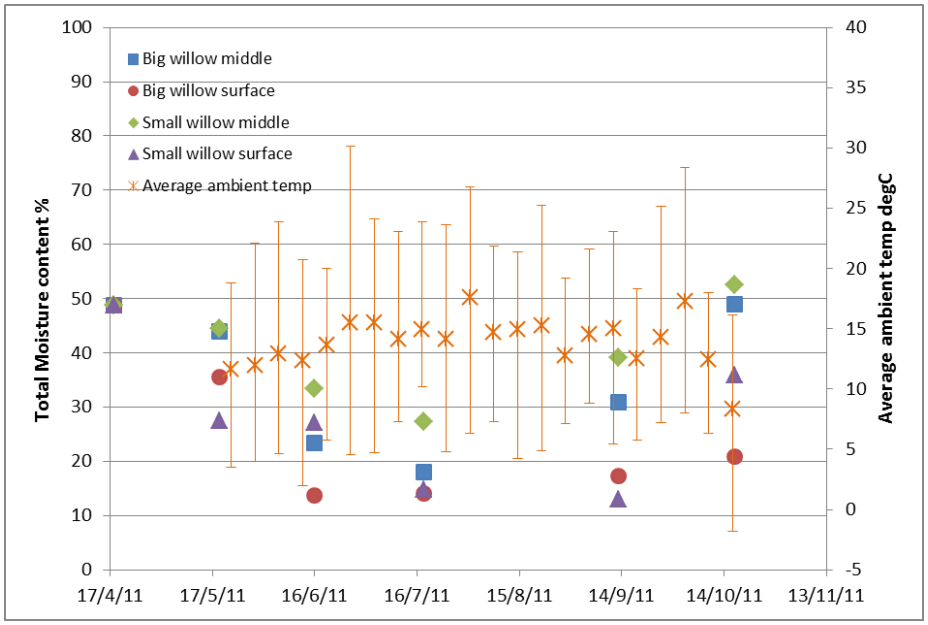

Figure 5-8. Total moisture content of Phase 1 Willow chips and weekly average ambient temperature

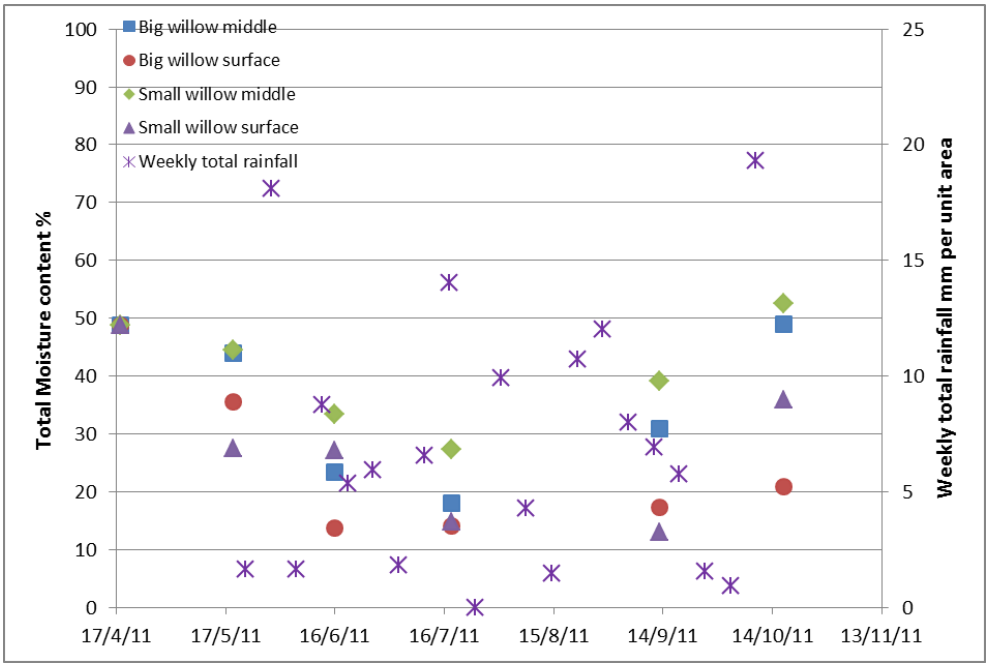

Figure 5-9. Total moisture content of Phase 1 Willow chips and weekly total rainfall per unit area

The data point in April 2011 corresponds to the freshly harvested Willow chips at the start of the storage period. The humidity, ambient temperature and rainfall measurements only started in May 2011 because of issues with the weather station data logger as described in Section 4.2. For each of the humidity and the ambient temperature data points, the weekly average value is displayed on the graphs with the error bars showing the minimum and maximum values each week. For the rainfall, the weekly total mm of rain is shown.

From the graphs, it can be seen that outdoor Willow piles dried gradually both at the surface and in the middle during the first three months in storage. However, from July 2011 onwards the weekly total rainfall as well as the rain frequency increased, resulting in an increase in the moisture content both on the surface and middle samples. The surface moisture content stayed lower than the moisture content at the middle most likely due to the drying effects brought about by being exposed to the wind and ambient temperature. The middle of both piles, on the other hand, saw a rapid increase in moisture

content after a period of rainfall with the levels reaching as high as the fresh fuel moisture content at the start of storage. The Willow's porous and fibous nature probably caused the rain water to penetrate the piles from the surface towards the middle, even though the piles were built with a conical shape in order to encourage the water running down the sides to the ground.

In terms of differences between the smaller and bigger Willow piles, the smaller pile dried more slowly (shown by the middle and surface moisture content of the small pile being higher than the middle and surface moisture content of the large pile throughout storage) and this can be explained by the lower temperatures developed in the small pile compared to the large pile (see Section 4.4.1). As might be expected, the smaller Willow chip pile became more saturated in water after frequent high rainfall due to easier and faster penetration of the water towards the middle of the pile.

5.3.2 Phase 2 Willow chip piles

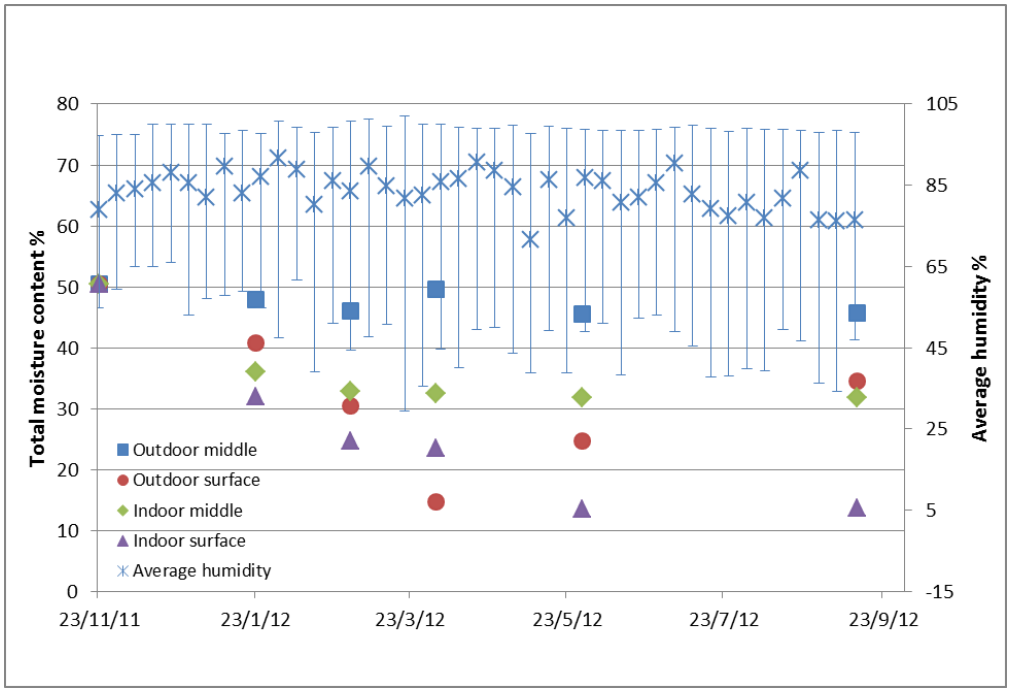

Figure 5-10. Total moisture content of Phase 2 Willow chips and weekly average humidity

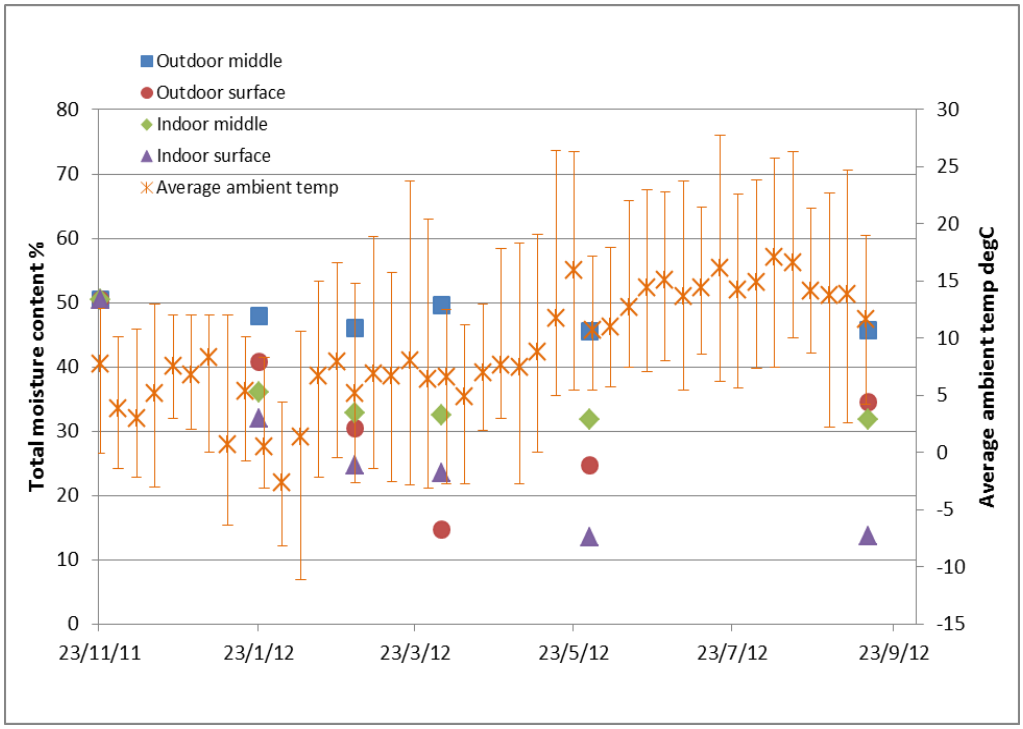

Figure 5-11. Total moisture content of Phase 2 Willow chips and weekly average ambient temperature

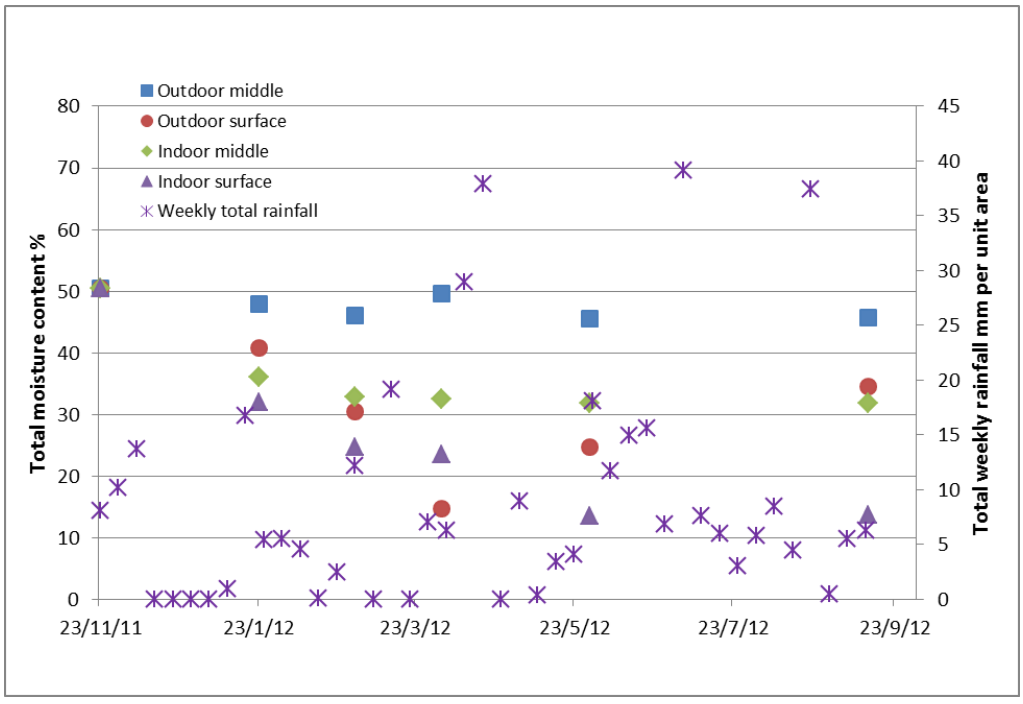

Figure 5-12. Total moisture content of Phase 2 Willow chips and weekly total rainfall per unit area

Figure 5-10 to Figure 5-12 show the moisture content of the Phase 2 Willow chips plotted alongside weekly average humidity, weekly average ambient

temperature and weekly total rainfall. The data point in November 2011 corresponds to the freshly harvested Willow chips at the start of the storage period. For each of the humidity and the ambient temperature data points, the weekly average value is displayed on the graphs with the error bars showing the minimum and maximum values each week. For the rainfall, the weekly total mm of rain is shown.

From the above graphs, a number of differences can be drawn out between the equally sized Phase 2 indoor and outdoor Willow chips piles. The middle of the indoor pile saw some drying with its moisture content dropping from about 50% down to about 30% in the first three months of storage but it then stayed constant at that level for the rest of the storage period. On the surface of this pile, a greater extent of drying took place with the moisture content reaching as low as 12%. The indoor Willow chip pile was stored in a ventilated area inside a barn which had two open sides, this would probably have contributed to better drying than a completely enclosed barn.

The outdoor Willow chip pile was influenced by the weather trends, as also observed in Phase 1. The middle of this pile saw a maximum moisture reduction of about 5%. From November 2011 to February 2012, the low extent of drying can be explained by the low average ambient temperature. From March to September 2012, the ambient temperature increased but so did the level and frequency of rainfall, which resulted in the middle of the pile retaining high levels of moisture. The surface of the outdoor pile dried gradually from November 2011 to March 2012 despite the cold ambient temperature; possibly due to the higher exposure to wind and easier evaporation path compared to the middle of the pile. However with the increased rainfall from March to August 2012, the moisture content on the surface of the pile increased once again.

5.3.3 Phase 1 thermally treated wood pellet piles

Figure 5-13 to Figure 5-15 show the total moisture content of the Phase 1 thermally treated wood pellets plotted against weekly average humidity, weekly average ambient temperature and weekly total rainfall.

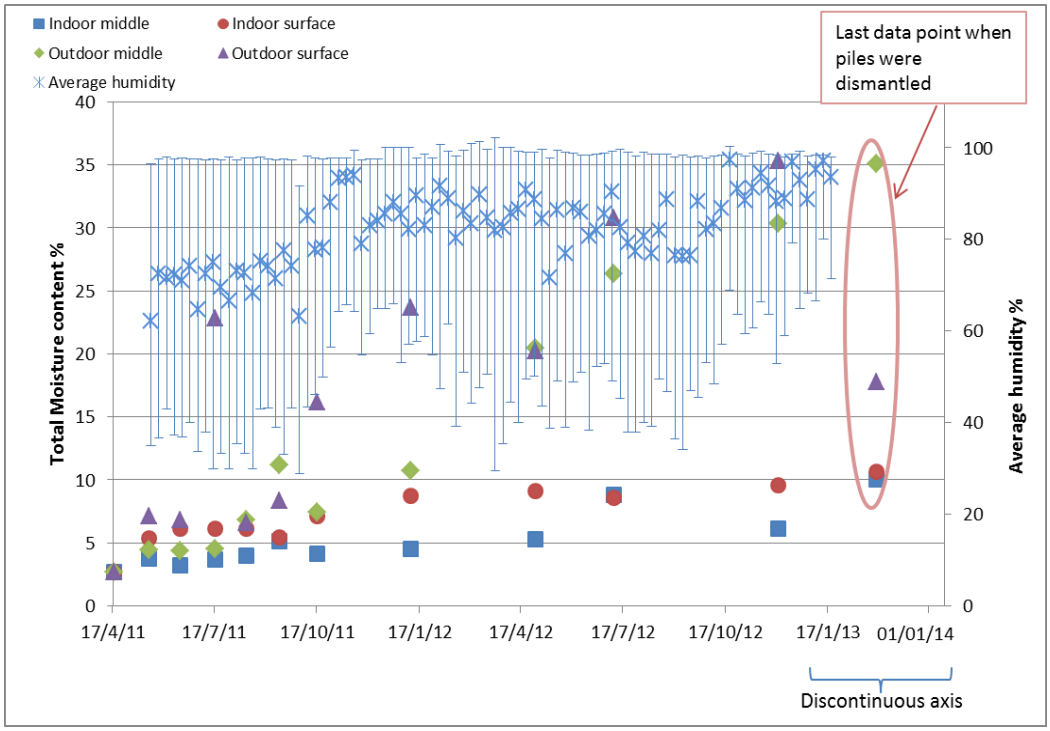

Figure 5-13. Total moisture content of Phase 1 thermally treated pellets and weekly average humidity

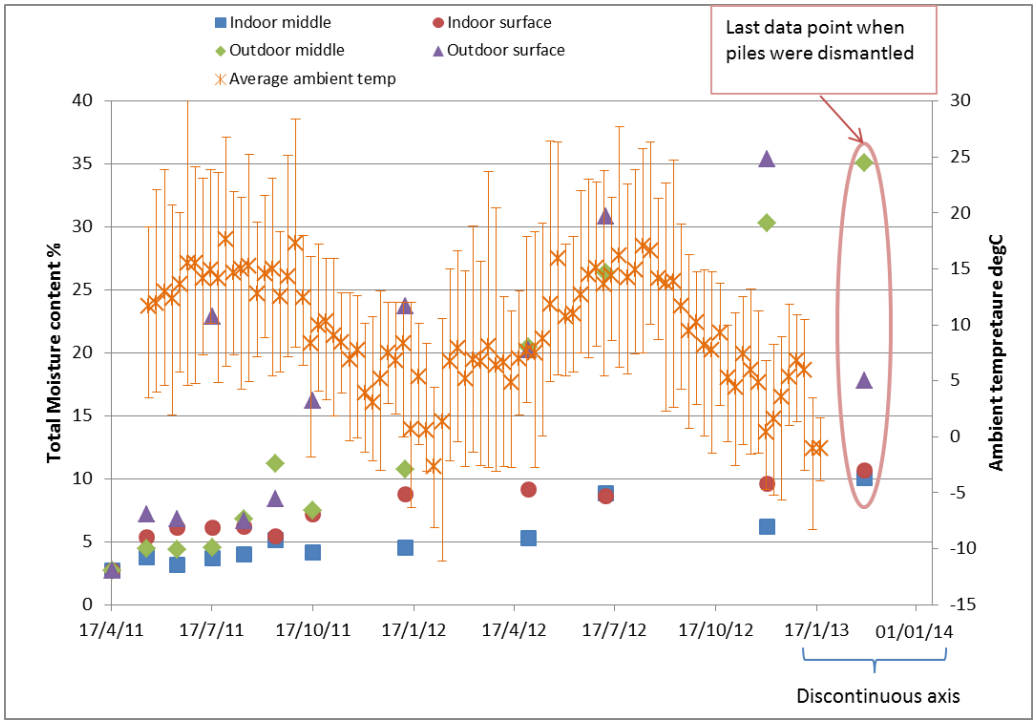

Figure 5-14. Total moisture content of Phase 1 thermally treated pellets and weekly average ambient temperature

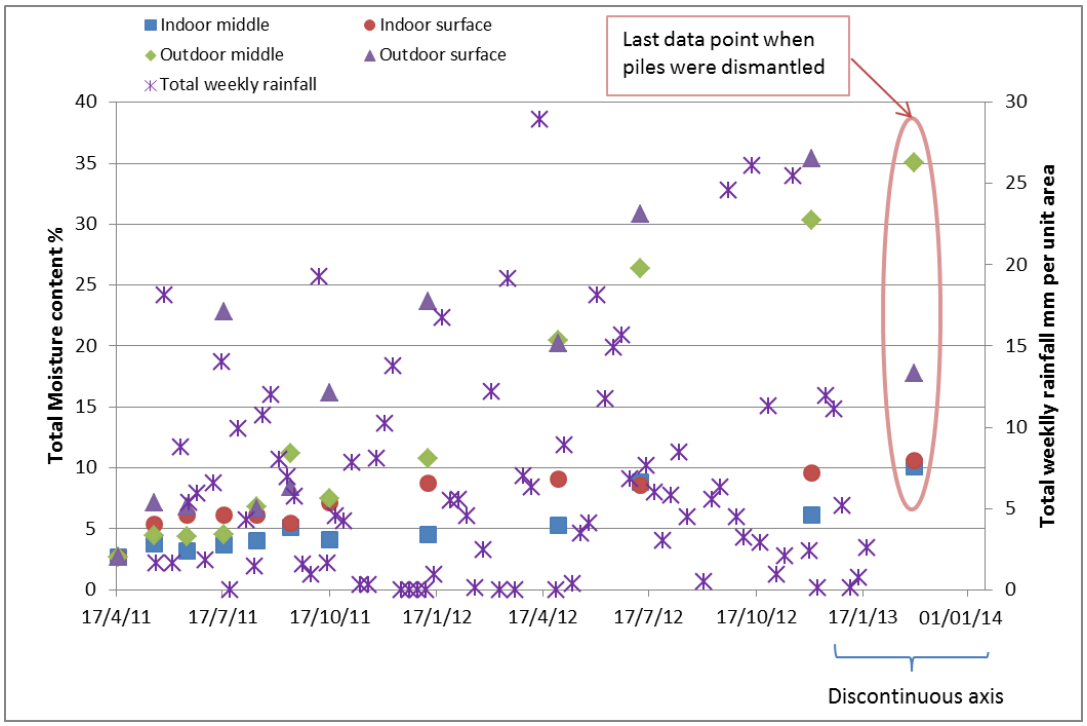

Figure 5-15. Total moisture content of Phase 1 thermally treated pellets and weekly total rainfall in mm per unit area

The data point in April 2011 corresponds to the fresh pellets at the start of the

storage period. The humidity, ambient temperature and rainfall measurements only started in May 2011 because of issues with the weather station data logger as described in Section 4.2. For each of the humidity and the ambient temperature data points, the weekly average value is displayed on the graphs with the error bars showing the minimum and maximum values each week. For the rainfall, the weekly total mm of rain is shown. The last data points on the graph correspond to the final samples taken in March 2014 on the day the piles were dismantled and removed. The relative humidity for the period January 2013 to March 2014 is not displayed on the graph.

The above three graphs show that both the indoor and the outdoor thermally treated wood pellet piles reacted to an increase in relative humidity as the trial progressed. The middle of the indoor pile saw a small increase in moisture content (1-2%) and then stayed stable. However for the surface of the indoor pile, the first six months of storage and exposure to humidity resulted in a steady rise in moisture content from 2 to 6%. In October 2011, the weekly average relative humidity saw a significant step increase of about 10% (from 75 to 85%) and this higher level of humidity prevailed for the remainder of the project. This would explain the further increase in the indoor pellet surface moisture content to 9%.

The outdoor thermally treated wood pellet pile was influenced by rainfall as well as humidity. In the first six months of storage from April to October 2011, the pellets displayed resistance to moisture ingress and absorption. The conical pile shape encouraged rainwater to run down the sides of the pile to the ground. The thermal treatment of the pellets improved their moisture resistance compared to untreated white wood pellets (Bergman and Kiel, 2005). From October 2011 onwards, the pellets on both the surface and in the middle of the outdoor pile became more prone to moisture intake. The weekly total rainfall and frequency as well as the weekly relative humidity all increased from October 2011, causing the pellets to be exposed to harsher conditions. In addition, in the autumn and winter months, the lower ambient temperature led to lower drying rates. The pellets on the surface saw large step increases in

moisture content in October and December 2011. The increasing ambient temperature (promoting drying) and lower average rainfall in April 2012 led to a drop in moisture content which then increased significantly again in July and December 2012 (31 and 35% respectively). The moisture content in the middle of the outdoor pile similarly increased significantly from October 2011 to December 2012 but consistently remained lower than the surface moisture content. This could be explained by the fact that the pellets on the surface were absorbing water very readily acting as a 'sponge', having lost their resistance to moisture ingress. This possibly meant that the flow of water towards the centre of the pile during rainy periods was lower, causing the middle of the pile to stay drier than the surface.

It is difficult to comment in detail on the moisture content of the final samples in March 2014 as there was a big gap between these samples and the previous ones. Also the weather data was not analysed for the period January 2013 to March 2014.

5.3.4 Phase 2 thermally treated wood pellet piles

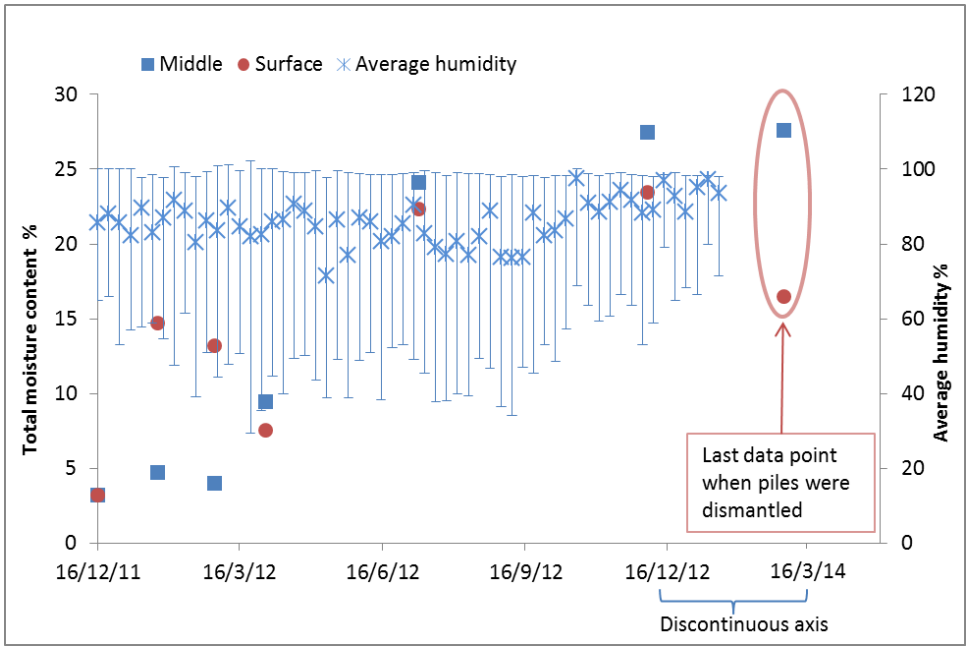

Figure 5-16. Total moisture content of Phase 2 thermally treated pellets and weekly average humidity

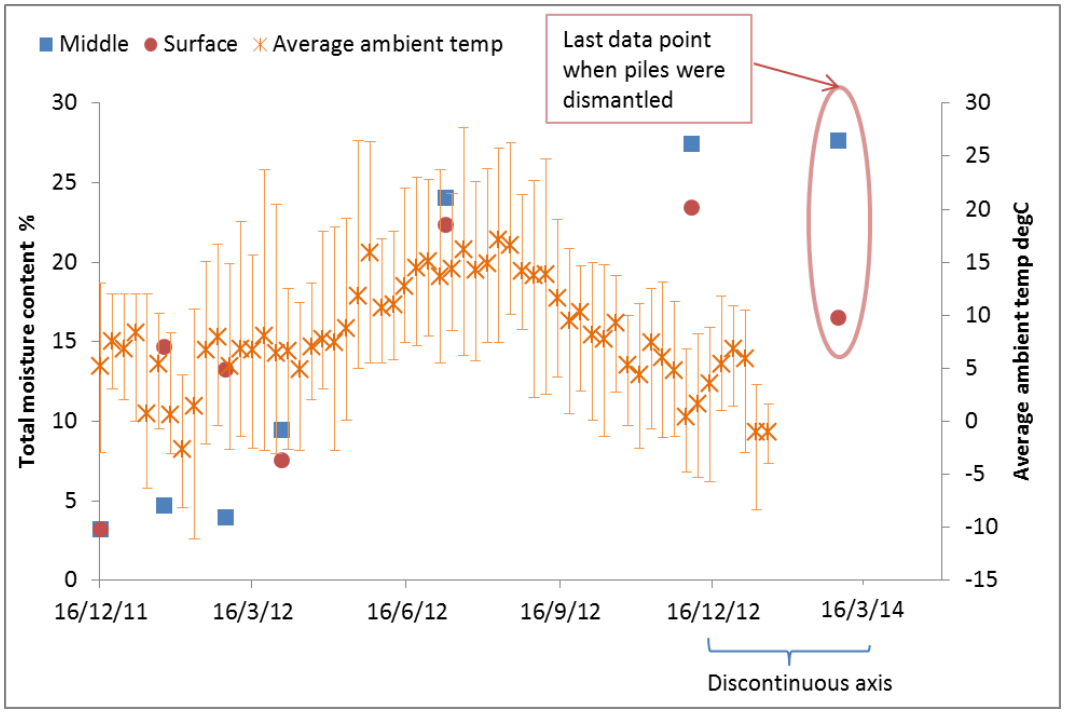

Figure 5-17. Total moisture content of Phase 2 thermally treated pellets and weekly average ambient temperature

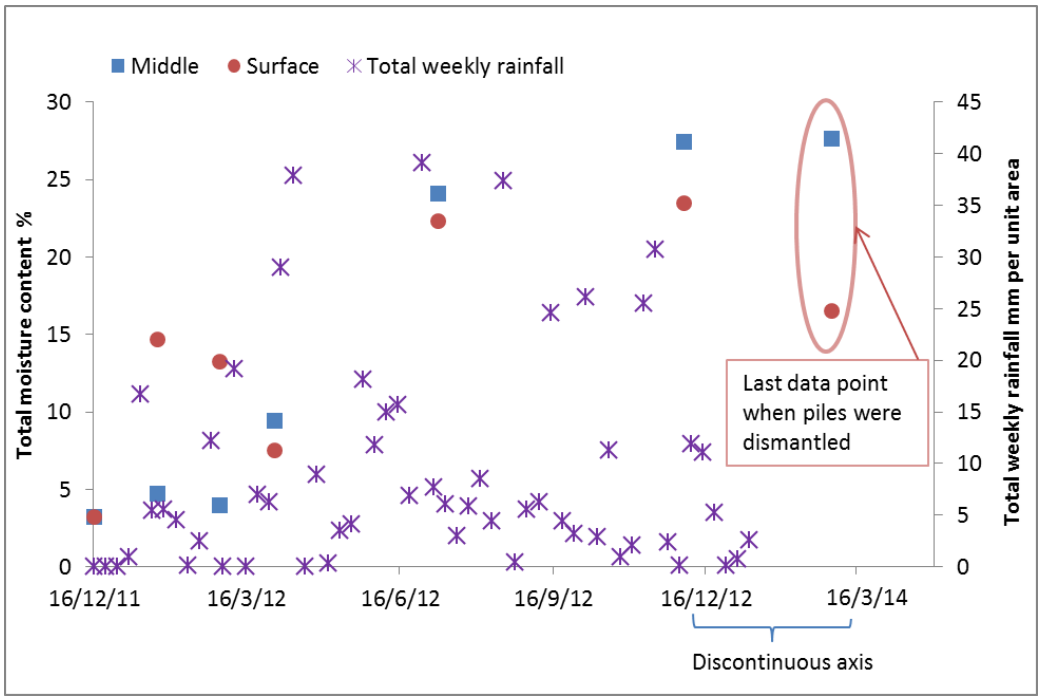

Figure 5-18. Total moisture content of Phase 2 thermally treated pellets and weekly total rainfall per unit area

Figure 5-16 to Figure 5-18 show the total moisture content of the Phase 2 thermally treated wood pellets plotted alongside the weekly average humidity, weekly average ambient temperature and weekly total rainfall. The data point in December 2011 corresponds to the fresh pellets at the start of the storage period. For each of the humidity and the ambient temperature data points, the weekly average value is displayed on the graphs with the error bars showing the minimum and maximum values each week. For the rainfall, the weekly total mm of rain is shown.

It is worth starting the discussion on the moisture behaviour of the Phase 2 outdoor thermally treated wood pellet pile by highlighting that throughout its storage, it was subjected to a high level of humidity (mostly 80% and above). This was higher than what was seen during the Phase 1 test period. Section 4.2.1 highlights the difference in humidity seen in Phase 1 and Phase 2.

High humidity and a total weekly rainfall of 17mm in mid January 2012 led to a large step in the surface moisture content from 3 to 15%. Increasing ambient temperatures in the spring as well as a relatively dry period in the last two weeks of March resulted in a decrease in the surface moisture content in April. However regular periods of high rainfall between April and December 2012 are believed to have caused the pellet's resistance to moisture to drop, with the surface moisture content rising consistently to reach as high as 23%.

For the middle of the pile, the moisture content did not change much in the first two months of storage. This is likely to be because the conical shaped pile caused the rain water to run down the sides of the pile with the pellets on the surface exhibiting resistance towards moisture ingress, leading to little flow towards the centre of the pile. However as the level of rainfall picked up dramatically from April 2012 onwards, water flow towards the middle of the pile increased as did the moisture content. The moisture content of the middle sample in December 2012 was as high as 27%.

An interesting observation when comparing the Phase 2 and Phase 1 outdoor thermally treated wood pellet piles was that at the end of Phase 2, the middle of the pile was wetter than the surface which is opposite to what was observed for Phase 1. The following explanations are suggested:

- In Phase 1 the pellets on the surface and in the top layers have lost all resistance to moisture due to significant mechanical degradation and therefore absorbed the water readily, maintaining high levels of moisture and therefore the middle stayed drier. The differences in extent of mechanical degradation between the Phase 1 and Phase 2 pellets are explained fully in Section 6.7
- In Phase 2, the surface pellets were less mechanically degraded and still showed some moisture resistance at the end of the storage period, hence the water flowed past them towards the middle of the pile, resulting in high levels of moisture there
- Although both sourced from the same supplier, The Phase 1 and Phase 2 pellets were almost certainly different in terms of raw material, degree of thermal treatment and hence showed different behaviour. This is only based on physical observations. The Phase 2 pellets were a lot lighter in colour and did not have a shiny appearance. The Phase 1 pellets were a lot darker coloured and exhibited a 'glassy' external appearance. Section 6.7 draws out the differences in mechanical properties between the two pellet types.

It is difficult to comment in detail on the moisture content of the final samples in March 2014 as there was a big gap between these samples and the previous ones taken. Also the weather data was not analysed for the period January 2013 to March 2014.

5.3.5 Phase 2 white wood pellets

The white wood pellet pile was stored indoors in the same open barn as the Phase 1 indoor thermally treated wood pellet pile and the Phase 2 indoor Willow chip pile.

Figure 5-19 to 5-21 show the moisture content of the pellets.

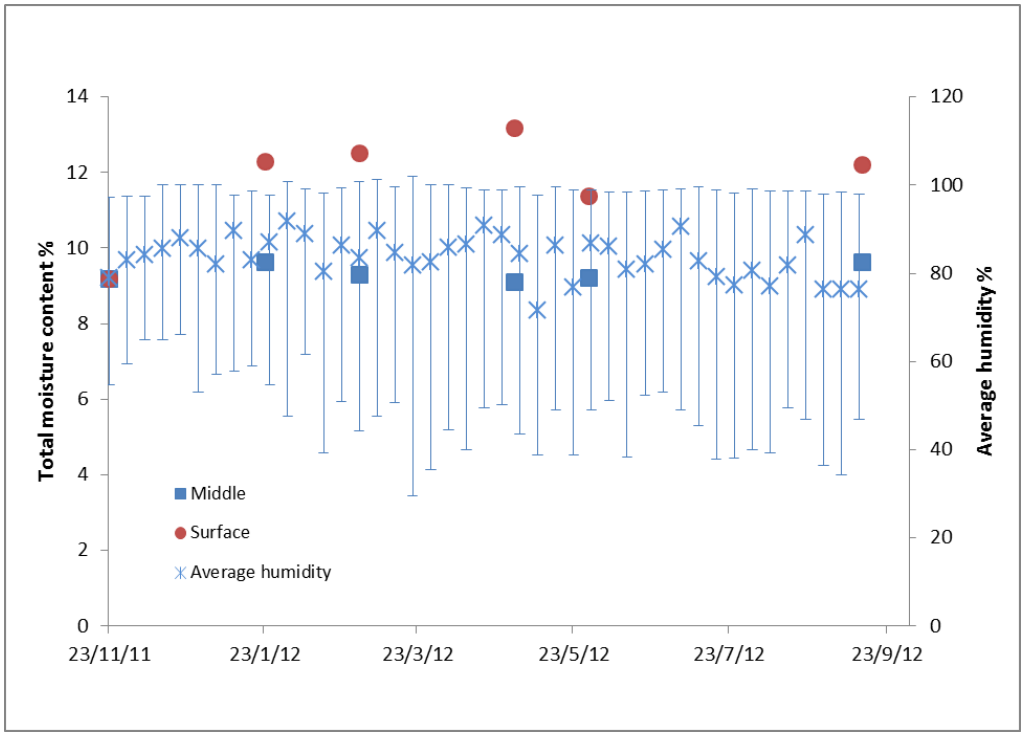

Figure 5-19. Total moisture content of Phase 2 white wood pellets and weekly average humidity

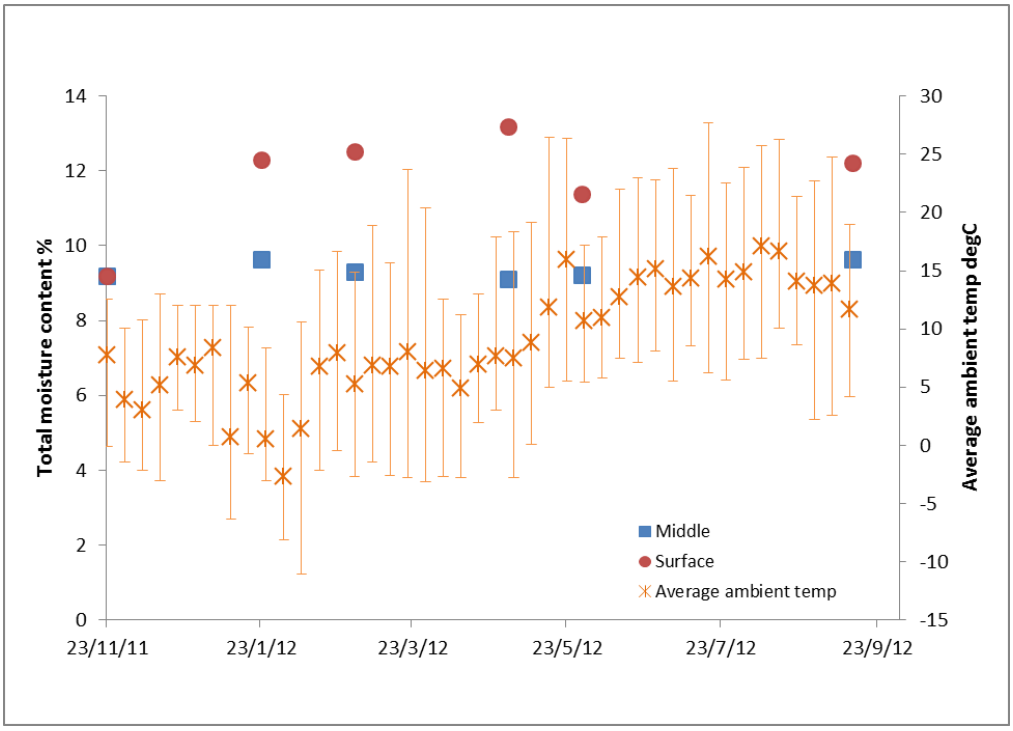

Figure 5-20. Total moisture content of Phase 2 white wood pellets and weekly average ambient temperature

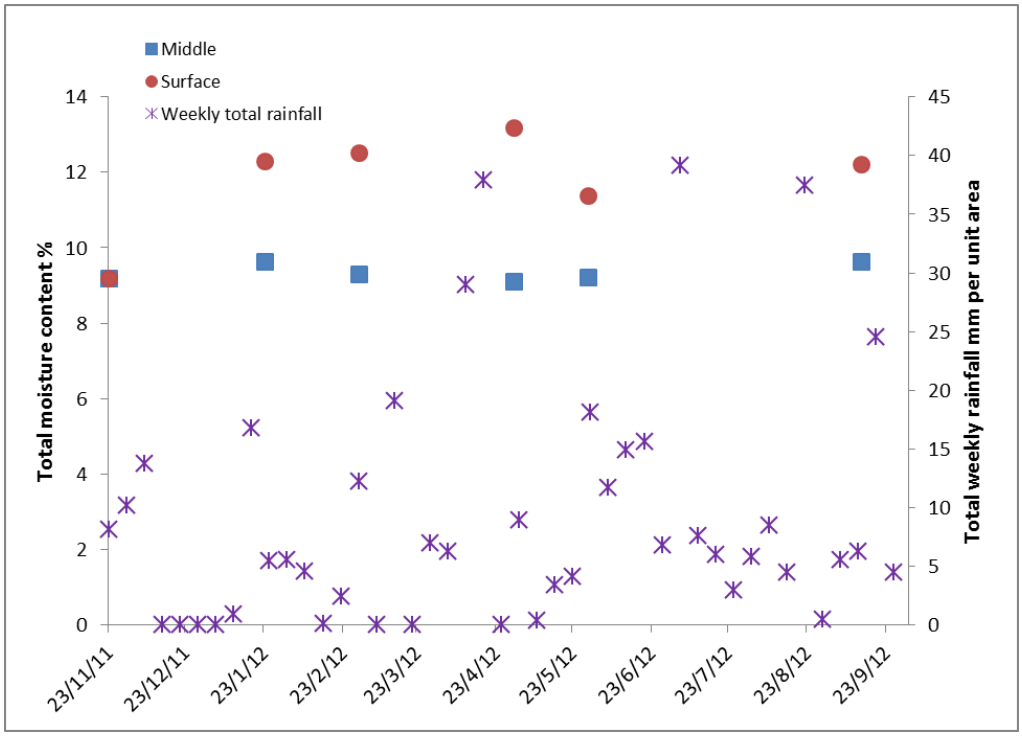

Figure 5-21. Total moisture content of Phase 2 white wood pellets and weekly total rainfall per unit area

Figure 5-19 to Figure 5-21 show the total moisture content of the Phase 2 white wood pellets plotted alongside the weekly average humidity, weekly average ambient temperature and weekly total rainfall. The data point in November 2011 corresponds to the fresh pellets at the start of the storage period. For each of the humidity and the ambient temperature data points, the weekly average value is displayed on the graphs with the error bars showing the minimum and maximum values each week. For the rainfall, the weekly total mm of rain is shown.

The above graphs show that hardly any change in the moisture content occurred in the middle of the white wood pellet pile. On the surface of the pile, due to the effects of humidity, the moisture content increased gradually from November 2011 to April 2012 from a value of 9% to 13%. As the ambient temperature increased in May 2012, a lower moisture content was seen. Significant step increases in the total weekly rainfall (April, July and August 2012) also led to a rise in surface moisture content potentially due to roof

leakage and rain getting entrained horizontally in the wind and wetting the pile inside the open barn.

From the trends in the moisture content of the different fuels, the main conclusions are as follows:

- Storing white wood pellets in an environment where the pellets are exposed to high humidity can result in the pellets' moisture content rising to as high as 13%. Section 6.6 fully describes the resulting impacts on the pellets' mechanical strength. Therefore white wood pellets should only be stored in a fully enclosed space where the humidity level is kept low. It is well known that outdoor storage of white wood pellets is totally unadvisable and the results of this work shows that storage in a covered open barn is also not viable because the pellets are highly sensitive to ambient relative humidity

- For the Willow chips, indoor storage with ventilation results in continuous drying of the chips on the surface but the chips in the middle of the pile undergo a smaller extent of drying with the moisture content remaining high. One way of ensuring that all the chips are dried is to turn the pile.

- In outdoor storage, the moisture content of the Willow chips is influenced by the weather pattern, especially the rainfall. When rainfall is low, both the surface and middle of the pile dry continuously, the extent of drying being higher for the chips on the surface of the pile. Pile turning would again help with achieving uniform drying. Drying is also faster in the summer months due to the higher ambient temperature. In both summer and winter, a period of high rainfall causes the chips absorb moisture again.

- Storing thermally treated pellets in a covered but ventilated storage environment (open barn in this project) results in a gradual increase in moisture content over time due to exposure to humidity but after 20

months in storage, the moisture content was still < 10%. A step increase in humidity results in a step increase in moisture content.

- In outdoor storage, the moisture content is highly influenced by humidity and rainfall, but the effects of rainfall are more dramatic and significant. In the first six months of Phase 1, the humidity averaged at 75% but rainfall was low. The outdoor pellets showed high resistance to moisture ingress with the moisture content of the pellets from both the surface and middle of the pile staying below 15%. From the seventh month onwards, both the humidity and rainfall increased and stayed continuously high and the outdoor pellets absorbed a lot of moisture.

- In countries with long periods of low humidity and rainfall, outdoor storage of Willow chips and thermally treated wood pellets would promote gradual drying of the fuels and pile turning could be performed to promote uniform drying

- In the UK, the weather is not very predictable and periods of continuously low rainfall are rare. Therefore it is more risky to store biomass fuels in outdoor stockpiles

5.4 Net calorific value

This section follows the section on fuel moisture content because of the direct impact of moisture on net calorific value. As the moisture content of any fuel increases, its net calorific value decreases.

The gross, or higher, calorific value is determined in the laboratory using a calorimeter. It can be defined as the total heat liberated by the complete combustion of the fuel. It is determined by measuring the heat removed when cooling the products of combustion to a standard reference temperature, and it includes the latent heat recovered from condensation of the water vapour

component. This water vapour forms as a result of the combustion of any hydrogen molecules contained within the fuel, and the vaporisation of any moisture present.

The net, or lower, calorific value equals the gross calorific value minus the latent heat of the water vapour formed from the combustion of hydrogen and from any moisture present in the fuel. The net value is more representative of the heat available in practice when fuels are burned in equipment such as furnaces and boilers. The latent heat of the water vapour contained in exhaust gases is not normally recoverable, except where low-temperature heat recovery involving condensation is used (CHP from DECC)

The same four test piles used to illustrate the changes with time of dry ash, DAF volatile matter and DAF calorific value are again used in this section. Figure 5-22 and Figure 5-23 below show the net calorific value (wet basis) of the Phase 1 thermally treated wood pellet piles and the Phase 2 Willow chip piles plotted against the moisture content.

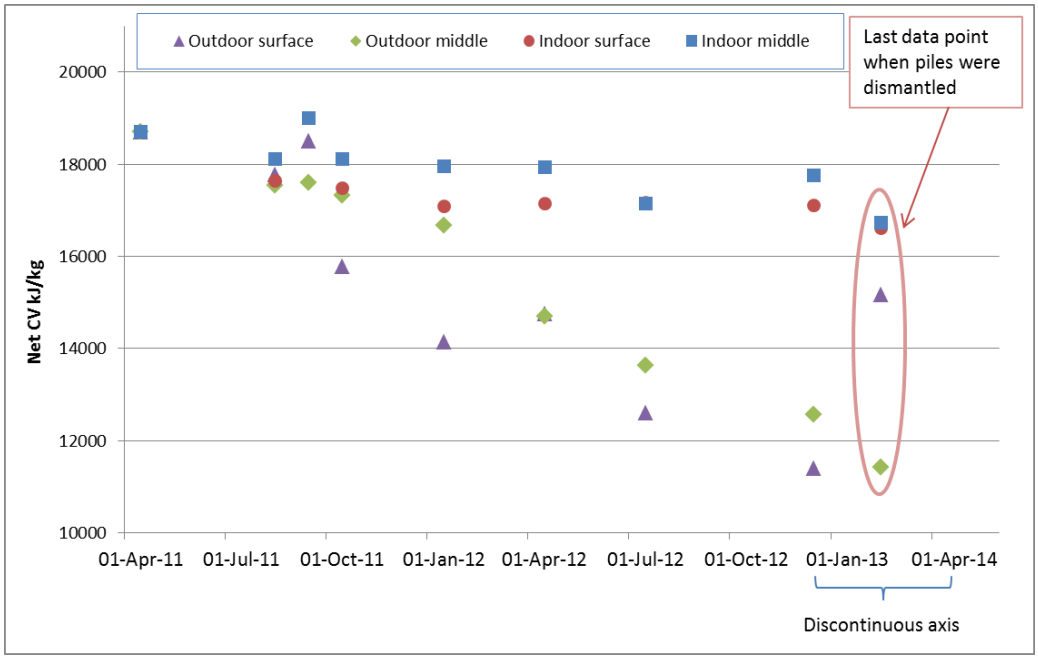

Figure 5-22. Net CV (wet basis) of samples from Phase 1 thermally treated wood pellet piles

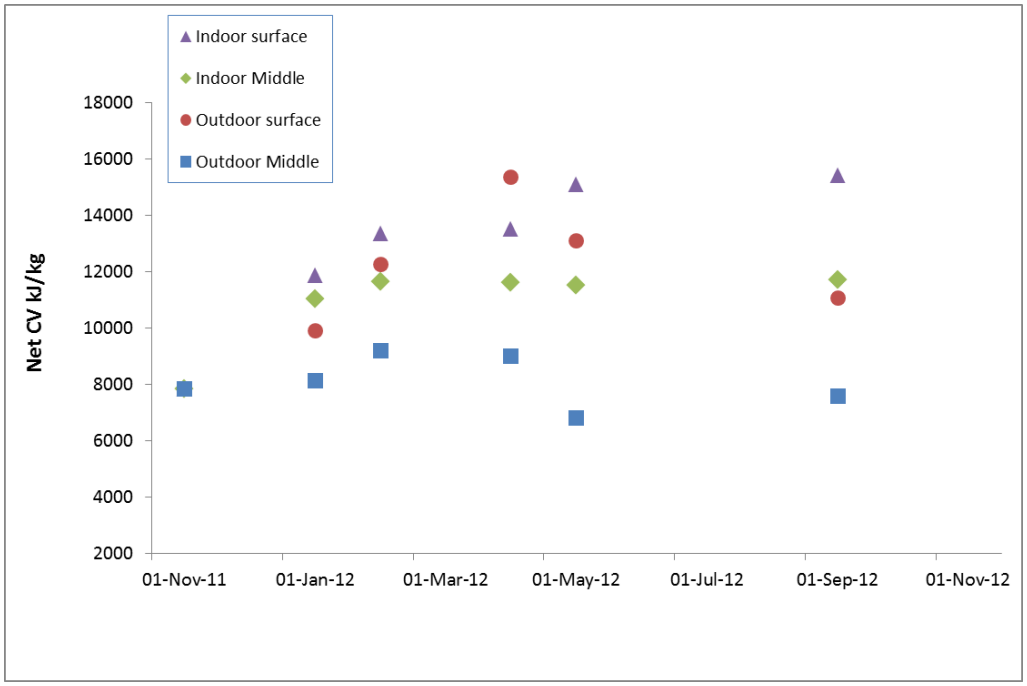

Figure 5-23. Net CV (wet basis) of samples from Phase 2 indoor and outdoor Willow chip piles

While similar trends were observed for the Phase 1 pellets and Phase 2 Willow chips in the dry ash content, DAF volatile content and DAF CV, for the net CV the pellets and the Willow chips exhibited different behaviour. This is because of the direct impact of moisture content on the net CV and the very different starting moisture contents of the two materials. The net CV trend for each of the above piles is explained below.

- For the indoor pellet pile, the pellets from both the surface and middle gradually absorbed moisture as time in storage increased, resulting in a decreasing net CV trend. The pellets on the surface absorbed more moisture, hence the lower net CV.
- The net CV of the pellets from the outdoor pellet pile also decreased as moisture content increased. The outdoor pile absorbed significantly more moisture than the indoor pile with the surface being wetter than the middle again, resulting in a lower net CV.
- The Phase 2 Willow chips' general trend was of an increasing net CV which was a result of drying and general decrease in moisture content.

The surface of the indoor pile dried more than the middle, as reflected by its higher net CV. The outdoor Willow pile was affected by the weather conditions. The cold months meant that the middle of the pile did not experience any significant drying, hence no significant changes in net CV were observed. The surface of the outdoor Willow pile dried in the first few months from November 2011 to April 2012, causing the net CV to increase. However from May 2012 onwards, due to increased rainfall, the moisture content rose again resulting in a drop in net CV.

Figure 5-24 and Figure 5-25 below show the strength of the correlation between net CV and moisture content for the Phase 1 thermally treated wood pellets and Phase 2 Willow chips respectively, hence laying the emphasis on the need to minimise the moisture intake. The R^2 value obtained for a linear trendline for each of the samples is shown on the graphs next to the respective sample. A strong linear correlation as per Equation 2 in Section 2.5.1.4 is shown.

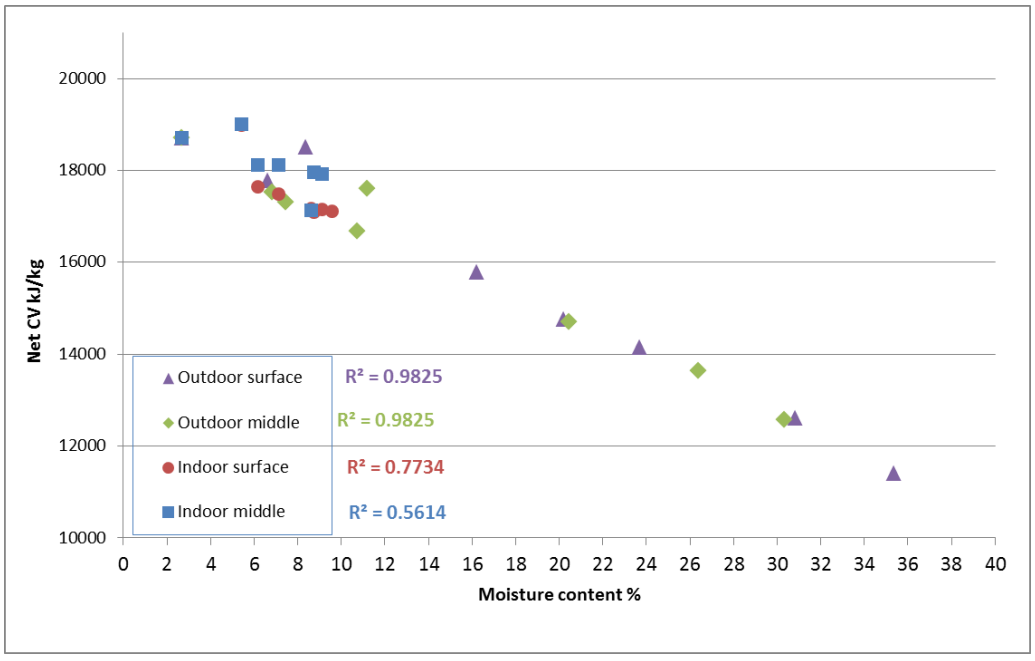

Figure 5-24. Net CV of Phase 1 thermally treated pellets against moisture content

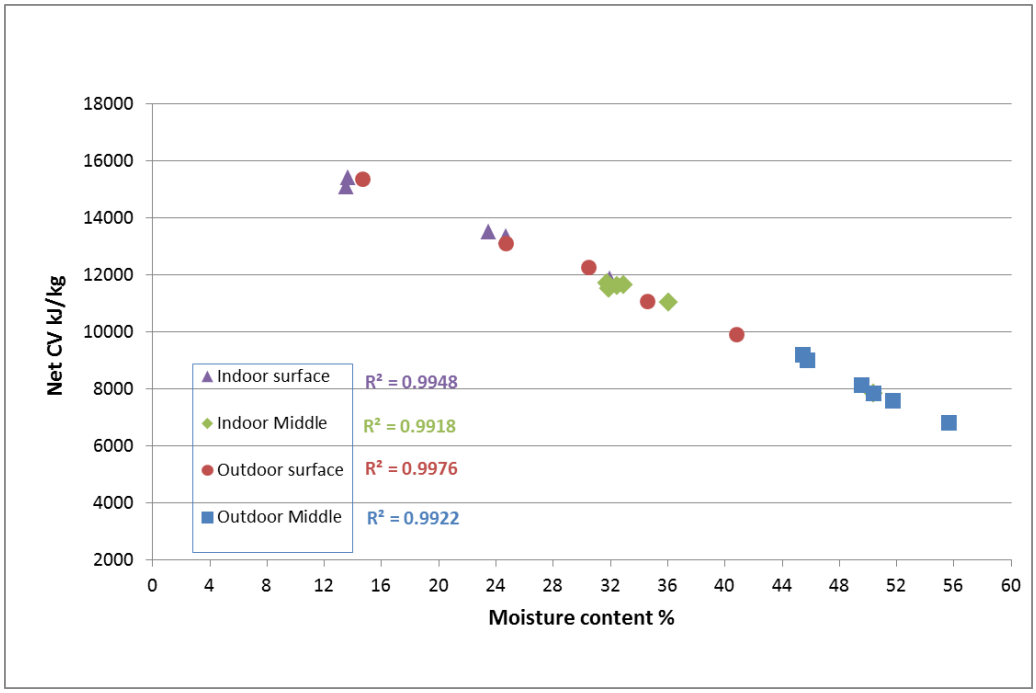

Figure 5-25. Net CV of Phase 2 Willow chips against moisture content

The main conclusions from this section on the impacts of storage on the net calorific value of biomass fuels are as follows:

- Thermally treated wood pellets showed a decrease in net calorific value during storage, the drop being more significant for the pellets stored outdoors as the increase in moisture content was higher

- For white wood pellets (Figure B27 in Appendix B), the net calorific value of the pellets from both the surface and the middle of the pile decreased in the first six months of storage. During the winter, the pellets absorbed moisture, with the increase in moisture content and hence decrease in net CV being larger for the pellets on the surface of the pile. From May 2012 onwards, the higher ambient temperature promoted natural drying of the pellets, resulting in a decrease in moisture content and an increase in net CV for both the surface and middle pellets

- Willow chips in indoor storage underwent gradual drying and increase in net CV. In outdoor storage, the moisture content and therefore net CV were influenced by the weather conditions, particularly rainfall.

6 Mechanical degradation of biomass pellets during storage

6.1 Introduction

This chapter focuses on the mechanical degradation of the pelletised fuels studied namely white wood pellets and thermally treated wood pellets.

The extent of degradation of mechanical properties was measured on a regular basis during both Phases 1 and 2 of the project. A range of tests were carried on the pellet samples from the stockpiles as listed below:

- Pellet durability
- Measurement of average pellet diameter, in order to assess the extent of moisture absorption and breakdown in pellet structure
- Pellet compression strength (axial and diametrical),
- Pellet inter-laminar shear modulus (stiffness).

In addition, inspections and visual monitoring was carried out, with photographs and scanning electron microscopy (SEM) images used to assess the changes in shape, texture, colour as well as crack formation and propagation.

Each of the test methods has been described in detail in Section 3.6 of the methodology chapter.

6.2 Data processing

For each fuel, the durability, diameter, compression strength and shear modulus were analysed against time in storage. A general trend could be

observed for most of the properties but there were also changes in trend throughout the storage, which led to the analysis of the mechanical data in combination with the weather data and the moisture levels in the pellets

As the pellets absorbed moisture, swelling occurred and as they dried afterwards, shrinkage occurred. Frequent and significant changes in moisture content upon exposure to humidity and rainfall therefore result in pellet weakening as a result of this cyclic growth and shrinkage.

Therefore, in the data analysis process, the Phase 1 and Phase 2 mechanical data was plotted alongside each of the average weekly relative humidity, average weekly ambient temperature and average weekly total rainfall against time in storage. The mechanical properties were also plotted against the pellet moisture content.

6.3 Results section structure

Three pellet types were studied in this project namely:

- Thermally treated pellets in Phase 1 of storage trials (April 2011 – January 2013)
- Thermally treated pellets in Phase 2 of storage trials (December 2011 – January 2013)
- White wood pellets in Phase 2 of storage trials (November 2011 – September 2012)

The results section of this chapter is split into three parts with each focusing on one of the pellet types. In each section, the full range of test results for the particular pellet will be presented and discussed. The photographs of the pellets and the SEM images will be shown first as they illustrate the textural and structural changes in the pellets which can be used to explain the trends seen in durability, diameter, compression strength and stiffness. The pellet durability

test results will then follow followed by the pellet diameter, the axial and diametrical compression strength and the pellet stiffness data.

Comparisons between Phase 1 and Phase 2 results, along with similarities and differences in the behaviours exhibited by the different pellets, will be made in a separate section at the end of the results.

6.4 Detailed results for the Phase 1 thermally treated wood pellets

6.4.1 Photographs of samples

Figure 6-1 to Figure 6-4 below show the fresh pellets at the start of storage in April 2011 and degraded pellets on the surface of the indoor and the outdoor thermally treated pellet pile in July and October 2011 after three and six months in storage respectively.

Figure 6-1. Fresh pellets April 2011

Figure 6-2. Pellets on surface of indoor pile in July 2011 (3 months storage)

Figure 6-3. Pellets on surface of outdoor pile in July 2011 (3 months storage)

Figure 6-4. Pellets on surface of indoor pile in October 2011 (6 months storage)

Figure 6-5Pellets on surface of outdoor pile in October 2011 (6 months storage)

A significant change in appearance was noticed in the pellets from the surface of the outdoor pile after three months. The fresh pellets (Figure 6-1) have a clearly smooth and shiny outer surface which is dark in nature. This is largely unchanged for those pellets stored indoors (Figure 6-2 and Figure 6-4), although there is evidence of small cracks in the surface which have not penetrated into the structure of the pellet. Figure 6-2 and Figure 6-4 show the outdoor stored pellets where there are clearly major cracks that have propagated through the pellet structure, leading to a multiple fractured appearance. The photographs show that storage has resulted in pellet

degradation, the extent being much larger for those stored outdoors compared to those indoors.

6.4.2 Scanning electron microscopy (SEM) images of pellets

Figure 6-6 to Figure 6-8 show SEM images of the circular cross section of: a fresh pellet in April 2011, a pellet from the surface of the indoor pile in October 2011 and a pellet from the surface of the outdoor pile also in October 2011 (six months storage).

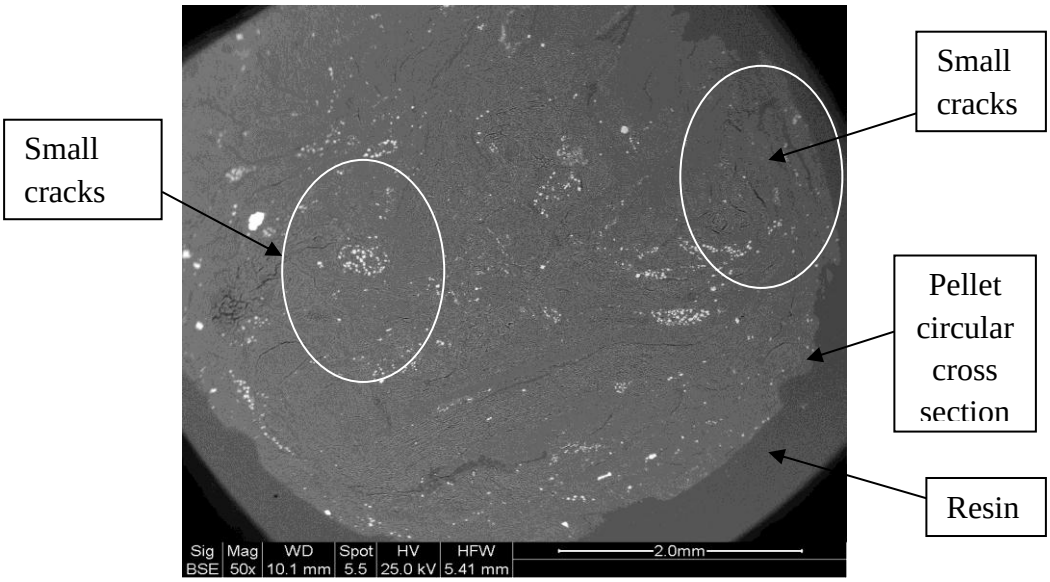

Figure 6-6. Circular cross section of fresh pellet April 2011

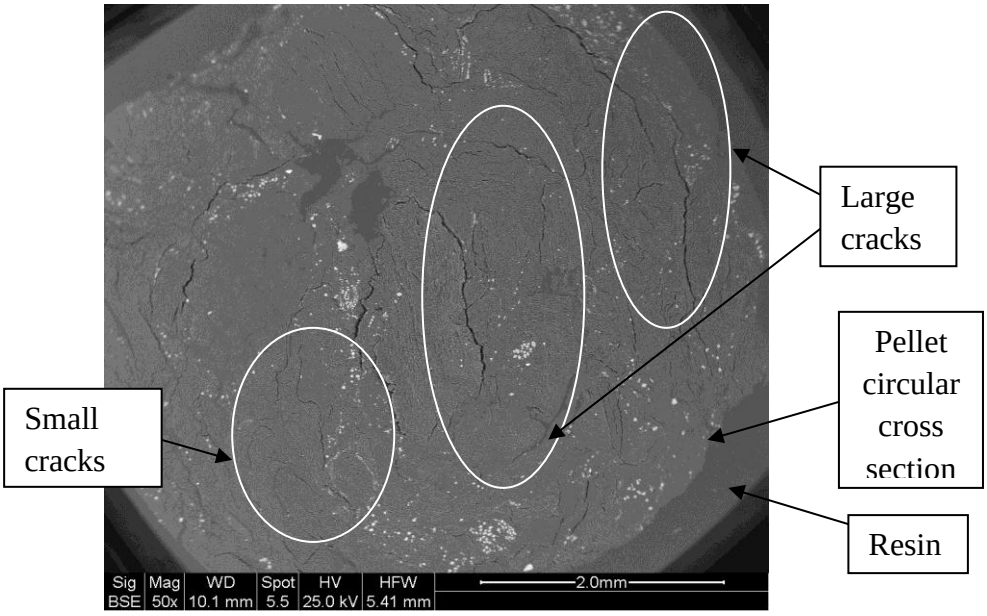

Figure 6-7. Circular cross section of pellet from surface of indoor pile October 2011 (6 months storage)

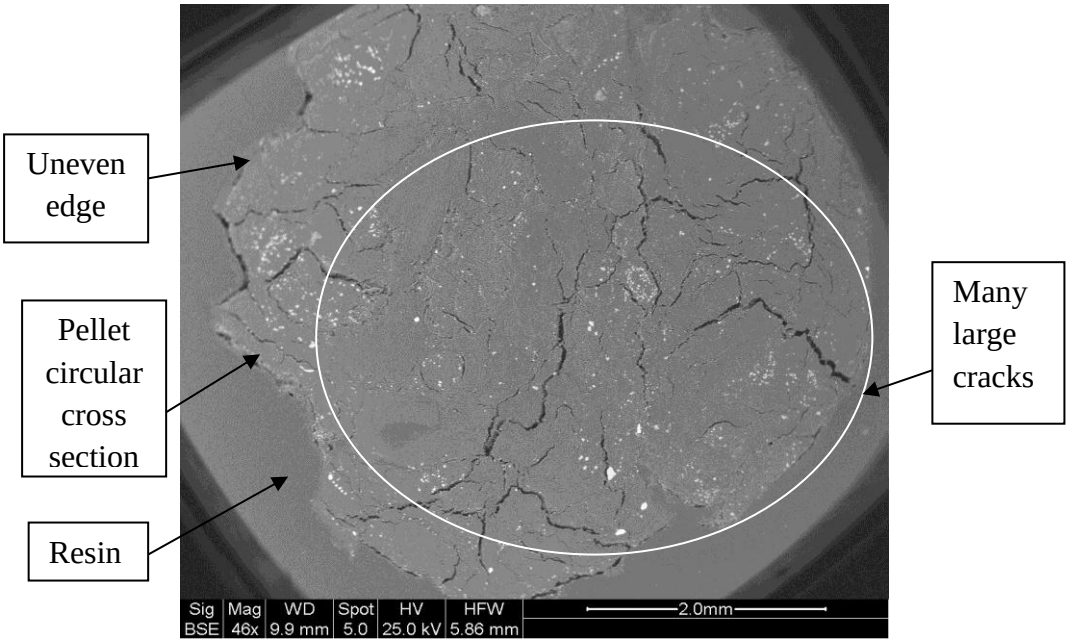

Figure 6-8. Circular cross section of degraded pellet from surface of outdoor pile October 2011 (6 months storage)

While the image of the fresh pellet (Figure 6-6) shows a few small cracks mostly towards the edge of the pellet, the image of the pellet from the indoor pile after six months in storage (Figure 6-7) clearly shows a few large cracks and a large number of small cracks. The cracks are contained within the whole pellet. The image of the pellet from the outdoor pile (Figure 6-8) shows an even larger extent of crack formation and propagation. There are multiple large cracks right across the pellet diameter and the pellet shows signs of its edge being damaged throughout the preparation process for SEM (see Section 3.6.1).

6.4.3 Durability

Figure 6-9 and Figure 6-10 show the durability (see Section 3.6.2 for test details) of the Phase 1 thermally treated wood pellets from both the surface and middle of the indoor and outdoor piles plotted alongside the weekly total rainfall and pellet moisture content against time in storage. The graphs showing the durability alongside the weekly humidity and ambient temperature are in Appendix C.

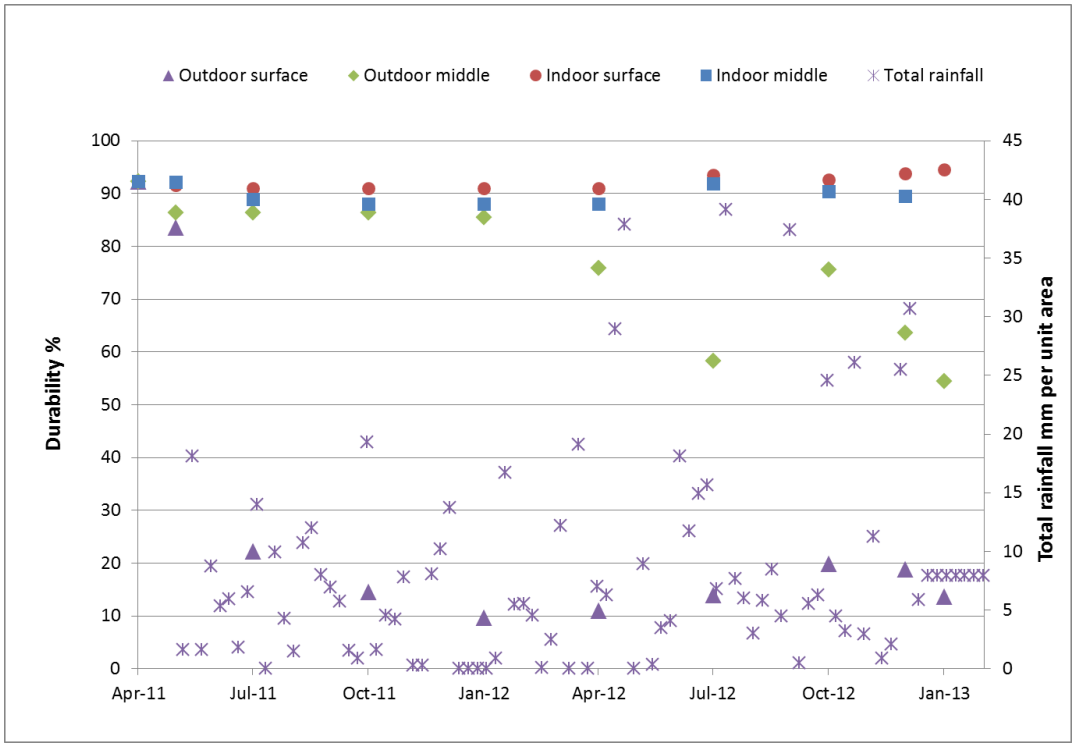

Figure 6-9. Durability of thermally treated wood pellets and weekly total rainfall

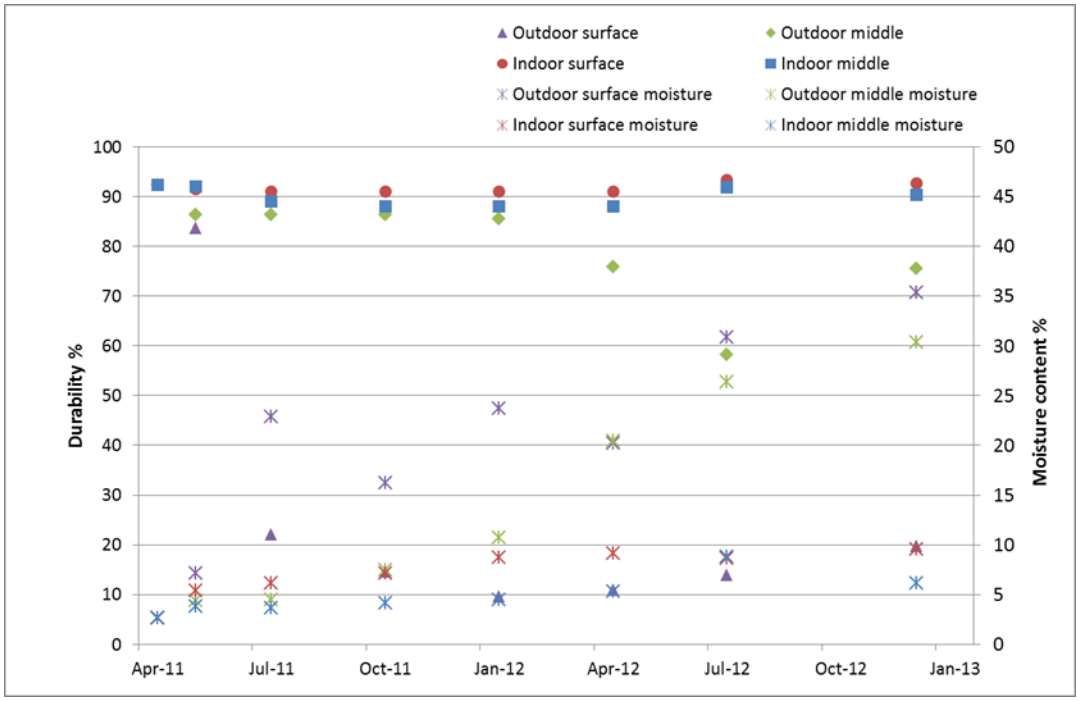

Figure 6-10. Durability of thermally treated wood pellets and pellet moisture content

There are fewer durability data points on Figure 6-10, compared to Figure 6-9. This is because the determination of the sample moisture content was not carried out as regularly as the pellet durability. The total moisture content shown on all the graphs in this section is a single value (no repeats) as drying at 105°C was only carried out on each monthly sample once. This was due to time constraints but also the weight of each sample taken from the piles was kept at ~ 300g to try and avoid too much material being removed from the piles, potentially causing movement of material within the piles. However sample variation for the moisture test was determined at the start and end of the storage period and the maximum sample variation range was 1%.

The measured durability of the pellets from both the surface and middle of the indoor pile did not change significantly throughout the storage period. There was exposure to humidity and ambient temperature inside the barn where the pile was located but this did not result in moisture uptake which was significant enough to affect the durability (Figure 6-10). The fresh pellets had a moisture content of 2.67% and in December 2012, the pellets on the surface of the

indoor pile had a moisture content of 9.57%, the indoor middle pellets being at a moisture content of 6.15%. The changes in indoor pellet durability were within 1% of the original pellet durability.

For the pellets stored outdoors, the changes in measured durability were significantly larger. The exposure of the outdoor pellets to humidity and rainfall (Figure 6-9) from April to July 2011 resulted in a large step increase of 20% in the moisture content of the pellets on the surface of the pile (Figure 6-10). This resulted in a 70% reduction in pellet durability. As the pellets absorb moisture, they swell and the layers within the pellets move outward and apply pressure onto the pellet wall, resulting in cracks as seen in Figure 6-5. Also, at the higher moisture level, the cellulose fibrils are packed more loosely within the wood (Ashby and Jones, 2006). These changes in structure make the pellet more susceptible to breakage during the durability test and hence also during handling and conveying. Both humidity and rainfall show a temporary drop in October 2011 followed by a rise again in January 2012 and this is reflected in the moisture content (Figure 6-10). From January to December 2012, the moisture content of the outdoor surface pellets followed a gradually increasing trend influenced by a general increase in humidity and rainfall (see Section 4.2). However, the step increases in moisture content are not as large as the one initially seen during the first three months of storage. Hence no further decreases in durability are observed. In fact from January to December 2012, the durability of the outdoor surface pellets recovered slightly, especially in July and December 2012 when the moisture content was as high as 30.82 and 35.36% respectively. This could be explained by the binding effect caused by the high moisture content during the durability test in the tumbler and the sieving afterwards. Particularly in the sieving, the pellet wetness could encourage smaller particles to stick together and also to the pellets and hence stay in the oversize fraction, hence yielding a higher durability result. The pellets in the middle of the outdoor pile exhibited a different behaviour to the pellets on the surface. The first nine months of storage from April 2011 to January 2012 did not see a significant decrease in pellet durability (7%). During that time, the moisture content of the pellets only increased from 2.7 to 10.7%. But as the relative humidity and more significantly rainfall increased

from January 2012 onwards, the pellets saw two large step increases in moisture content in April and July 2012 (10% and 16% respectively), which led to a drop in durability. The pellet durability changed from 85 to 75% from January to April 2012 and then further decreased to 59% in July 2012. In the last five months of 2012, there is a further increase in moisture content but only by 4%. Therefore the durability recovered and the same binding effect described for the surface pellets could also be contributing to a higher durability result. Therefore at high pellet moisture levels, the durability test did not return a realistic value because of tendency of stickiness. It was observed that when the pellets were at high moisture content, the cleaning of both the durability tester and the sieve proved more difficult.

In order for the strong impact of moisture content on the durability to be appreciated, Figure 6-11 below shows the durability plotted against pellet moisture content.

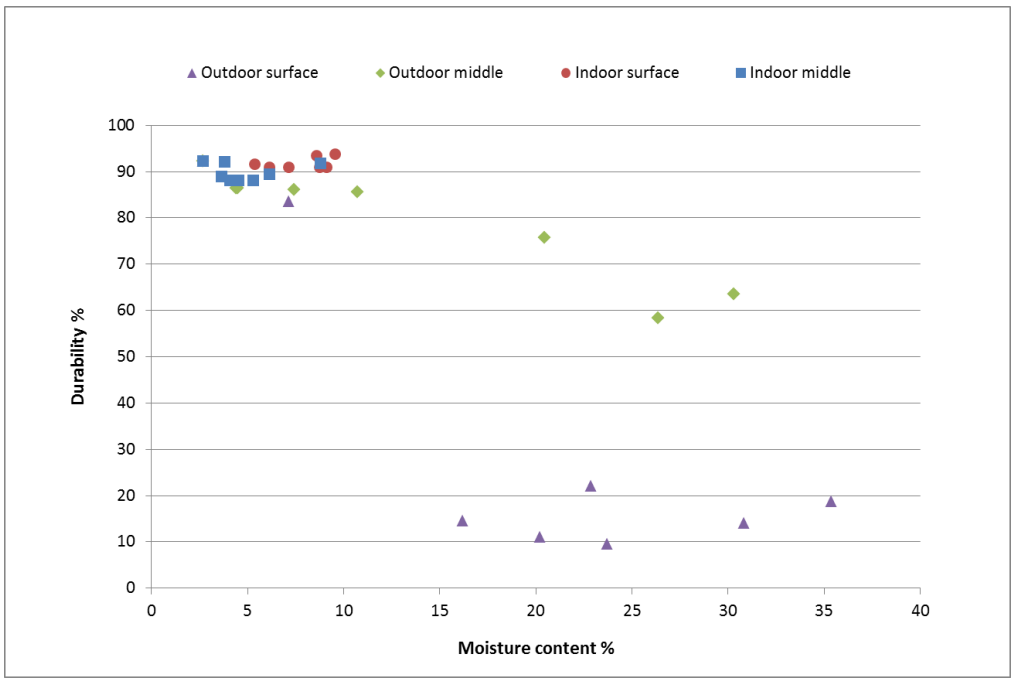

Figure 6-11. Pellet durability of Phase 1 thermally treated wood pellets against moisture content

The two weather parameters which affected the moisture content of the pellets and hence the durability the most were humidity and rainfall. The ambient

temperature did result in drying but the temperature behaviour throughout the duration of the project followed a day and night and summer and winter cycle. No significant step increases were noticed, unlike the humidity and rainfall.

Therefore in the remaining sections of this chapter, the mechanical property will be plotted alongside the moisture data, together with either relative humidity or rainfall. All the other graphs generated in the mechanical data analysis will be shown in Appendix C.

6.4.4 Pellet Diameter

Figure 6-12 and Figure 6-13 show the diameter of the Phase 1 thermally treated pellets plotted alongside weekly average relative humidity and pellet moisture content. The pellet diameter measurement, along with the compression tests and flexure tests were introduced in the ninth month of Phase 1. Error bars were generated to indicate sample variation by measuring the diameter of ten pellets per sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

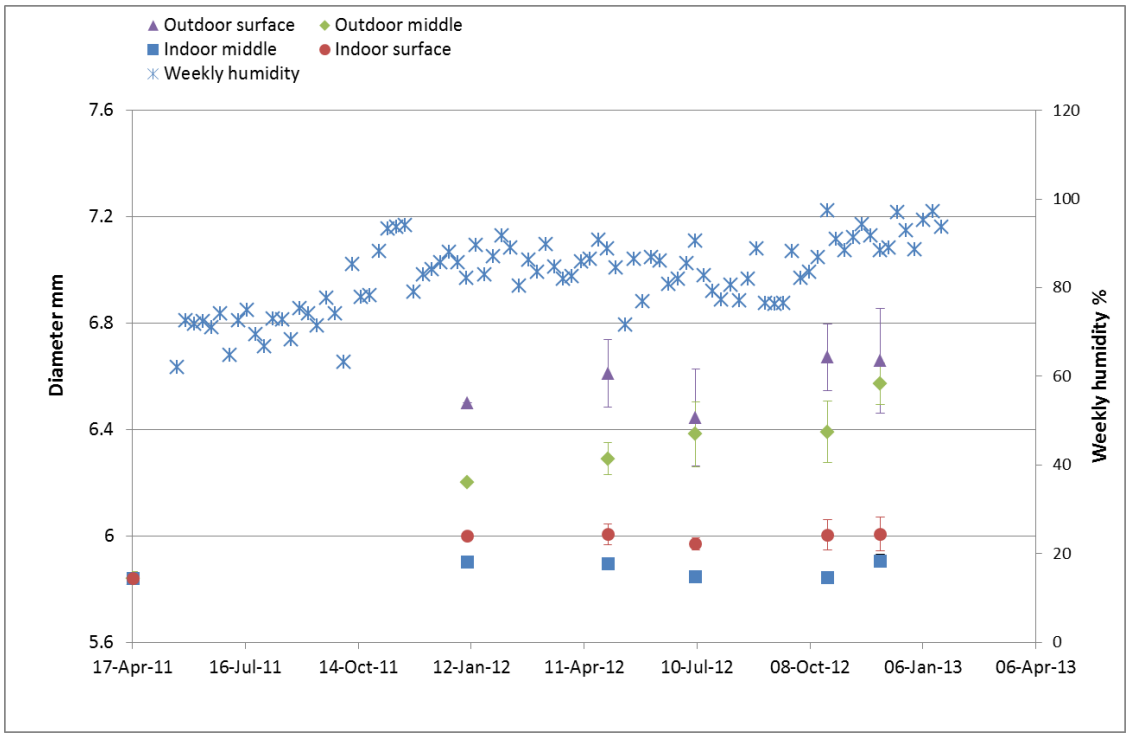

Figure 6-12. Diameter of Phase 1 thermally treated wood pellets with average weekly humidity

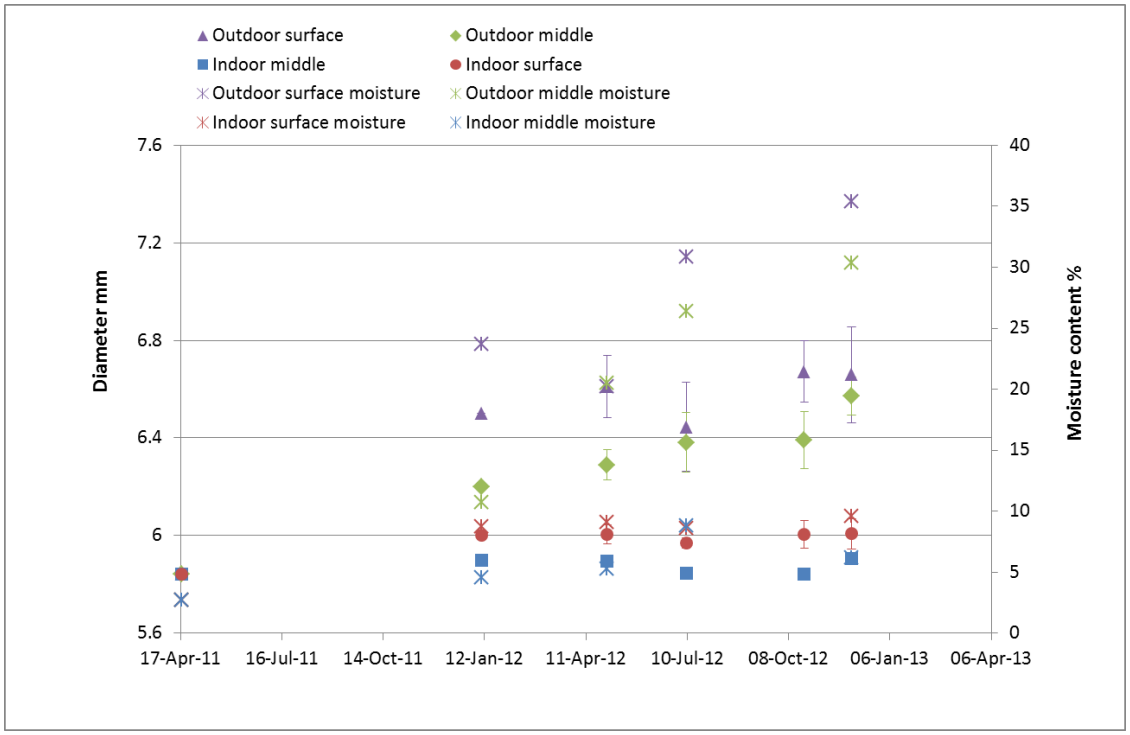

Figure 6-13. Diameter of Phase 1 thermally treated wood pellets with pellet moisture content

Both the indoor and outdoor pellets increase in diameter upon exposure to humidity (Figure 6-12). The consistent trend throughout the storage trials was for the indoor pellets middle sample to show the smallest increase in diameter, with the ranking then being indoor surface, outdoor middle and outdoor surface samples respectively. The outdoor surface sample maximum increase in diameter was 0.8mm while the maximum increase for the indoor middle sample was 0.3mm. The variation was also larger for the outdoor pellets compared to the indoor ones.

This shows that as the degree of exposure to humidity and rainfall increases, so does the degree of pellet swelling due to moisture absorption. In fact Figure 6-13 shows a strong linear relationship between the moisture content of the pellets and the pellet diameter. Another observation is the drop in the diameter of the indoor pellets following a drop in relative humidity and a rise in temperature in the summer months (July - October 2012, Figure 6-12). The reduction in moisture content and swelling during those months also resulted in

a recovery of durability (Figure 6-13). For the outdoor pellets, the rainfall was high in summer 2012 and hence the high moisture content and large diameter (Figure 6-13).

6.4.5 Pellet axial compression strength

In Figure 6-14, the axial compression strength of the Phase 1 thermally treated pellets is shown alongside the pellet moisture content. Error bars were generated to indicate sample variation by carrying out the test on five pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

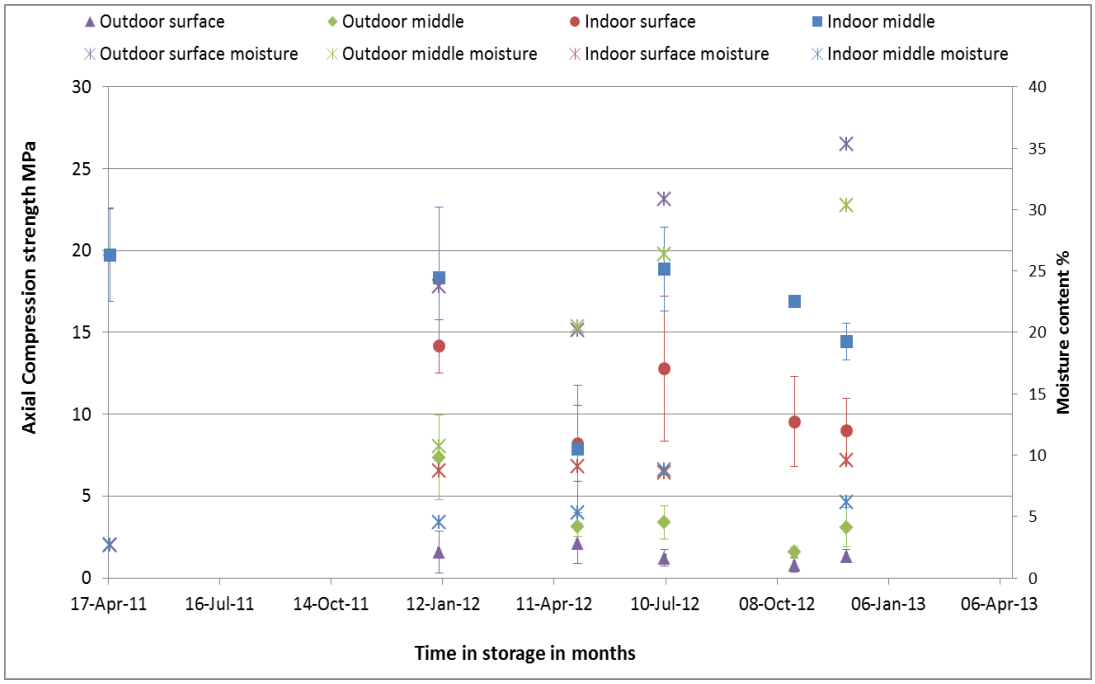

Figure 6-14. Axial compression strength of Phase 1 thermally treated wood pellets with pellet moisture content

The axial compression test (Section 3.6.3.1) is measuring the likelihood that the pellet will fail if loaded in compression along the length of the pellet, if aligned vertically in storage. The axial compression strength relates to the pressure sustained by the pellet. The INSTRON mechanical tester used for this

test was operated at a load cell capacity of 5kN at a ramp rate of 1mm per minute. The pellets on both the surface and in the middle of the indoor pile suffer a gradual drop in axial compression strength, with the indoor middle compression strength being consistently lower than the indoor surface equivalent due to more exposure to humidity and heat. In Figure 6-14, the axial compression strength values for the indoor pile in April 2012 are lower than the rest of the data set. While the diameter and moisture content of the indoor pellets in April 2012 matched those of the other pellet samples (Figure 6-12), the average pellet length was larger for the April 2012 indoor pellet sample compared to all the other pellet samples, resulting in a higher aspect ratio (length to diameter ratio). This could have contributed to an increased tendency in the pellet to fail by cracking (Al-Sahawneh, 2013), and hence a lower compression strength.

The outdoor pellets experienced a much larger drop in axial compression strength, with the values for pellets from the surface being consistently lower than the middle. This is consistent with the pellet durability trends seen in Section 6.4.3, including the slight recovery in December 2012.

An interesting observation is that the axial compression strength of the indoor and outdoor middle pellets showed a more significant drop in values when compared to pellet durability. Durability tests showed no significant change for pellets stored indoors whereas reductions from a minimum of 25% to a maximum of 30% were seen for the axial compression strength. The two tests are very different in nature. In the durability test, the pellets are tumbled at high speed and although they experience forces as they rotate around and bounce against each other, the forces are not continuous and of increasing magnitude. In the axial compression test, a force of increasing magnitude is applied to the pellet continuously until the pellet fractures, providing a value which is checked across multiple pellets in a repeatable manner.

There is an inverse relationship between the pellet moisture content and axial compression strength (Figure 6-14) with the indoor middle pellets having the lowest moisture content and highest compression strength and the outdoor surface pellets having the highest moisture content and the lowest compression

strength. This builds on the evidence seen in the photographs of the pellets (Figure 6-1 to Figure 6-5) and the durability test results (Figure 6-10). The fresh pellets and the pellets stored indoors showed a much larger variation (indicated by error bars) than the pellets stored outdoors. Five pellets from each of the samples were used in this test. The large variation in the fresh pellets could be reflecting that the batch might not have been very uniform, possibly due to differences in the thermal treatment and pelleting processes. And because the pellets stored indoors did not suffer significant mechanical degradation, the variation did not change. For the outdoor pellets however, the extent of mechanical degradation was higher and the failing tendency of all the pellets in the axial compression test increased significantly, hence the smaller variation.

An undergraduate project was carried also out to investigate the fracture mechanics of the pellets in this test. Digital microscopy was used to photograph the pellets before and after each test. Two pellets were imaged in this way for each sample, and care taken to ensure that it was the same pellets each time. Figure 6-15 and Figure 6-16 below show the photographs of the fresh pellets before and after axial compression testing respectively.

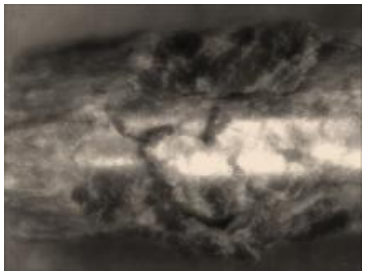

Figure 6-15. Before testing

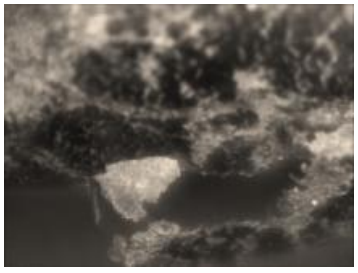

Figure 6-16. After testing

Pellets which undergo axial testing appear to fail by barrelling, where the middle of the pellet 'blows outward'.

6.4.6 Pellet diametrical compression strength

Figure 6-17 shows the diametrical compression strength of the Phase 1 thermally treated wood pellets plotted alongside pellet moisture content. Error bars were generated to indicate sample variation by carrying out the test on five

pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

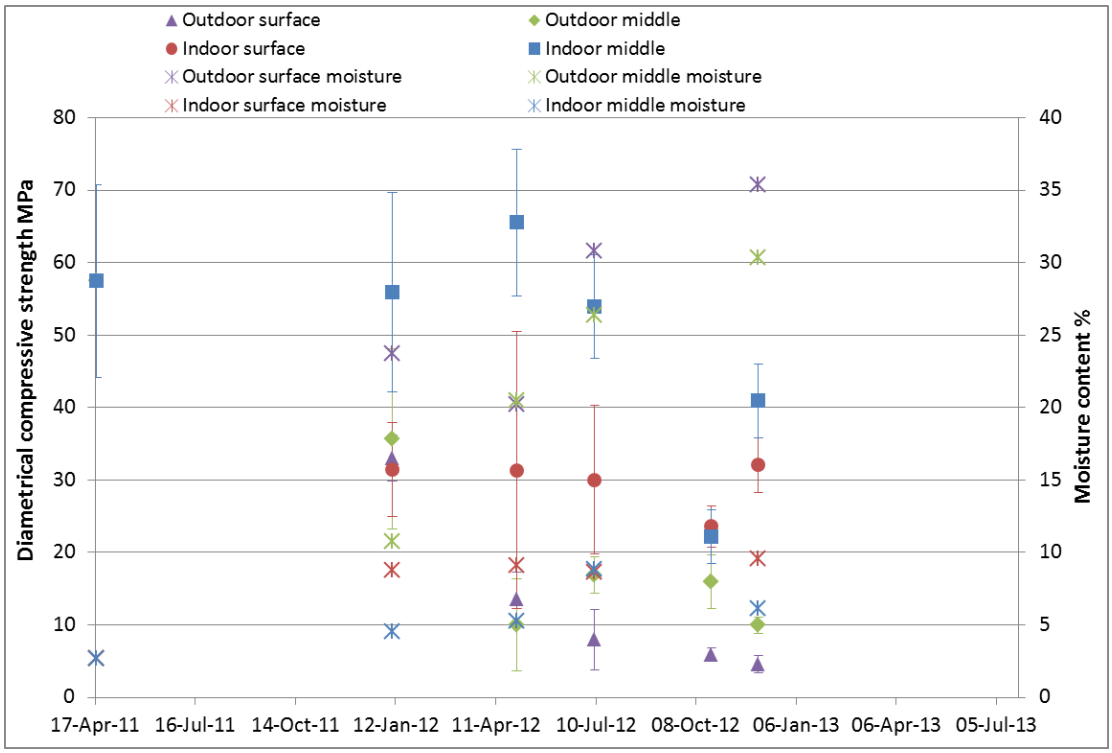

Figure 6-17. Diametrical compression strength of Phase 1 thermally treated wood pellets and pellet moisture content

The first observation is that the diametrical compression strength of the pellets is higher than the axial compression strength. This is because in the axial test, the pellet is positioned vertically between two plates (see Section 3.6.3.1) and the area of contact is smaller, resulting in a larger pressure on the pellet. In both tests, the INSTRON mechanical tester used for this test was operated at a load cell capacity of 5kN at a ramp rate of 1mm per minute

In terms of trends in diametrical compression strength, there is a strong similarity with axial compression strength trends. As exposure level to humidity, rainfall and heat increased from indoor middle through indoor surface, outdoor middle and outdoor surface pellets, the diametrical compression strength decreased accordingly.

The following observations were consistent for both axial and compression strength:

- The drop in the compression strength for the indoor middle pellets ranged between 25 and 30%
- The compression strength of the pellets from the surface of the indoor pile almost halved
- The compression strength of the pellets from the middle of the outdoor pile decreased by a factor of 4
- The compression strength of the pellets from the surface of the outdoor pile decreased five fold

In Figure 6-17, the compression strength of the indoor pellets (surface and middle) in December 2012 has a higher value than in October 2012. However the measurement ranges for these samples overlap and the changes in compression strength which could indicate a slight recovery falls within the normal sample to sample variation.

The fracture mechanics were also determined for the pellets undergoing the diametrical compression test as described in Section 6.4.5 for axial compression. Figure 6-18 and Figure 6-18 below show the photographs of the fresh pellets before and after diametrical compression testing respectively.

Figure 6-18. Before testing

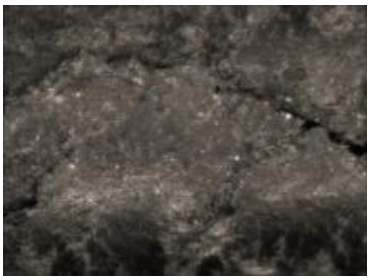

Figure 6-19. After testing

In diametric testing, the pellet is flattened, such that the straight cracks appear all the way down each of the side which were equally furthest away from the two compression surfaces.

6.4.7 Pellet inter-laminar shear modulus (stiffness)

The inter-laminar shear modulus of the Phase 1 thermally treated pellets is presented alongside pellet moisture content in Figure 6-20. Error bars were generated to indicate sample variation by carrying out the test on ten pellets per sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

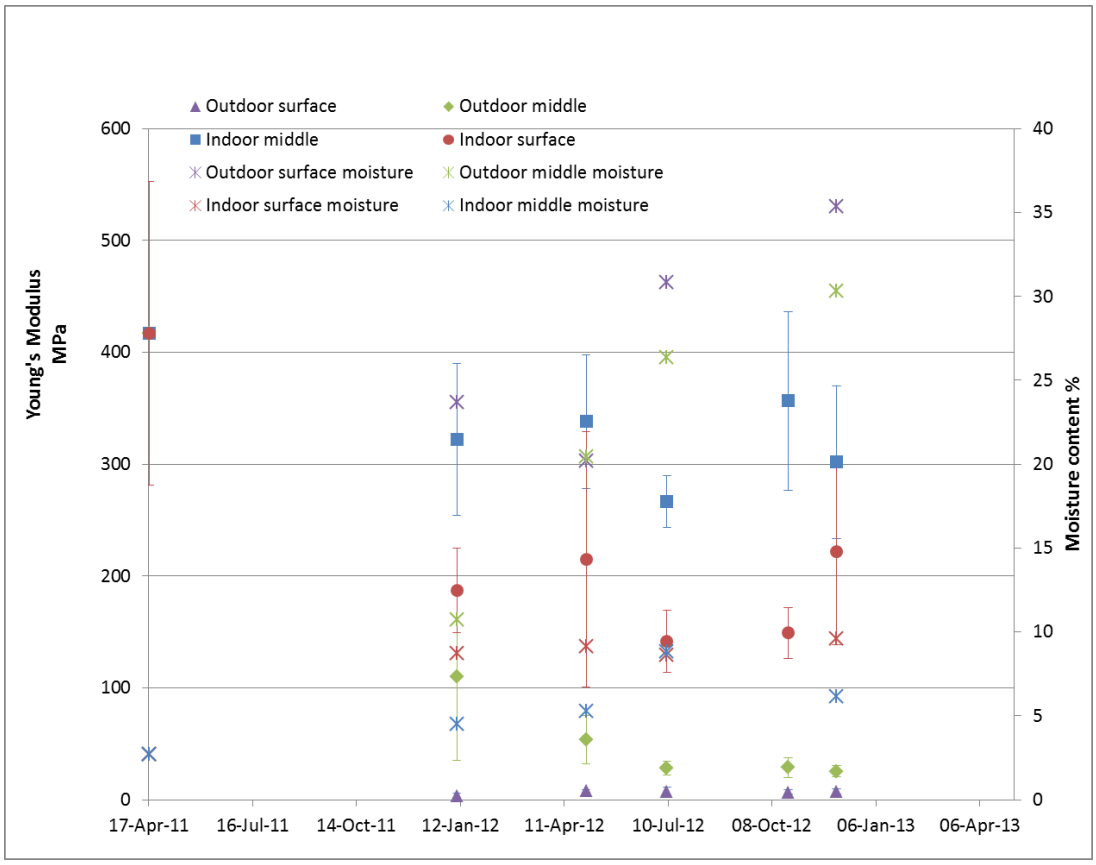

Figure 6-20. Young's modulus of Phase 1 thermally treated wood pellets and pellet moisture content

As for the axial compression strength and diametrical compression strength, the pellets on the surface of the outdoor pile suffered the biggest drop in shear modulus, followed by the outdoor middle followed by the indoor surface followed by the indoor middle pellets. The similarities and differences between the shear modulus and the two compression strength tests data are as follows:

- The drop for the indoor middle pellets ranged between 25 and 30% for all of the axial and diametrical compression strengths and the Young's modulus
- The compression strengths (axial and diametrical) and Young's modulus of the pellets from the surface of the indoor pile almost halved
- The drop in shear modulus of the outdoor pellets however was larger than for the compression strengths, with almost a 100% reduction in December 2012 compared to the fresh pellets in April 2011, indicating that the potential for pellets to fail in this mode is significantly impacted by the storage method

As for the diametrical compression strength (Figure 6-17), the Young's modulus values for the indoor pellets increased in the last few months of storage. However the measurement ranges for these samples overlap and the changes in shear modulus which could indicate a slight recovery fall within the normal sample to sample variation.

The fracture mechanics were also determined for the pellets undergoing the shear test test as described in Section 6.4.5 for axial compression. Figure 6-21 and Figure 6-21 show the photographs of the fresh pellets before and after inter-laminar three point shear testing respectively.

Figure 6-21. Before testing

Figure 6-22. After testing

The flexure tests cause 'splintering' whereby a crack propagates into the pellet at a shallow angle to the surface.

6.5 Detailed results for the Phase 2 thermally treated wood pellets

6.5.1 Photographs of samples

Figure 6-23. Fresh pellets December 2011

Figure 6-24. Pellets on surface of outdoor pile June 2012 (6 months storage)

Figure 6-23 and Figure 6-24 show the fresh thermally treated wood pellets at the start of Phase 2 and the pellets sampled on the surface of the pile after six months in storage. Similarly to Phase 1, while the fresh Phase 2 pellets have a smooth texture and shiny appearance (albeit less 'glassy' appearance than the Phase 1 pellet), the stored pellets have cracks and a much rougher texture which reflect surface degradation. From visual inspection, the Phase 1 and Phase 2 outdoor thermally treated wood pellet piles showed the following differences:

- The fresh Phase 1 pellets were much darker in colour than the fresh Phase 2 pellets, reflecting a higher degree of thermal treatment

- However, as outdoor storage progressed, the Phase 2 pellets appeared less degraded as the pellets had fewer cracks and breaks. This could be because the pellets were made from a different raw material which was more resistant to mechanical degradation
- No dust generation was observed around either pile

6.5.2 Scanning electron microscopy (SEM) images of Phase 2 thermally treated wood pellets

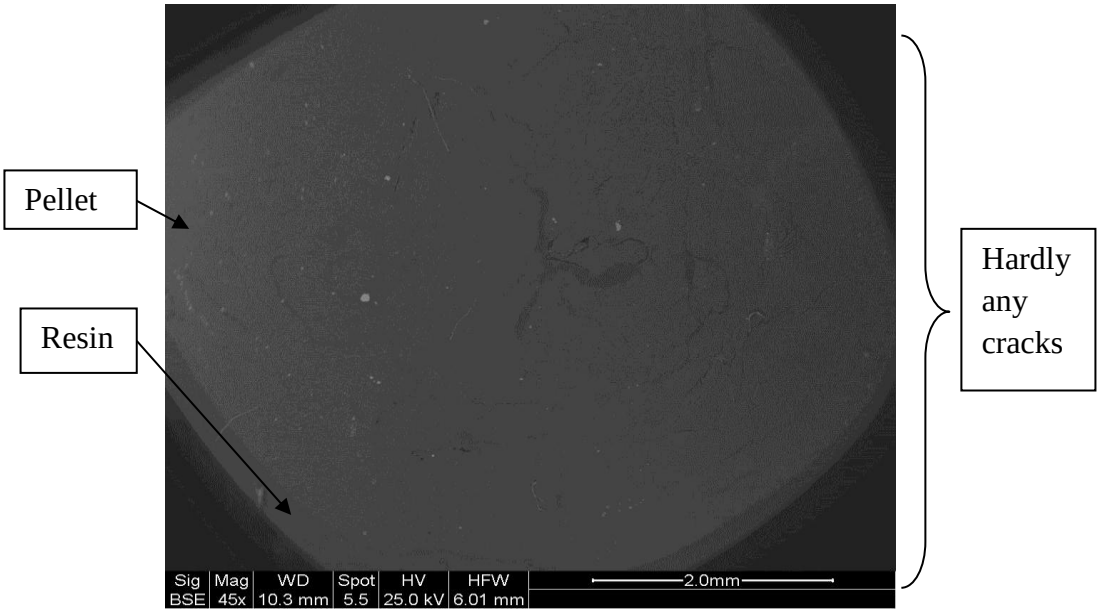

Figure 6-25. Circular cross section of fresh pellet December 2011

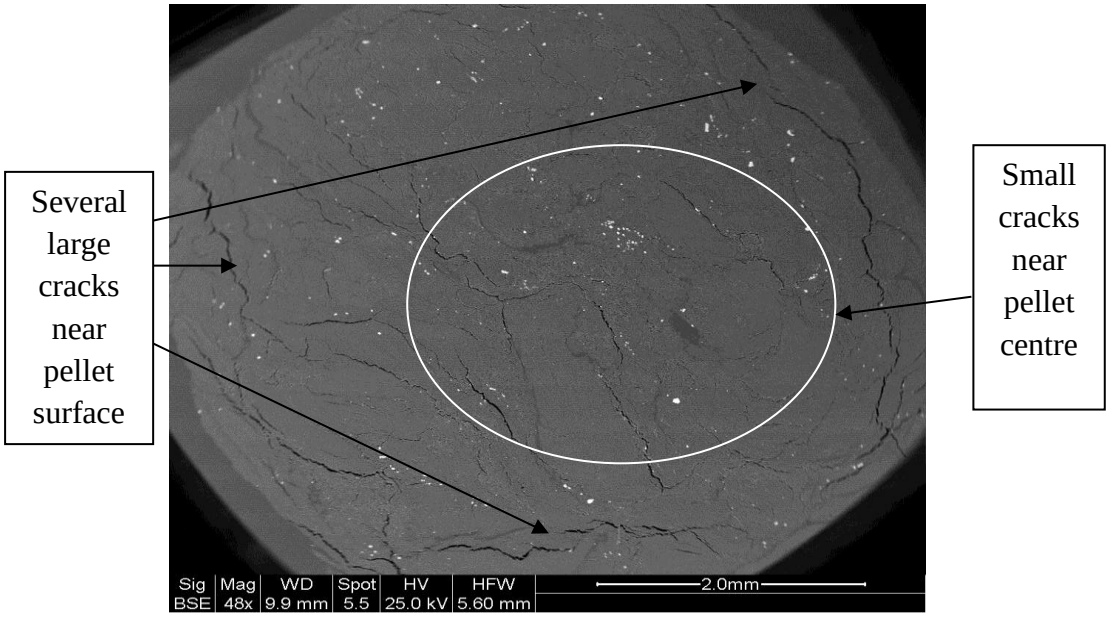

Figure 6-26. Circular cross section of pellet from surface of outdoor pile May 2012 (six months storage)

As expected, the outdoor pellet (Figure 6-26) shows multiple cracks across the pellet, the largest ones being aligned with the surface of the pellet, showing that the outer layer was flaking away. The internal layers of the pellets also showed signs of shocks with cracks slowly developing. The fresh pellet (Figure 6-25), hardly displays any cracks.

6.5.3 Durability

Figure 6-27 and Figure 6-28 below the durability of the Phase 2 outdoor thermally treated wood pellets plotted alongside the weekly total rainfall and pellet moisture content respectively, the graphs having the same formats as Figure 6-9 and Figure 6-10. Figure 6-29 shows the durability plotted against the pellet moisture content.

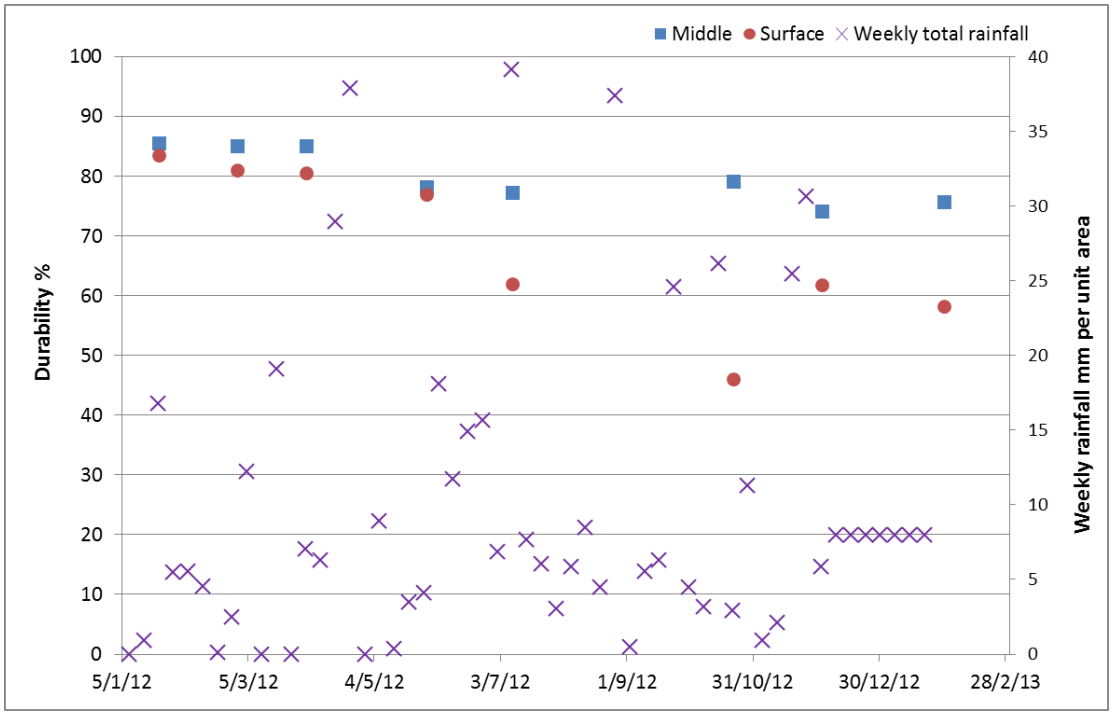

Figure 6-27. Durability of Phase 2 outdoor thermally treated wood pellets with weekly total rainfall

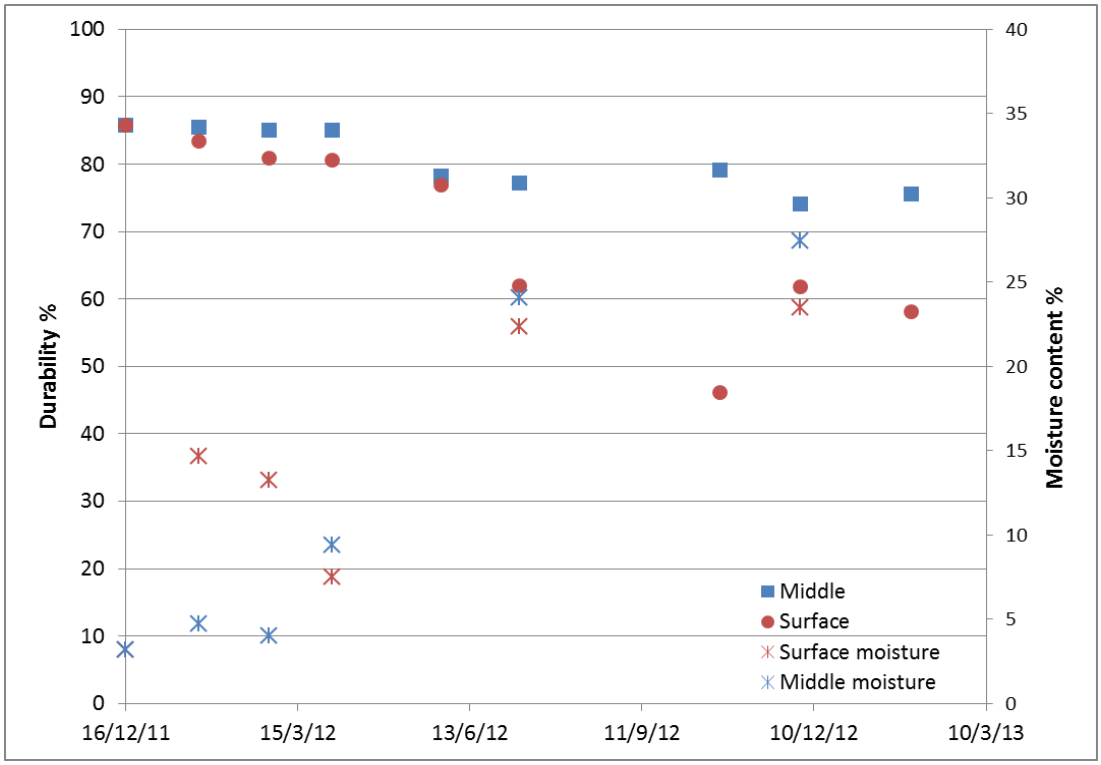

Figure 6-28. Durability of Phase 2 outdoor thermally treated wood pellets with pellet moisture content

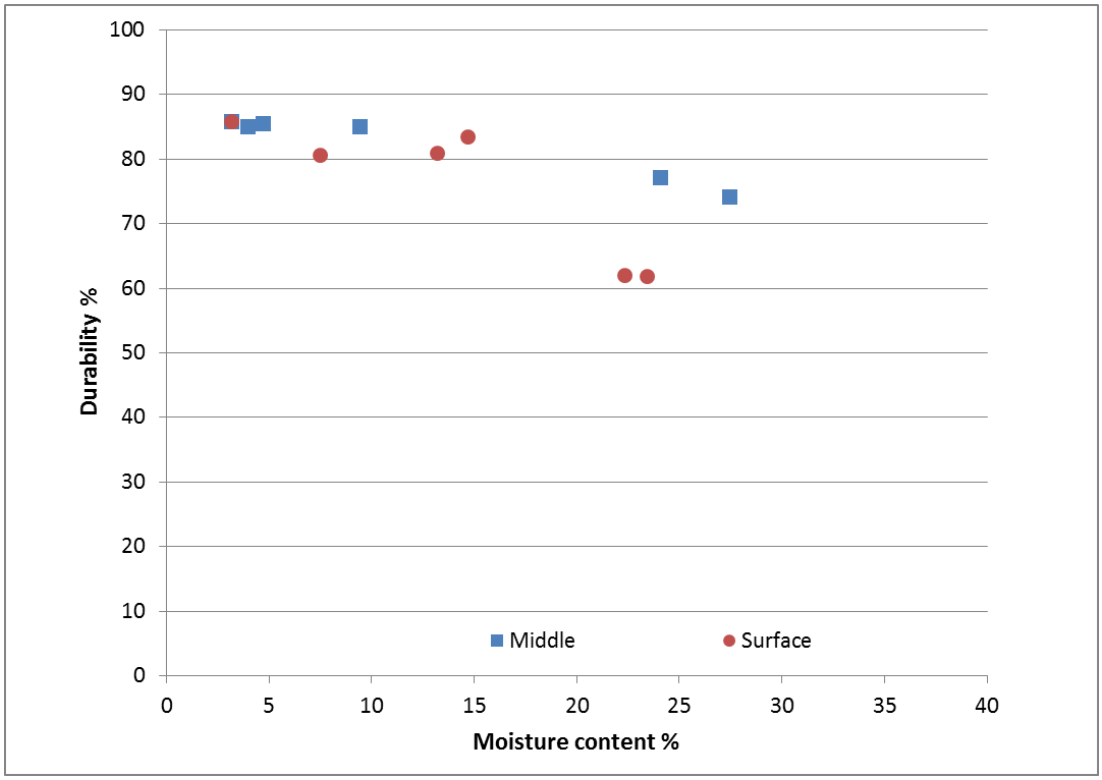

Figure 6-29. Durability of Phase 2 outdoor thermally treated wood pellets against moisture content

The main observations from the durability graphs are as follows:

- In the first three months of storage (December 2011 to March 2012), the weekly total rainfall was lower than average resulting in a pellet moisture content of below 15%. This gave rise to no significant change in the durability of the pellets in the middle of the pile, although the pellets on the surface suffered a 3% decrease in durability.

- From the middle of March onwards, the weekly total rainfall increased and remained consistently high until November 2012. 2012 was an unusually wet year as described in Section 4.2.3. The total rainfall in the first twelve months of Phase 1 was 275 mm per unit area compared to 480 mm per unit area in the first twelve months of Phase 2. This is reflected by a significant step increase in the moisture content of both the surface sample (22%) and middle sample (24%) pellets in July 2012. The maximum reduction in durability of the middle sample pellets was 10%, from 85 to 75%. For the surface sample pellets, the

maximum drop was 40%, from 85 to 45%. This compares to Phase 1 values of 40 and 70% reduction in durability for the middle and surface pellets respectively

- In October 2012, the durability of the outdoor surface pellets is at its lowest which could have been caused by a further increase in moisture content, unfortunately no moisture determination was carried out that month (Figure 6-28). In fact this is very likely due to the high rainfall in September and October 2012 (Figure 6-27).

- In December 2012, the durability of the outdoor surface pellets recovered. This could be because the moisture content stabilised. Also the effect of higher moisture content (above 25%) on the stickiness of particles during the durability test could be contributing to the higher measured durability value here as well. In future work, the durability of pellets with a moisture content above 25% should be studied alongside other measures so that the effectiveness of this industrially-used test for pellet strength can be drawn out

- There was a smaller difference between the durability of the surface pellets and those of the middle pellets compared to Phase 1. The pellets used in Phase 1 were different from the ones used in Phase 2 and there could have been differences in the raw material/s and also the thermal treatment process, which resulted in the Phase 2 pellets being more resistant to mechanical degradation upon exposure to humidity, heat and rainfall

6.5.4 Pellet Diameter

In this section, the pellet diameter data will be presented alongside the weekly average humidity (Figure 6-30) and the pellet moisture content (Figure 6-31), the graphs being in similar format to Figure 6-12 and Figure 6-13. Error bars were generated to indicate sample variation by measuring the diameter of ten pellets per sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

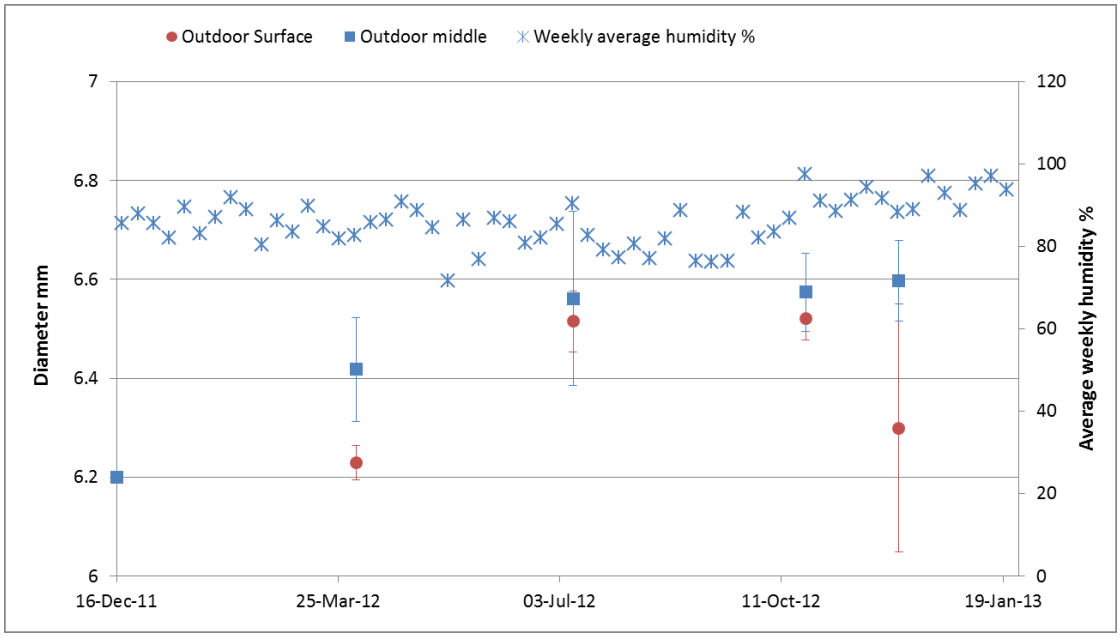

Figure 6-30. Diameter of Phase 2 thermally treated wood pellets and weekly average humidity, note extremely high levels of humidity compared to Phase 1

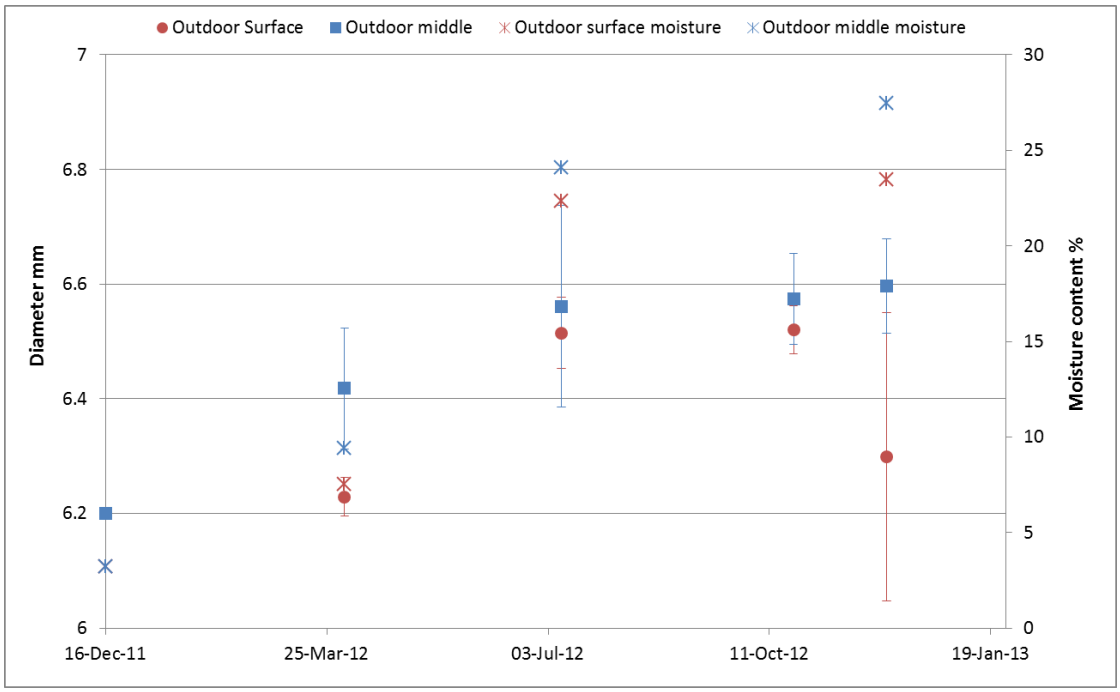

Figure 6-31. Diameter of Phase 2 thermally treated wood pellets with pellet moisture content

The following observations can be made from the Phase 2 pellet diameter trends:

- There is large variation in the pellet diameter, particularly in July and December 2012
- The relative humidity remained high throughout most of Phase 2 with a value above 75%. However the step increases in moisture content in April, July and December 2012 can be linked to the high rainfall close to the sampling dates (see Figure 6-27 above). This was accompanied by an increase in the pellet moisture content
- The unexpectedly low diameter of the surface pellets in December 2012 could be explained by the very large variation in the data
- An interesting observation is the consistently higher moisture content and hence larger diameter of the pellets in the middle compared to the pellets on the surface of the pile. This higher moisture content of the middle pellets was explained in Section 5.3.4.

6.5.5 Pellet axial compression strength

Figure 6-32 shows the axial compression strength of the Phase 2 thermally treated wood pellets with pellet moisture content in the same format as Figure 6-14. Error bars were generated to indicate sample variation by carrying out the test on five pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

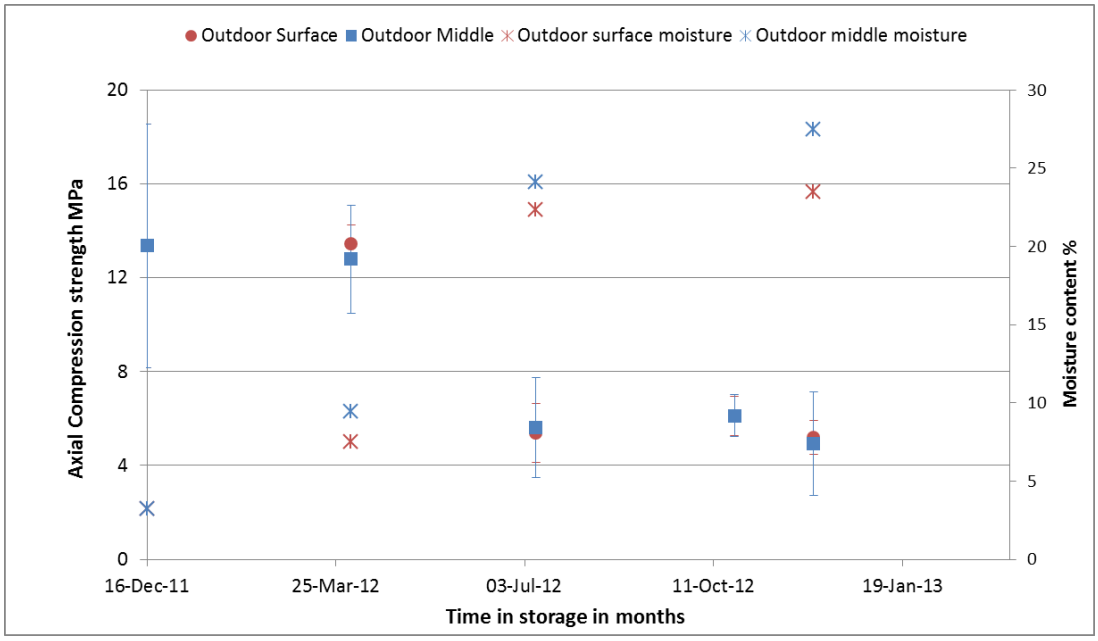

Figure 6-32. Axial compression strength of Phase 2 thermally treated pellets with pellet moisture content

As observed for durability, the changes in axial compression strength were small in the first three months of storage; the moisture content did not rise above 9% (Figure 6-32). From March to July 2012, there was a large step increase in moisture content due to continuously high rainfall and this is accompanied by a large step decrease in axial compression strength. The moisture levels remained high with a consistent behaviour in the axial compression strength with a reduction for the middle and surface pellets to approximately 40% of original value. It can also be observed that surface and middle pellets are exhibiting very similar behaviour, in a similar manner to the durability results. This is different to the results seen from Phase 1 tests.

6.5.6 Pellet diametrical compression strength

The trend in diametrical compression strength plotted alongside pellet moisture content (Figure 6-33) will be presented here. Error bars were generated to indicate sample variation by carrying out the test on five pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

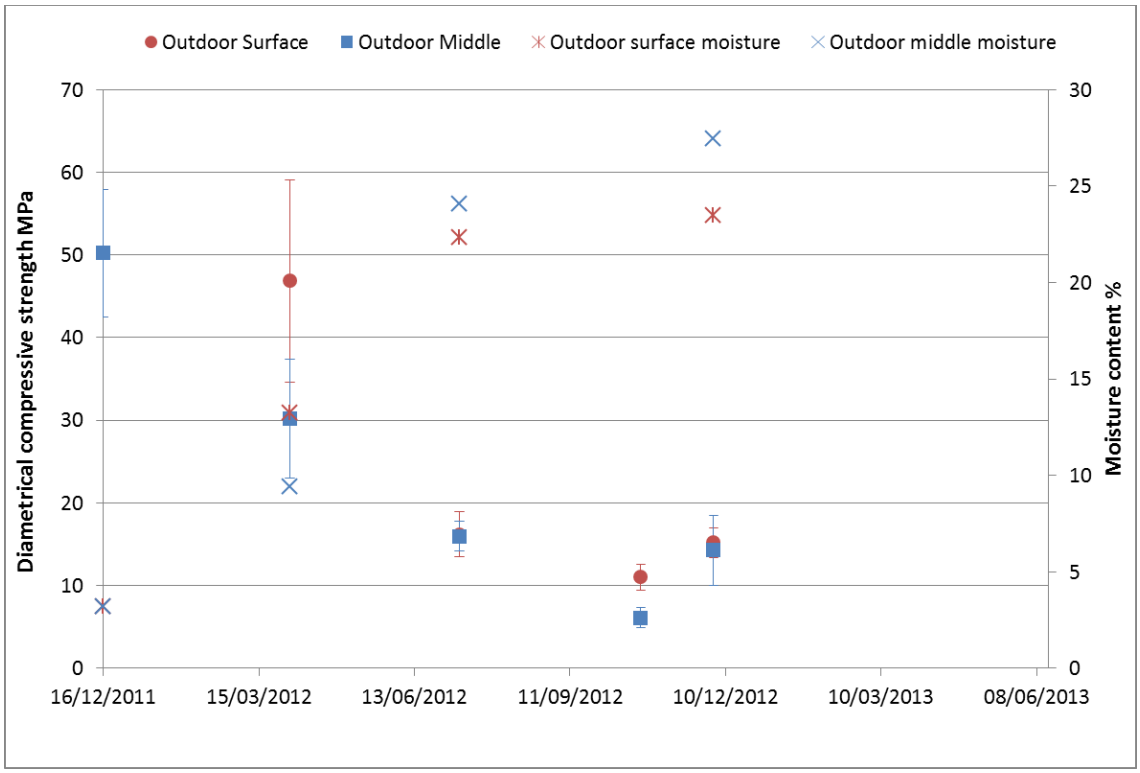

Figure 6-33. Diametrical compression strength of Phase 2 thermally treated pellets with pellet moisture content

With regard to Figure 6-33, it can be observed that similarly to Figure 6-32, in July 2012 there was a significant drop in strength when moisture increased for both pellet types. A significantly larger variation in results for March was seen compared to axial compression which was also seen in Phase 1. From July onwards, there was no significant variation observed for pellet types and both surface and middle pellets show very similar values for strength and moisture. This is different to Phase 1.

6.5.7 Pellet inter-laminar shear modulus (stiffness)

Figure 6-34 below shows the inter-laminar shear modulus of the Phase 2 thermally treated wood pellets with pellet moisture content. Error bars were generated to indicate sample variation by carrying out the test on ten pellets per

sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

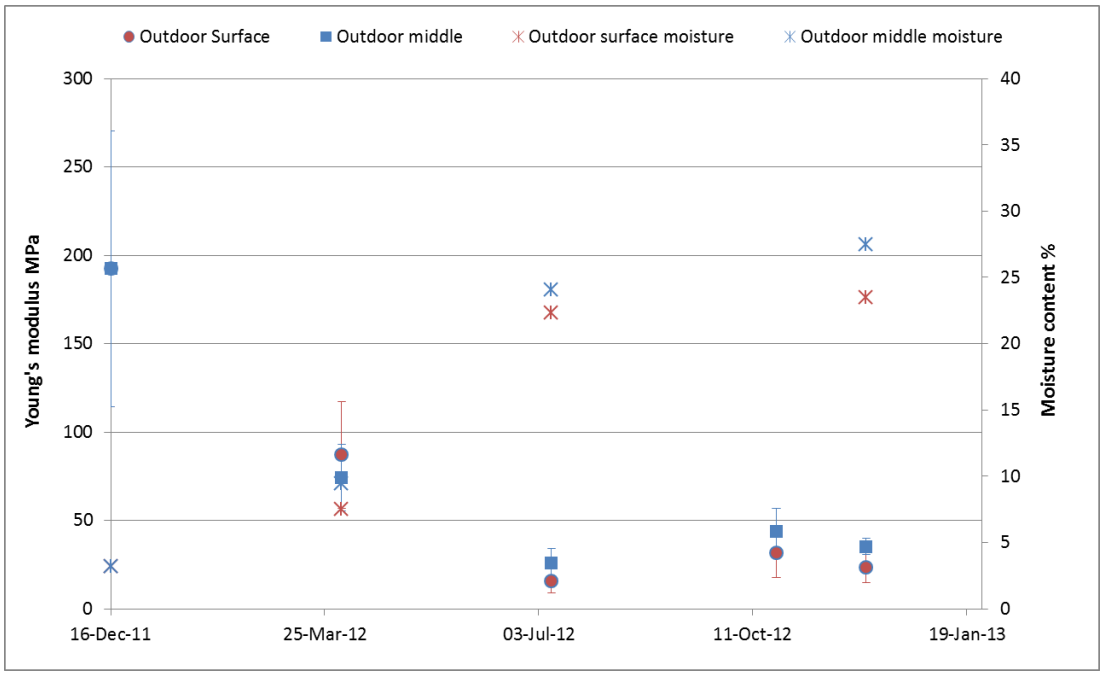

Figure 6-34. Inter-laminar shear modulus of Phase 2 thermally treated pellets with pellet moisture content

Compared to pellet durability and axial and diametrical compression strengths, there is a large step decrease in Young's modulus from December 2011 to March 2012 for both the surface and middle pellets. Exposure to continuously high relative humidity linked to high rainfall (Figure 6-30 and Figure 6-27) appears to increase the tendency of pellets to break under three point forces as this is seen in Phases 1 (Figure 6-20) and 2. As the rainfall, and hence moisture level increased, in July 2012, the degradation in Young's modulus continued accordingly. As in Phase 1, the drop in shear modulus is large. As seen in previous tests, the results for the surface and middle pellets were very similar.

6.6 Detailed results for the Phase 2 white wood pellets

6.6.1 Photographs of samples

The Phase 2 white wood pellets, stored indoor, showed a very different behaviour from thermally treated pellets with degradation occurring at a much faster pace. Figure 6-35 shows the pellets at the start of storage. To illustrate the speed at which the pellets degraded, photographs of the pellets taken after one, four and six months in storage (Figure 6-36 to Figure 6-38) are shown.

Figure 6-35. White wood pellets at start of trial in Nov 2011

Figure 6-36. White wood pellet on surface of pile after 1 month

Figure 6-37. White wood pellets on surface of pile after 4 months

Figure 6-38. White wood pellets on surface of pile after 6 months

After one month in storage (Figure 6-36), swelling and disintegration of the pellets could be observed. Very few pellets have retained their original shape and many pellets have cracked and burst. After four and six months in storage, pellet degradation is even worse with most pellets having been broken down to what appears to be the original particle size prior to pelletisation. This very high level of pellet degradation in an open barn environment shows that white wood pellets are best stored in a fully enclosed environment with no exposure to the outside environment.

In the top 20cm layer, there was a lot of dust but whole pellets could be hand picked for the mechanical tests to be carried out. Figure 6-39 shows the surface of the pile after nine months in storage.

Figure 6-39. Surface of pile consisting of pellets and dust after nine months in storage

Further into the pile also contained a lot of dust. It was therefore difficult to insert the sampling probe into the middle of pile. Therefore after January 2012, no middle samples were taken from the white wood pellet pile.

When the pile was deconstructed in September 2012 after nine months in storage, the deconstruction took place in a layer by later approach. This was primarily carried out to protect the thermocouple assemblies inside the pile. But it also enabled the very core of the pile to be reached during the process. A sample was manually taken at the middle of the pile for testing. An interesting observation was that the core of the pile was a lot less dusty than the surface and layers close to the surface. Figure 6-40 shows the middle of the pile which was reached during a layer by layer deconstruction approach. This could be a result of the dusty layers near the surface of the pile acting as a barrier to the inner layers within the pile, reducing the exposure to humidity and heat and preventing moisture ingress.

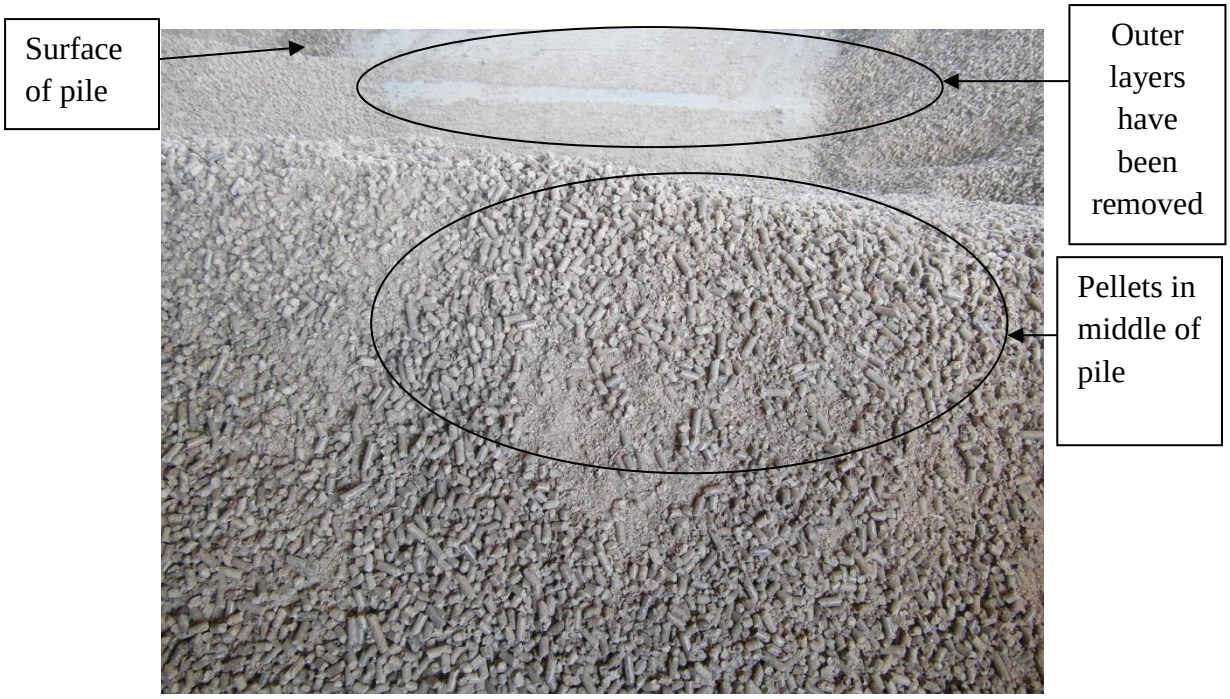

Figure 6-40. Centre of pile during deconstruction process after ten months in storage

6.6.2 Scanning electron microscopy (SEM) images of pellets

Figure 6-41 and Figure 6-42 show the circular cross sections of the fresh pellet at the start of Phase 2 and the degraded pellet on the surface of the pile after six months in storage. It was very difficult after the first three months of storage to find a long enough pellet to prepare for SEM. They had to be handpicked from a sample.

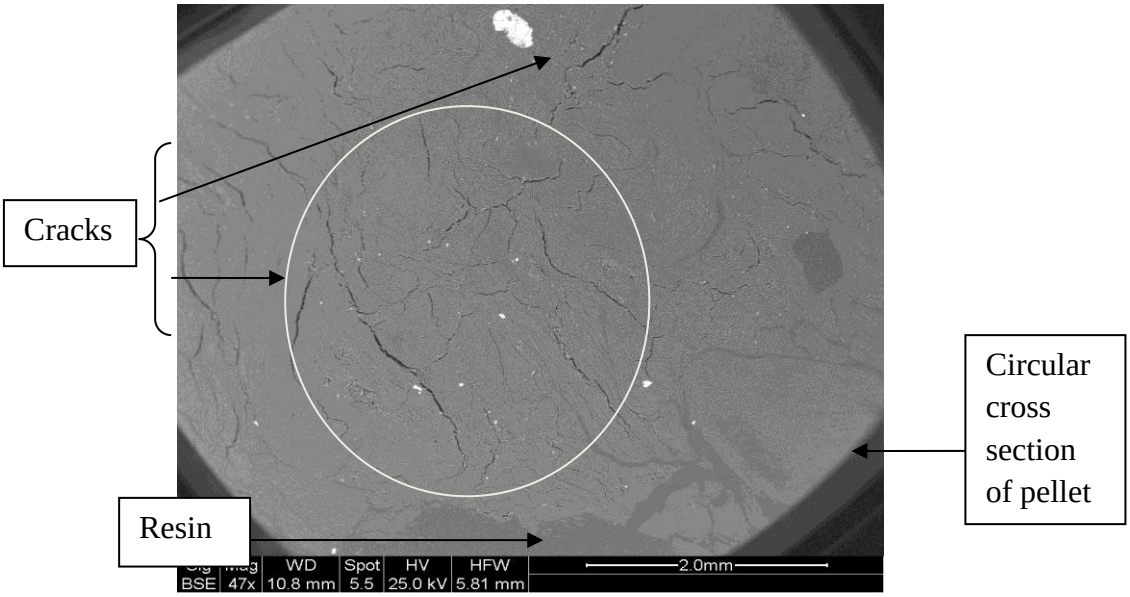

Figure 6-41. Circular cross section of fresh pellet November 2011

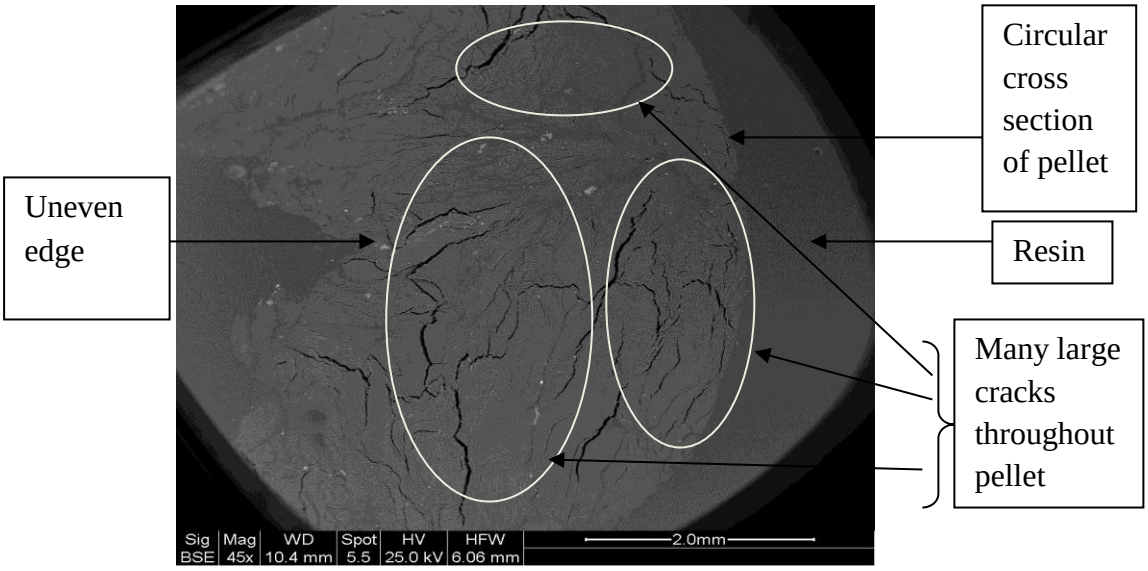

Figure 6-42. Circular cross section of degraded pellet from surface of pile May 2012 (6 months storage)

The SEM image of the fresh pellet (Figure 6-41) shows that cracks were present throughout the pellet at the start of storage. This is different to what was observed in the fresh thermally treated pellets for both Phases 1 and 2 (Figure 6-6 and Figure 6-25). The thermal treatment resulted in a stronger pellet. This was reflected in the strength test results.

After six months in storage, the white wood pellet had more numerous and larger cracks throughout the pellet. There were also signs of its edge being damaged during the preparation process for SEM (see Section 3.6.1)

6.6.3 Durability

Figure 6-43 shows the durability of the white wood pellets plotted alongside weekly average humidity. As this pile was stored in an open barn in covered storage, the data will not be presented alongside rainfall.

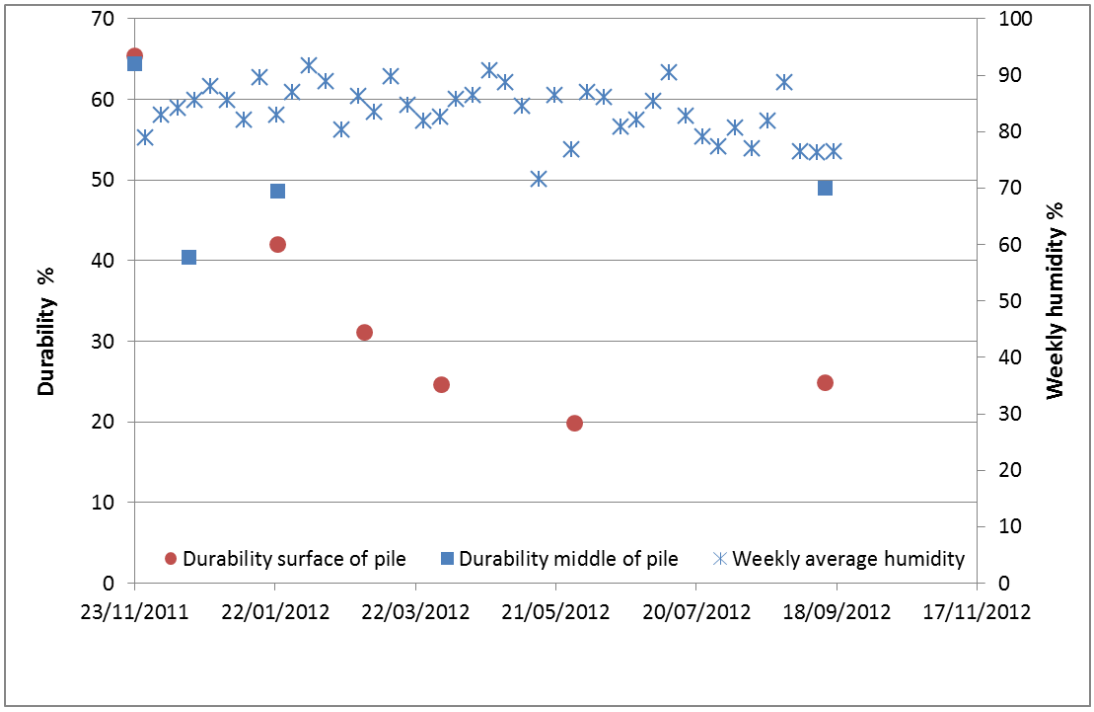

Figure 6-43. Durability of white wood pellets from surface of pile and average weekly humidity

Figure 6-44 shows the pellet durability plotted against moisture content for the white wood pellets. The middle pellets had moisture content which stayed mostly unchanged at about 9%.

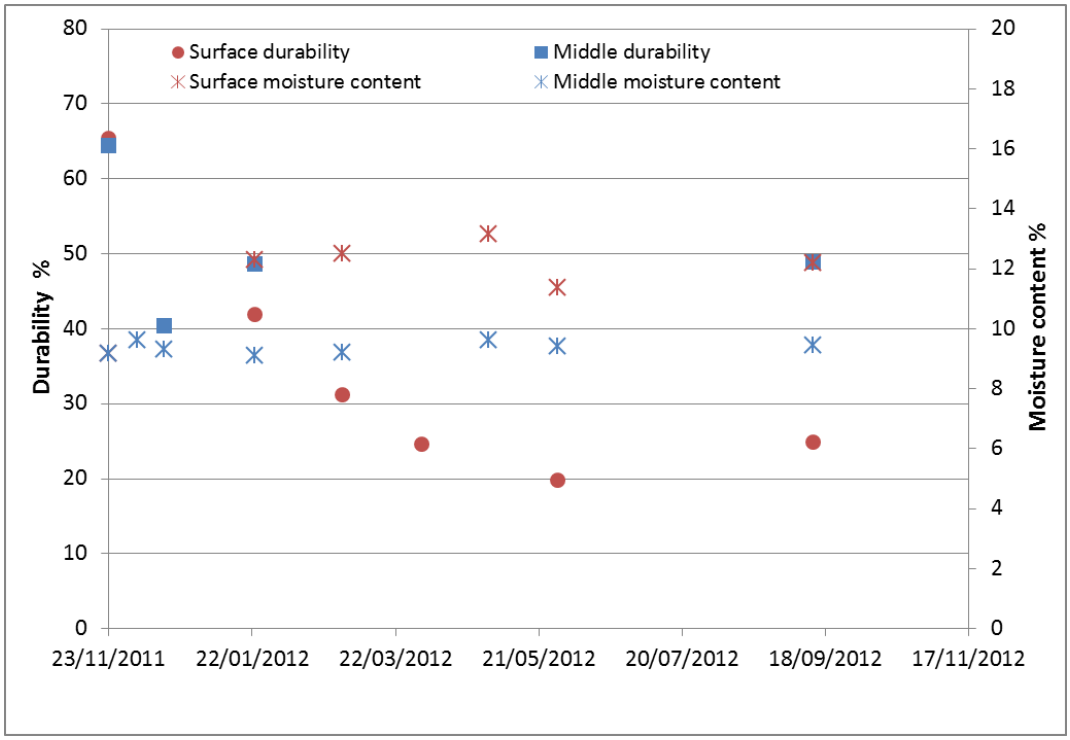

Figure 6-44. Durability of white wood pellets and pellet moisture content

The durability of both the surface and middle pellets decreases with exposure to humidity which brings about an increase in the pellet moisture content. For the pellets on the surface of the pile, the first two months of storage (November 2011 to January 2012) resulted in a 3% increase in pellet moisture content and a 20% decrease in pellet durability (Figure 6-44). As storage progresses from January to September 2012, the durability decreases gradually but more slowly than in the first two months. This is because the moisture content stabilises at around 12% from the third month of storage onwards. For the pellets from the middle of the pile, the initial drop in durability is 25% and then the durability stabilises. This could be because as the pellets near the edge of the pile disintegrated and got progressively dustier, the pellets at the middle were protected against moisture ingress.

6.6.4 Pellet Diameter

Figure 6-45 and Figure 6-46 below show the diameter of the Phase 2 white wood pellets plotted alongside the weekly average humidity and the pellet

moisture content. Error bars were generated to indicate sample variation by measuring the diameter of ten pellets per sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

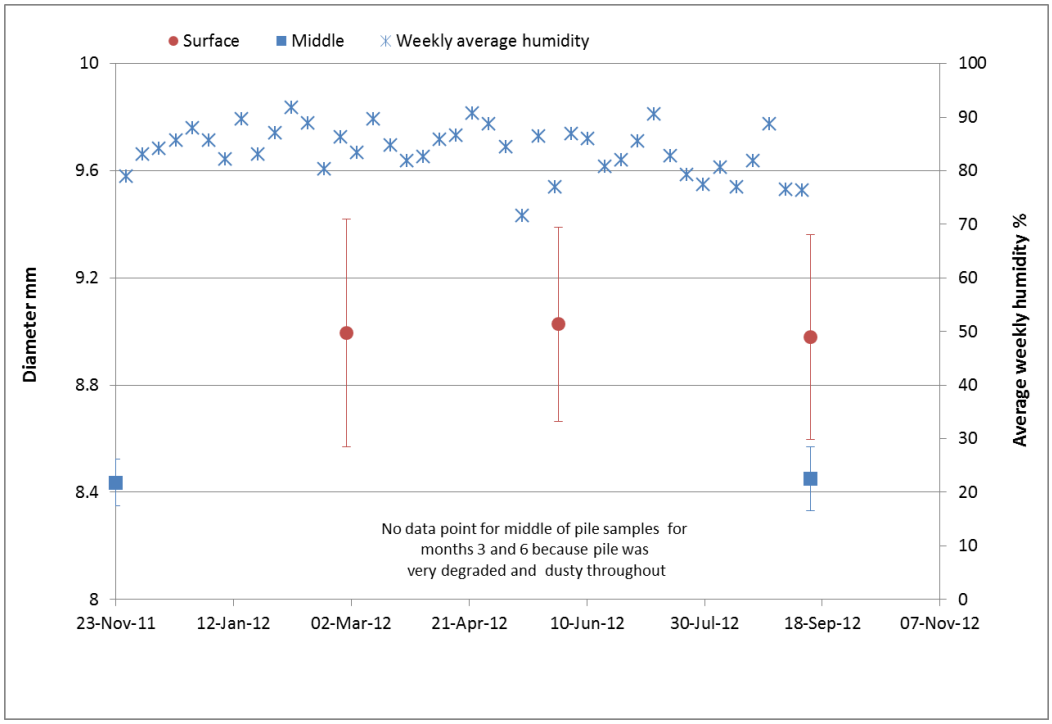

Figure 6-45. Diameter of Phase 2 white wood pellets with average weekly humidity

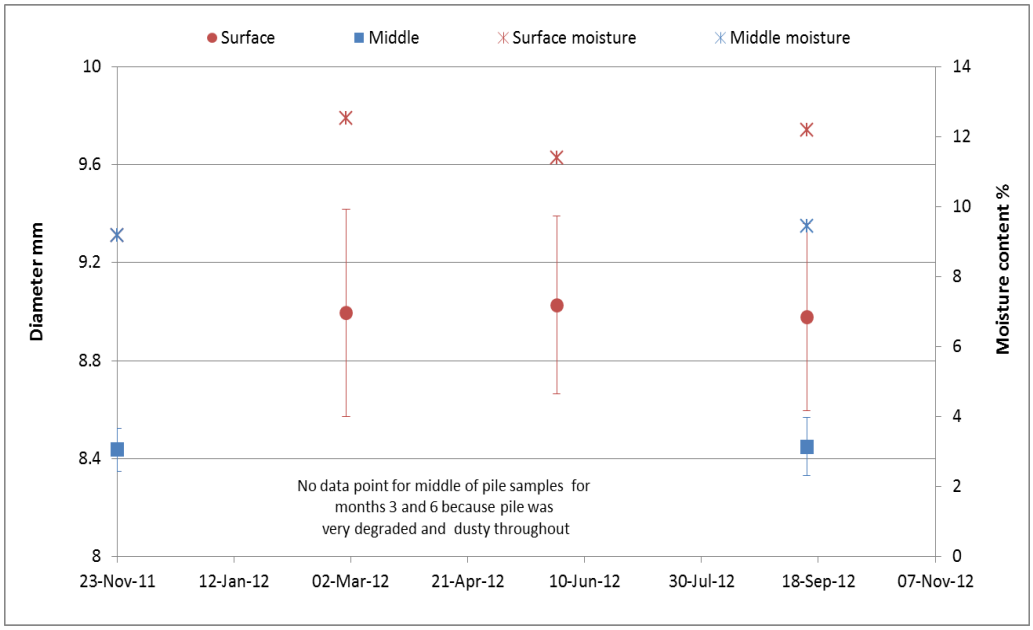

Figure 6-46. Diameter of Phase 2 white wood pellets with pellet moisture content

Upon continuous exposure to humidity, the moisture content of the surface pellets increased by 4%, leading to an increase in the diameter of about 0.5cm. The pellets at the middle of the pile, on the other hand, hardly saw any change in the moisture content and hence the diameter remained at 8.4cm. Again the link between moisture content and pellet diameter is illustrated. The layers near the surface of the pile acted as a barrier to the inner layers which were therefore less exposed to humidity. This is why the middle of the pile was less degraded than the surface after ten months in storage (Figure 6-39 and Figure 6-40).

6.6.5 Pellet axial compression strength

The axial compression of the pellets is presented alongside the pellet moisture content (Figure 6-47. Axial compression strength of Phase 2 white wood pellets and **pellet moisture content**

Error bars were generated to indicate sample variation by carrying out the test on five pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

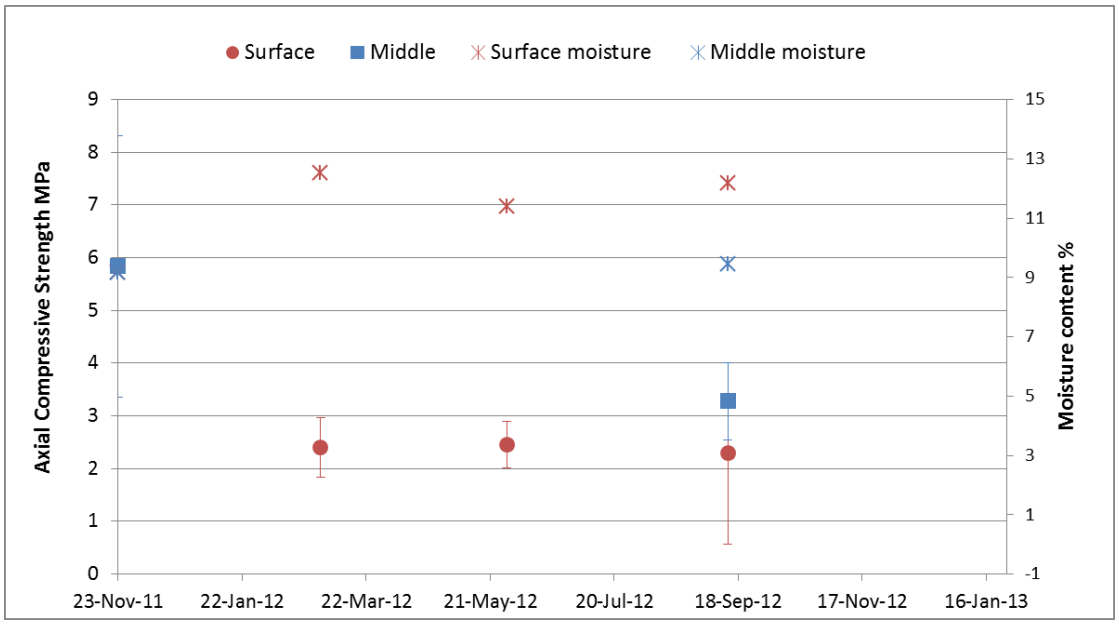

Figure 6-47. Axial compression strength of Phase 2 white wood pellets and pellet moisture content

There was a large step decrease in axial compression strength of the surface pellets from November 2011 (6 MPa) to February 2012 (2.4 MPa). Further on, the axial compression strength remained stable at around 2 MPa. The pellets in the middle of the pile suffered a 3 MPa drop in axial compression strength after ten months in storage. The degradation is larger for the surface pellets due to higher exposure to ambient temperature and humidity. The laboratory based project on the degradation of wood pellets when exposed to humidity and heat (Appendix D) showed that both weather parameters contribute to a loss in the mechanical strength of pellets.

When compared with the Phase 1 indoor thermally treated wood pellets, the white wood pellets suffered a larger decrease in axial compression strength. The fresh white wood pellets at the start of storage also had a lower axial compression strength. A full comparison between the three pellet types will be made in Section 6.7.

6.6.6 Pellet diametrical compression strength

Figure 6-48 shows the diametrical compression strength of the Phase 2 white wood pellets with pellet moisture content. Error bars were generated to indicate sample variation by carrying out the test on five pellets per sample. Because of a small population consisting of five pellets, the error bars represent the range (minimum and maximum values).

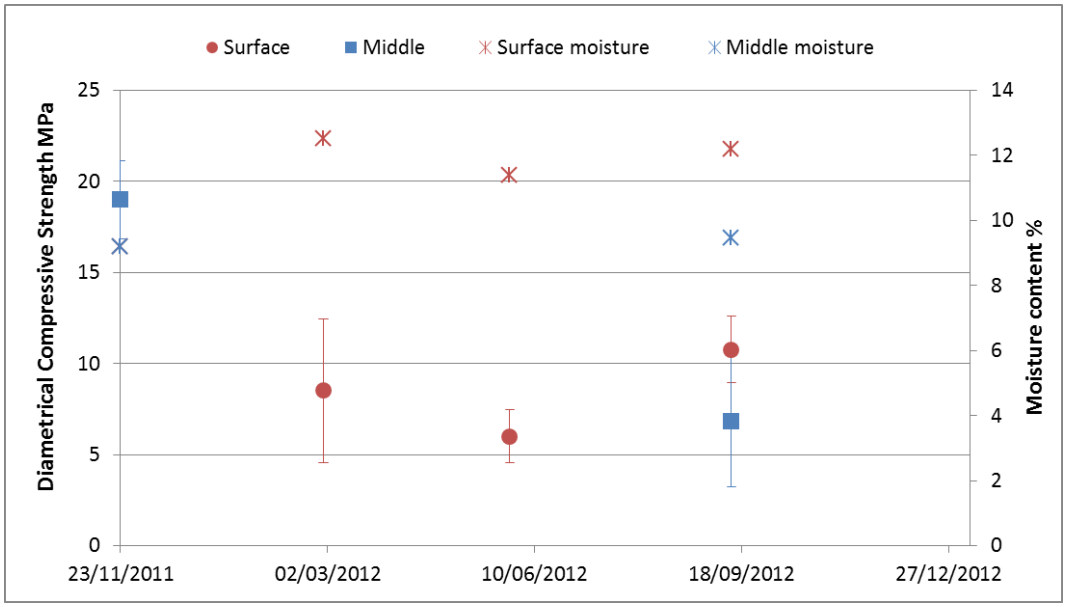

Figure 6-48. Diametrical compression strength of Phase 2 white wood pellets with pellet moisture content

The diametrical compression strength of both the surface and middle pellets decreased with time in storage. At the end of the storage period in September 2012, the diametrical compression strength of the middle pellets seems lower than that of the surface pellets. However, this could be due to large sample variation of the middle pellets.

6.6.7 Pellet inter-laminar shear modulus (stiffness)

Finally, the inter-laminar shear modulus of the white wood pellets is presented alongside the pellet moisture content (Figure 6-49). Error bars were generated to indicate sample variation by carrying out the test on ten pellets per sample. Because of a small population consisting of ten pellets, the error bars represent the range (minimum and maximum values).

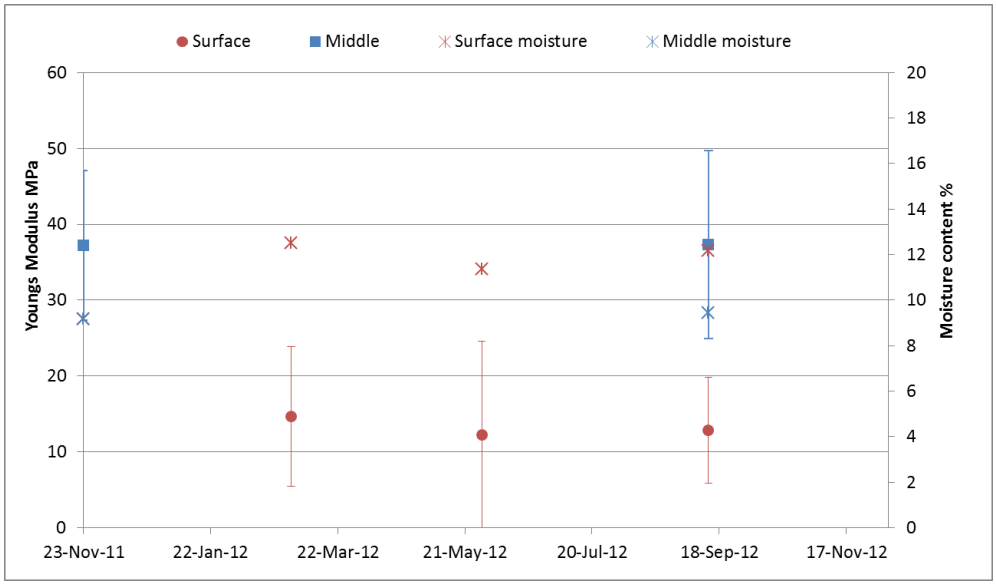

Figure 6-49. Young's modulus of Phase 2 white wood pellets with pellet moisture content

The trends in the Young's modulus of the white wood pellets on the surface of the pile are consistent with the trends in axial compression strength, undergoing a large step decrease in the first three months of storage and then the compression strength stabilising at about 12 MPa. The pellets from the middle of the pile, which could only be recovered at the end of the trial, did not show any drop in shear modulus. However the sample variation was large with a range of 25-50MPa, indicating a substantial variability as seen in other tests.

6.7 Comparison between the three pellet types

In this section, the comparison between the mechanical behaviour of Phase 1 and Phase 2 thermally treated pellets and the Phase 2 white wood pellets will be made.

The different comparisons are summarized below:

- The mechanical properties of the fresh Phase 1 thermally treated pellets at the start of storage were different to those of the fresh Phase 2 thermally treated pellets and the white wood pellets, as illustrated in

Table 6-1. The moisture content of the pellets at the start of storage is also shown.

Table 6-1. Mechanical properties of pellets at the start of storage

Pellet type	Moisture content %	Diameter mm	Durability %	Axial compression strength MPa	Diametrical compression strength MPa	Inter-laminar shear modulus MPa
Phase 1 thermally treated	2.69	5.8 Variation: Negligible	92	20 Variation: (17-22)	57 Variation: (44-70)	417 Variation: (280-550)
Phase 2 thermally treated	3.20	6.2 Variation: Negligible	86	13 Variation: (8-19)	50 Variation: (43-58)	192 Variation: (110-270)
Phase 2 white wood	9.18	8.4 Variation: (8.35-8.5)	64	6 Variation: (3.5-8.5)	19 Variation: (16-21)	37 Variation: (28-48)

- Table 6-1 shows that for the fresh pellets at the start of storage, the Phase 1 thermally treated pellets had the highest durability, axial and diametrical compression strengths and shear modulus, with the Phase 2 white wood pellets having the lowest values. The moisture content and diameter of the pellets followed the reverse sequence. These differences were to be expected because the pellets had different raw materials, manufacturing and pelletisation processes and pre and post shipping storage as well as transport and handling. The Phase 1 thermally treated pellets had a lower moisture content, smaller diameter and higher mechanical durability, strength and stiffness when compared to the Phase 2 thermally treated pellets. Sample variation was larger for the thermally treated wood pellets than for the white wood pellets.

- Throughout storage, the outdoor Phase 2 thermally treated pellets exhibited higher resistance to mechanical degradation than the outdoor Phase 1 pellets, especially the pellets on the surface of the piles. This is reflected in the percentage larger drops in all of durability, axial and diametrical compression strengths and shear modulus seen for the Phase 1 pellets. This behaviour is likely to be due to the different raw materials used in the phase 1 and phase 2 pellets and the differences in the thermal treatment and pelletisation processes used. Table 6-2 shows the pellet moisture content and mechanical properties after nine months in storage.

Table 6-2. Mechanical properties of pellets after nine months in storage

Pellet type	Moisture content %	Diameter mm	Durability %	Axial compression strength MPa	Diametrical compression strength MPa	Inter-laminar shear modulus MPa
Phase 1 thermally treated indoor surface	8.74	6.0 Variation: (5.93-5.99)	91	14.16 Variation: (12.51-16.25)	31.43 Variation: (25.05-42.17)	187.22 Variation: (124.03-250.09)
Phase 1 thermally treated indoor middle	4.52	5.9 Variation: (5.84-5.86)	88	16.49 Variation: (14.31-18.88)	55.92 Variation: (33.92-67.39)	322.23 Variation: (238.71-454.32)
Phase 1 thermally treated outdoor surface	23.70	6.5 Variation: (6.2-6.68)	9.58	1.57 Variation: (0.36-3.61)	33.06 Variation: (28.24-35.95)	3.78 Variation: (1.37-6.92)
Phase 1 thermally treated outdoor middle	10.73	6.1 Variation: (5.97-6.31)	85.53	7.35 Variation: (4.55-9.65)	35.69 Variation: (26.16-57.28)	109.69 Variation: (26.92-243.12)
Phase 2 thermally treated outdoor surface	22.34	6.5 Variation: (6.48-6.56)	46.07	2.94 Variation: (8-19)	11.01 Variation: (8.99-13.29)	23.63 Variation: (16.12-36.83)
Phase 2 thermally treated outdoor middle	24.08	6.6 Variation: (6.50-6.65)	79.07	6.12 Variation: (8-19)	6.12 Variation: (4.81-7.43)	43.91 Variation: (27.30-69.87)

Pellet type	Moisture content %	Diameter mm	Durability %	Axial compression strength MPa	Diametrical compression strength MPa	Inter-laminar shear modulus MPa
Phase 2 white wood indoor surface	12.19	9.0 Variation: (8.6-9.4)	24.87	2.29 Variation: (0.73-4.2)	10.76 Variation: (9.09-18.86)	12.84 Variation: (3.23-34.33)
Phase 2 white wood indoor middle	9.45	8.4 Variation: (8.3-8.55)	48.94	3.28 Variation: (2.71-4.36)	6.85 Variation: (3.95-11.95)	37.32 Variation: (17.76-61.64)

- In Phase 2, the moisture content and mechanical properties of the surface and middle pellets appear closer together after nine months of storage than for the Phase 1 pellets. This shows that the larger the difference in moisture content, the larger the contrast in mechanical properties

- The white wood pellets started off with much lower mechanical durability, strength and stiffness values and still had the lowest mechanical properties after nine months in storage except when compared to the Phase 1 pellets from the surface of the outdoor pile. After nine months in storage, the Phase 1 outdoor surface pellets exhibited the lowest mechanical strength and stiffness

6.8 MSc Project work

A short term project was carried out by a Masters student in Mechanical Engineering and supervised by the author at the University of Nottingham during the summer of 2012 to understand the impacts of humidity, heat and precipitation on the mechanical degradation of wood pellets. Three different pellets were subjected individually to humidity, humidity and heat and precipitation on a laboratory scale and the changes in moisture content, pellet durability, compression strength and shear modulus measured. A paper has been written on this work and will be sent to the journal 'Bioresource Technology' for peer reviewed publication and it can be found in Appendix D.

This short term Masters project showed that exposure of the different pellet types to high humidity led to an increase in moisture content and a decrease in pellet mechanical strength. When humidity is combined with heat, the rate of mechanical degradation increases. Precipitation also affects the pellets significantly and in the case of non-thermally treated pellets, disintegration was very rapid following precipitation. This work showed that for the changes in

mechanical properties during the long term storage of pellets to be fully understood, the mechanical data had to be interpreted alongside the weather data.

7 Biological degradation of biomass fuels during storage

7.1 Introduction

In this chapter, the biological activity which occurred on the different fuels during storage is discussed. Biomass is biodegradable and will decay in storage due to fungal and bacterial activity. The presence and growth of micro-organisms on biomass fuels can lead to the following issues (Noll and Jirjis, 2012):

- Reduction in fuel quality which can affect handling, milling and combustion, for example change in the CV, destruction of biomass structure affecting mechanical properties, agglomeration of biomass due to *Micela* formation, encouraging infestation, odour problems
- Self-ignition of the stockpiles catalysed by the microbial activity
- Occupational health hazards to workers on site if they are exposed to the fungi and bacteria

Chipped wood has the greatest potential for microbial growth (Boehmer et al., 2009). The storage conditions can greatly influence microbial numbers, essentially following the composting process if moisture conditions are optimal. Fungi are superior to bacteria in metabolising the main compounds of wood (Noll and Jirjis, 2012) and so biomass piles act as reservoirs of fungal spores. Moving or disturbing significant volumes of biomass fuel (chips/pellets) can result in the release of a large quantity of spores which can then be inhaled or ingested by workers or deposited on their skin (Grisoli et al., 2009).

In the typical outdoor environment the baseline level of bioaerosols naturally present is variable, depending on location and time of year, but 1,000 cfu/m3 air is not unusual and levels of viable microorganisms may be considerably

higher in outdoor air during the summer months (CIBSE, 2000). A bioaerosol is a microorganism and/or any other tiny biological particle suspended in the air, ranging in size from 0.5 to 100+ microns. It can be of microbial, plant or animal origin and as simple as airborne cells such as live or dead bacteria, fungal spores or perhaps viruses, pollens and cell fragments (Gladding, 2014).

Within the 'Indoor Environment Guidance Document CIBSE TM 26: 2000', the authors cite the work of a number of experts in the field who considered the results of sampling a number of air conditioned and mechanically ventilated buildings in the UK.' From these data this guidance document suggests that total bioaerosol levels at or above 1000 CFU per m3 should provide the action level at which further microbial investigations should be considered. Although this recommendation does not constitute a formal indoor exposure limit, it does provide a context within which to place bioaerosol levels detected in other indoor and potentially outdoor environments.

In developing guidelines for monitoring to protect public health in the vicinity of composting sites emitting bioaerosols, the Environment Agency have established what they consider to be baseline levels against which they compare emissions of bioaerosols of concern; these being the known respiratory allergen *Aspergillus Fumigatus* mould and Gram-negative bacteria capable of producing endotoxin. Their baseline levels are 500 CFU/m3 and 1000 CFU/m3 for these respectively. In addition to microorganisms, (Gladding, 2014) highlights the need to also monitor the concentrations of the following species: endotoxins, (1-3)-*B*-D-Glucan and dust. In a review by HSL of compost bioaerosols potentially effecting the respiratory health of workers (Swan et al, 2003), data on typical bioaerosol levels were summarised for a number of workplaces and these data can be used to benchmark bioaerosol measurements, generated by in-house monitoring. It is worth mentioning at this point that this type of data is rather scarce.

It was important in this long term biomass storage project to understand the potential and extent of the biological degradation of the Willow chips, thermally treated wood pellets and white wood pellets. Biological analysis was

a small part of the project and was partly contracted out to Mologic UK (Mologic UK).

Fresh samples, as well as samples after three and six months in storage, were sent to Mologic without any drying or pre-treatment. They were analysed for fungal count and identification, with subsequent analysis and interpretation included here carried out by the author. The microbiologist at Mologic generated images of each of the fungal species present on the biomass samples and also performed a fungal count and identification for each fungus. The information was sent to the author for interpretation in order to determine what the data set meant in the context of the project. From the data analysis, recommendations can be made to biomass users.

The methodology used by Mologic in determining the fungal identity and count was described in Section 3.5.

7.2 Presentation of results

The data provided by Mologic for the biological analysis consisted of the following:

- The count in colony forming units (CFU) per gram of wood (chip/pellet) of the different fungi identified on the Willow chip and wood pellet samples at the start of storage and after three and six months of storage. The count represents the fungal growth on the wood (chip/pellet) itself. It is different and not to be confused with the count of airborne species which could be released from the wood during pile handling.
- Images of the each of the fungi growing on agar plates
- DNA sequences of each of the fungi

In this chapter, a selection of the data after full analysis has been carried out will be presented, which will include:

- Photographs of the fresh and degraded fuels
- The count in colony forming units (CFU) per gram of wood of the different fungi identified on the Willow chip and wood pellet samples at the start of storage and after three and six months of storage
- Photographs of two of the main fungi growing on each of the fuels

For each of the fuel samples, a photograph of the degraded samples is shown followed by the complete fungal count on the fresh and degraded samples from the surface and middle of each of the stockpiles. A few photographs of the main fungi present on the samples are also included.

The Willow chips data (Phase 1 and Phase 2) is shown first followed by the thermally treated wood pellets (Phase 1 and Phase 2) and finally the Phase 2 white wood pellets results will be discussed.

Following the detailed biological results, the resulting occupational health implications of storing the types of biomass investigated in this project will be discussed

The last section in this chapter focuses on further work which can be carried out to improve understanding of the health hazards which biomass storage represent to workers.

7.3 Phase 1 Willow chips

Figure 7-1 and Figure 7-2 show the photographs of the freshly harvested Willow chips at the start of storage in April 2011 and the degraded Willow chips from the surface of the 3.8x3.8x2.5m outdoor pile in October 2011 after six months in spring/summer storage.

Figure 7-1. Fresh Willow chips from surface of 3.8x3.8x2.5m outdoor pile, April 2011

Figure 7-2. Degraded Willow chips from surface of 3.8x3.8x2.5m outdoor pile, October 2011

On the photograph of the degraded Willow, mould can be observed on the wood chips and strands of fungus can be seen linking the different pieces of wood. White and brown/black moulds are both present on the Willow chips. Figure 7-2 is representative of the whole surface of the pile.

Table 7-1 shows the full list of fungi and count for the Phase 1 Willow chip determined by Mologic.

Table 7-1. Phase 1 Willow chips fungal type and count in colony forming units per gram of wood (CFU/g)

Fungus type	Apr 2011 Fresh	Month 3 Jul 2011 BS	Month 3 Jul 2011 BM	Month 3 Jul 2011 SS	Month 3 Jul 2011 SM	Month 6 Oct 2011 BS	Month 6 Oct 2011 BM	Month 6 Oct 2011 SS	Month 6 Oct 2011 SM
Aspergillus fumigatus	Null	2.E+07	1.E+07	2.E+07	1.E+06	2.E+07	5.E+07	2.E+07	8.E+06
Aspergillus tubingensis	Null	Null	Null	Null	Null	Null	Null	1.E+06	Null
Aureobasidium	1.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Candida	2.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Cladosporium	2.E+04	Null	Null	Null	Null	Null	Null	Null	Null
Cryptococcus	3.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Diplodina	3.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Fusarium	1.E+04	Null	Null	1.E+06	Null	Null	Null	Null	Null
Hypocrea	Null	2.E+06	1.E+06	1.E+06	2.E+06	Null	Null	Null	Null
Lichteimia	Null	Null	Null	Null	Null	Null	Null	1.E+06	Null
Metschnikowia	2.E+03	Null	Null	Null	Null	Null	Null	Null	Null
Mucor	1.E+02	Null	Null	Null	Null	Null	Null	Null	Null
Phanerochaete	Null	Null	Null	Null	Null	2.E+06	1.E+07	Null	2.E+06
Phoma	2.E+04	Null	Null	Null	Null	Null	Null	Null	Null
Rhizopus oryzae	Null	Null	4.E+06	Null	Null	Null	Null	Null	Null
Rhizopus microsporus	Null	Null	2.E+06	3.E+06	4.E+07	1.E+06	1.E+07	1.E+06	1.E+06
Trichoderma	Null	3.E+06	Null	Null	Null	Null	Null	Null	Null

The five pathogenic (with the potential to harm human health) fungi are shown in red. A few of the fungi only appeared on one sample on only one occasion. This is likely to be because the storage trials took place in a natural rural farm environment where airborne fungi were likely to land on the piles from the surrounding environment.

The month at which the sample was taken is shown in the top row and the samples are labelled as follows:

BS – 3.8x3.8x2.5m pile, surface sample

BM – 3.8x3.8x2.5m pile, middle sample

SS – 2.4x2.4x1.7m pile, surface sample

SM – 2.4x2.4x1.7m pile, middle sample

Table 3-1 in Chapter 3 contains detailed information on the characteristics of each of the above piles.

The main observations from Table 7-1 are as follows:

- There were nine fungal species detected on the fresh Willow chips, none of which are pathogenic. The maximum count was in the order 10^5 CFU/g

- After three months in storage, all the fungi types initially seen on the fresh Willow chips were no longer present. This could be attributed to the heat generation in the piles which led to high temperatures and therefore the elimination of the mesophilic (non-thermally resistant) fungi. As described in Section 4.4.1, both the 2.4x2.4x1.7m and 3.8x3.8x2.5m Willow piles saw a significant rise in pile temperature in the first few weeks of storage (the middle of larger pile reached a temperature of 73°C while the middle of the smaller pile reached 62°C). The maximum temperature for the growth of mesophilic fungi is between 30 and 40°C above which they long longer survive (Nilsson, 1965).

- Four new fungi types were detected in the Willow piles after three months in storage namely *Aspergillus Fumigatus*, *Hypocrea*, *Rhizopus (Oryzae and Microsporus)* and *Trichoderma*. In their work on chipped Willow storage, (Scholz et al., 2005) also reported the presence of *Aspergillus* and *Rhizopus*, both of which are thermophilic fungi and can

tolerate temperatures up to 60°C. (Conrad et al., 2009) and (Noll et al., 2010a) have reported that after a temperature change, a shift in the fungal community composition from mesophilic to thermophilic species is to be expected, with predominantly thermophilic micro-organisms frequently found in wood chip piles where high temperatures have been recorded (Novinscak et al., 2009, Adams and Frostick, 2009). During storage, the microorganisms naturally present in low number begin to multiply using the wood as a nutrient source. As they do so their metabolic activity causes an increase in temperature. This in turn encourages greater microbiological activity and the warmer conditions leads to stimulated growth of thermotolerant and thermophilic species compared to mesophilic types (Boehmer et al., 2009)

- After six months in storage, there is still significant presence of *Aspergillus* and *Rhizopus*. The presence of the *Phanerochaete* fungus was also reported. The *Hyprocrea* fungus on the other hand, was reported after three months, was no longer present

Figure 7-3 and Figure 7-4 below show photographs of the *Aspergillus Fumigatus* and *Rhizopus Microsporous* fungi growing on agar plates in the laboratory.

Figure 7-3. Aspergillus Fumigatus (from Mologic UK)

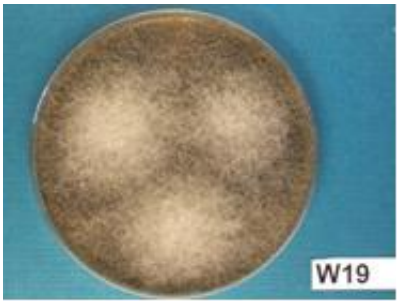

Figure 7-4. Rhizopus Microsporus (from Mologic UK)

7.4 Phase 2 Willow chips

Figure 7-5 and Figure 7-6 show the fresh Willow chips at the start of Phase 2 in November 2011 and the degraded Willow chips from the surface of the 3.8x3.8x2.5m outdoor pile in May 2011, after six months in winter/spring storage.

Figure 7-5. Fresh Willow chips from surface of 3.8x3.8x2.5m outdoor pile, November 2011

Figure 7-6. Degraded Willow chips from the surface of 3.8x3.8x2.5m outdoor pile, May 2011

It is harder to notice mould and strands of fungi for the Phase 2 Willow chips simply by visual inspection of the surface of the piles.

Table 7-2 shows the full list of fungi and count for the Phase 2 Willow chips

Table 7-2. Phase 2 Willow chips fungal type and count in colony forming units per gram of wood (CFU/g)

Fungus type	Fresh	Month 3 OS	Month 3 OM	Month 3 IS	Month 3 IM	Month 6 OS	Month 6 OM	Month 6 IS	Month 6 IM
Aspergillus fumigatus	Null	Null	9.E+06	Null	3.E+06	Null	4.E+06	Null	1.E+07
Aspergillus tubingensis	Null	Null	Null	Null	Null	Null	Null	Null	Null
Aureobasidium	3.E+05	Null	Null	Null	Null	1.E+06	Null	1.E+06	Null
Bionetrica	Null	Null	1.E+06	Null	Null	Null	Null	Null	Null
Candida	Null	2.E+05	Null	Null	Null	Null	Null	Null	Null
Cladosporium	Null	1.E+05	Null	1.E+05	Null	4.E+06	Null	Null	Null
Didymella	Null	6.E+05	Null	Null	Null	Null	Null	Null	Null
Endocymes	Null	Null	Null	Null	1.E+07	Null	Null	Null	3.E+07
Eupenicillium	Null	Null	Null	5.E+05	Null	Null	Null	Null	Null
Hypocrea	Null	Null	Null	Null	Null	Null	Null	Null	1.E+06
Lecythopora	Null	Null	Null	Null	Null	Null	1.E+06	Null	Null
Mortierella	Null	Null	Null	1.E+04	Null	Null	Null	Null	Null
Mucor	Null	Null	Null	4.E+04	Null	Null	Null	Null	Null
Penicillium	1.E+05	2.E+06	3.E+06	Null	3.E+06	1.E+05	Null	1.E+06	6.E+06
Phanerochaete	Null	Null	Null	Null	Null	Null	1.E+06	Null	Null
Phoma	1.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Pichia	2.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Rhodotorula	1.E+05	Null	Null	Null	Null	Null	Null	Null	Null
Truncatella	Null	1.E+05	Null	Null	Null	6.E+05	Null	Null	Null

The five pathogenic fungi are again shown in red. Once again, a few of the fungi only appeared on one sample on only one occasion probably for the same reasons noted above

The month at which the sample was taken is shown in the top row and the samples are labelled as follows:

OS – Outdoor 3.8x3.8x2.5m pile, surface sample

OM – Outdoor 3.8x3.8x2.5m pile, middle sample

IS – Indoor 3.8x3.8x2.5m pile, surface sample

IM – Indoor 3.8x3.8x2.5m pile, middle sample

The main observations from Table 7-2 are as follows:

- There were fewer fungi detected on the fresh Phase 2 Willow chips compared to fresh Phase 1 chips (Table 7-1). Phase 2 started in November 2011 when it was colder (average temperature in first three months was 5°C) than when Phase 1 started in April 2011 (average temperature in first three months was 13°C). This confirms the visual inspections

- After three months in storage, all the fungi present on the fresh Willow except *Penicillium* had disappeared. As described in Section 7.3 for Phase 1 Willow chips, this can be attributed to the heat generation and temperature rise in the Willow piles in the first few weeks in storage (middle of indoor pile reached 60°C while middle of outdoor pile reached 57°C).

- As for Phase 1, *Aspergillus Fumigatus* was present on the Phase 2 Willow chips after three months in storage. However, the fungus was only seen in the middle of the piles and not on the surface. This is because the surfaces of the piles was exposed to the cold ambient temperatures (-6 to 20°C range over the first six months in storage in Phase 2 compared to a range of 3 to 26°C in the first six months of

Phase 1). Even in the middle samples of the Phase 2 Willow piles (range of 8 to 60°C in the first six months of storage), the count is lower than in the middle of the large Willow pile in Phase 1 (range of 9 to 73°C in the first six months of storage). It should be noted that in Phase 2, both the indoor and outdoor Willow piles were of the same size as the large Willow pile in Phase 1 (3.8x3.8x2.5m).

- There was still a significant presence of *Aspergillus* detected after six months of storage, in the middle of both the outdoor and indoor Willow chip piles in May 2012. Even though the ambient and pile temperatures were higher at this time (~ 15°C), the *Aspergillus* was still not present on the surface of the piles. Figure 7-7 shows the count of *Aspergillus Fumigatus* on equally sized (3.8x3.8x2.5m) outdoor Willow chip piles in Phases 1 and 2.

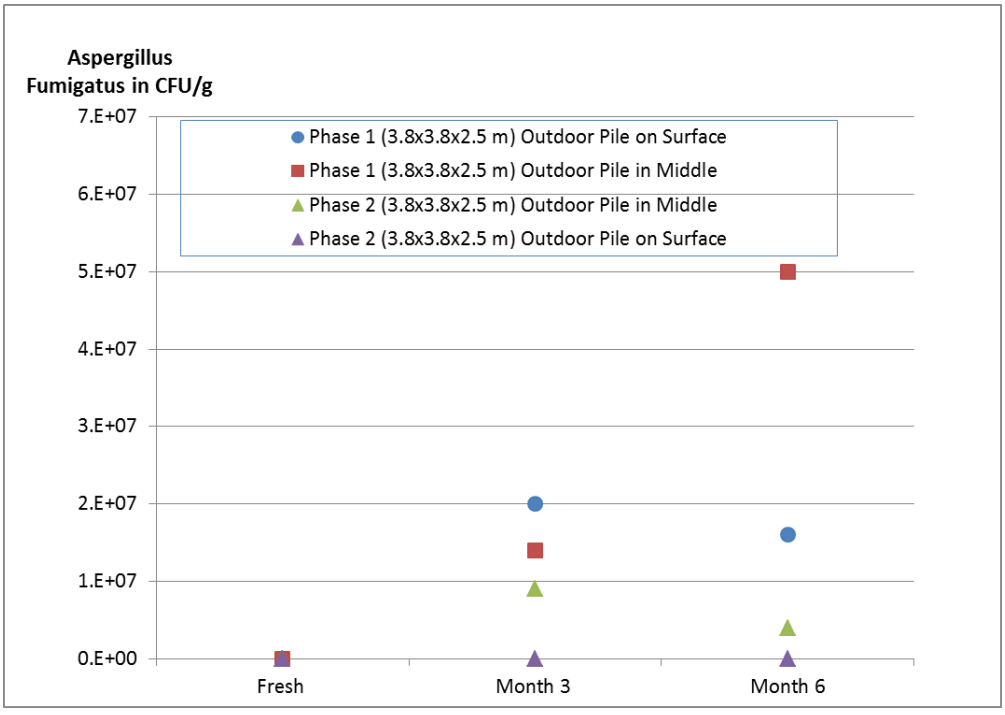

Figure 7-7. Change in the count (CFU/g of wood) of Aspergillus Fumigatus as Phases 1 and 2 progressed

- The surface of the Phase 2 outdoor Willow pile was sustaining the growth of *Aureobasidium, Cladosporium, Penicillium and Truncatella* while *Hypocrea, Endocymes* and *Penicillium* were found on the surface of the indoor Willow pile. Apart from the *Penicillium* fungus, which

appeared on all of the fresh and degraded samples, the presence of the other four fungi was less consistent. This is likely to be because the storage trials took place in a natural rural farm environment where airborne fungi were likely to land on the piles from the surrounding environment

- There was a close relationship between the ambient and pile temperatures and the number and count of fungi with both decreasing when temperatures reduced

Figure 7-8 and Figure 7-9 show the *Aureobasidium* and *Clasdosporium* fungi growing on agar plates in the laboratory

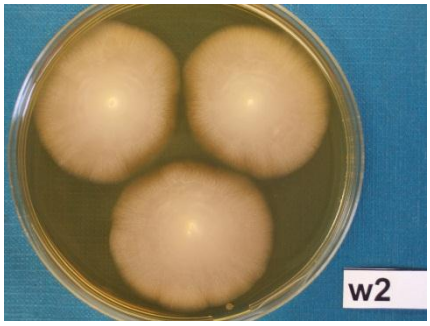

Figure 7-8. *Aureobasidium* (from Mologic UK)

Figure 7-9. *Cladosporium* (from Mologic UK)

7.5 Phase 1 thermally treated wood pellets

Figure 7-10 and Figure 7-11 show the fresh pellets at the start of storage in April 2011 and the degraded pellets from the surface of the outdoor pile after six months in storage in October 2011

Figure 7-10. Thermally treated wood pellet pile from the surface of outdoor pile (fresh pellets at the start of Phase 1 in April 2011)

Figure 7-11. Thermally treated wood pellet pile from the surface of outdoor pile (six months storage)

White mould can be seen on the degraded pellets from the surface of the outdoor pellet pile. The presence of white mould became noticeable after the third month in storage in July 2011, see Figure 7-12

Figure 7-12. Thermally treated wood pellet pile from the surface of outdoor pile (three months storage)

As the time in storage increased from three to six months, the presence of the white mould became more noticeable.

Table 7-3 shows the full list of fungi and count for the Phase 1 thermally treated wood pellets.

Table 7-3. Phase 1 thermally treated wood pellets fungal type and count (CFU/g)

Fungus type	Fresh	Month 3 OS	Month 3 OM	Month 3 IS	Month 3 IM	Month 6 OS	Month 6 OM	Month 6 IS	Month 6 IM
Aspergillus fumigatus	Null	2.E+03	2.E+03	Null	8.E+02	Null	Null	Null	Null
Cladosporium	Null	Null	Null	Null	Null	3.E+04	Null	Null	1.E+02
Penicillium	Null	Null	Null	2.E+03	Null	Null	Null	Null	Null
Rhizopus microsporus	Null	7.E+02	Null	Null	1.E+02	Null	Null	Null	Null
Sporidiobolus	Null	Null	Null	Null	Null	3.E+04	Null	Null	Null

The month at which the sample was taken is shown in the top row and the samples are labelled as follows:

OS – Outdoor 2.4x2.4x1.5m pile, surface sample

OM – Outdoor 2.4x2.4x1.5m pile, middle sample

IS – Indoor 2.4x2.4x1.5 pile, surface sample

IM – Indoor 2.4x2.4x1.5m pile, middle sample

The main observations from Table 7-3 are as follows:

- There was no fungal presence on the fresh pellets presumably because of the thermal treatment at elevated temperatures effectively sterilizing them
- As storage progressed, the pellets were exposed to airborne fungi and a few species were reported after three and six months in storage, mostly on the surface of the piles
- *Sporidiobolus, Cladosporium and Penicillium* were detected after three months along with *Aspergillus Fumigatus* and *Rhizopus Microsporus*. The white mould seen in Figure 7-11 and Figure 7-12 can be attributed to one or more of these fungi. The count for all of the fungi was low (maximum 10^4 CFU/g).
- The low counts of the *Aspergillus* and *Rhizopus* fungi on the indoor thermally treated wood pellets, compared to what was seen on the outdoor Willow chips (count in the order of 10^6-10^7 CFU/g), reflect that these species were not actively growing on the thermally treated pellets and that they were most likely present through contamination from the natural farm environment.

Figure 7-13 and Figure 7-14 show *Penicillium* and *Sporidiobolus* fungi growing on agar plates in the laboratory

Figure 7-13. *Penicillium* (from Mologic UK)

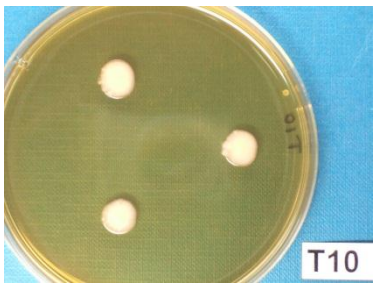

Figure 7-14. *Sporidiobolus* (from Mologic UK)

7.6 Phase 2 thermally treated wood pellets

As for the Phase 1 thermally treated wood pellets stored outdoor, the biological degradation of the Phase 2 pellets was gradual and the spread of white mould increased with time in storage. White mould was noticeable on the pellets after four months in storage, with the mould intensity increasing gradually from then on. Figure 7-15 to Figure 7-19 below show the following:

- Fresh pellets in December 2011 at the start of storage
- Pellets after 3 months in storage in March 2012
- Pellets after 4 months in storage in March 2012
- Pellets after 5 months in storage in April 2012
- Pellets after 6 month in storage in June 2012

Figure 7-15. Fresh thermally treated wood pellets at the start of storage, December 2011

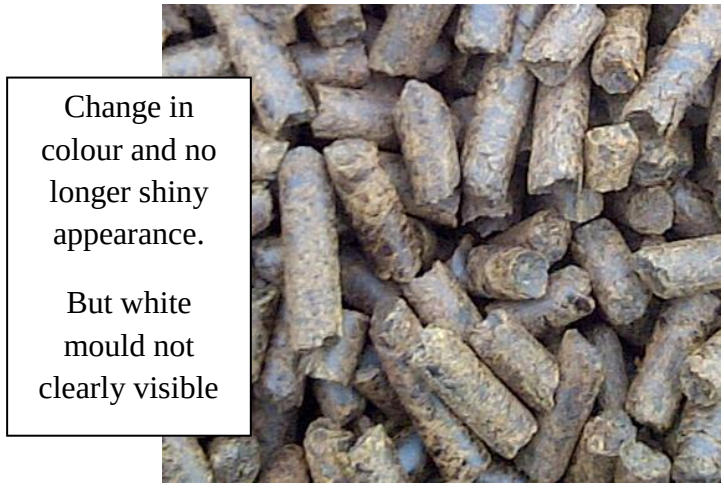

Figure 7-16. Thermally treated wood pellets from the surface of outdoor pile after three months in storage, March 2012

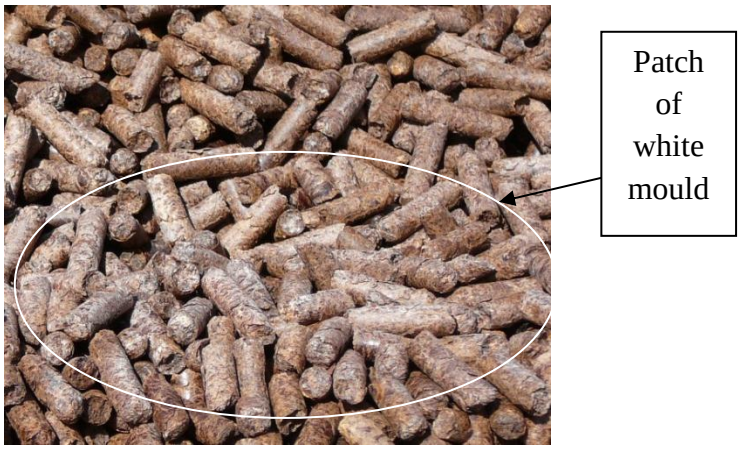

Figure 7-17. Thermally treated wood pellets from the surface of outdoor pile after four months in storage, April 2012

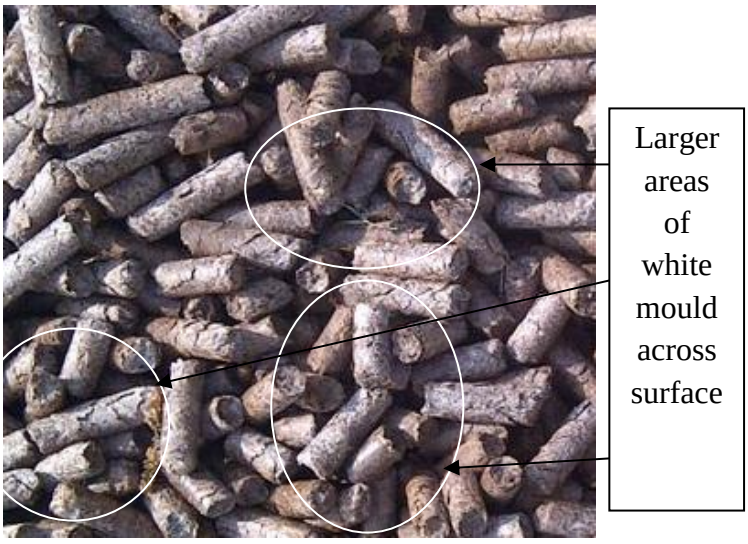

Figure 7-18. Thermally treated wood pellets from the surface of outdoor pile after five months in storage, May 2012

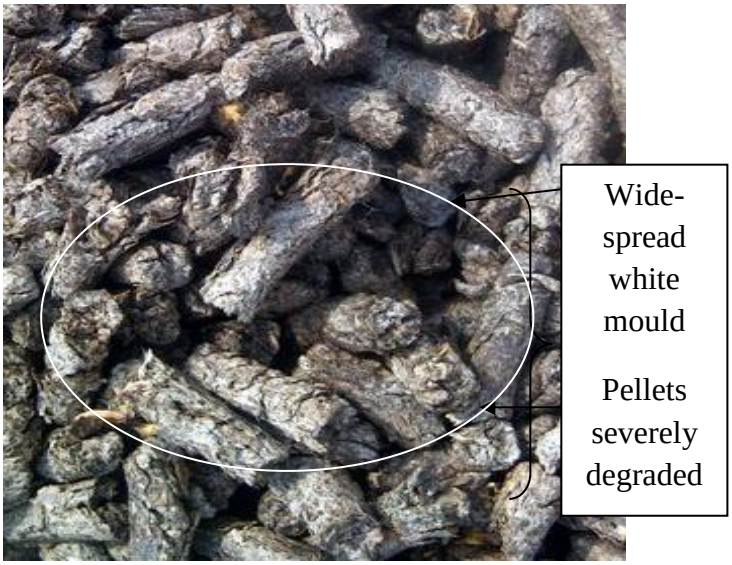

Figure 7-19. Thermally treated wood pellet pile from the surface of outdoor pile (six months storage, June 2012)

After six months in storage, white mould growth can be observed on the pellets. By visual inspection, the mould concentration on the degraded Phase 2 pellets (Figure 7-19) appears higher than on the degraded Phase 1 pellets (Figure 7-11).

Table 7-4 shows the full list of fungi and count for the Phase 2 thermally treated wood pellets

Table 7-4. Phase 2 thermally treated wood pellets fungal type and count (CFU/g)

Fungus type	Fresh	Month 3 OS	Month 3 OM	Month 6 OS	Month 6 OM
Amorphotheca	Null	Null	Null	3.E+05	9.E+05
Aureobasidium	Null	Null	Null	3.E+04	Null
Cladosporium	Null	7.E+04	5.E+02	Null	9.E+04
Mucor	Null	Null	Null	1.E+03	Null
Sydowia	Null	Null	Null	1.E+04	Null
Sporidiobolus	Null	2.E+04	Null	Null	1.E+04

The month at which the sample was taken is shown in the top row and the samples are labelled as follows:

OS – Outdoor 2.4x2.4x1.5m pile, surface sample

OM – Outdoor 2.4x2.4x1.5m pile, middle sample

The main observations from Table 7-4 are as follows:

- Again there was no fungal presence on the fresh pellets.
- During outdoor storage, the pellets were exposed to airborne fungi and a few species were reported after three and six months in storage. The white mould seen in Figure 7-17 to Figure 7-19 can be attributed to one or more of these fungi.
- The *Aureobasidium* and *Cladosporium* fungi present on the outdoor pellets were also located on the outdoor Willow chips situated a few metres from the pellet pile. It is possible they could have resulted from contamination from the Willow pile. The *Amorphoteca*, *Mucor*, *Sydowia* and *Sporidiobolus* were not present on the Willow chips. However, the storage trials took place in a natural rural farm environment where airborne fungi were likely to land on the piles from the surrounding environment
- The count for all of the fungi was lower than what was seen on the Willow chips (maximum 10^5 CFU/g) and no pathogenic types were identified

Figure 7-20 and Figure 7-21 show the *Amorphoteca* and *Mucor* fungi growing on agar plates in the laboratory

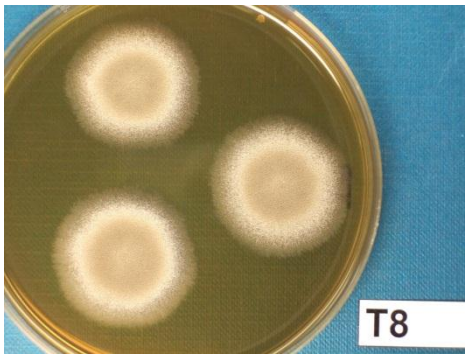

Figure 7-20. *Amorphoteca* (from Mologic UK)

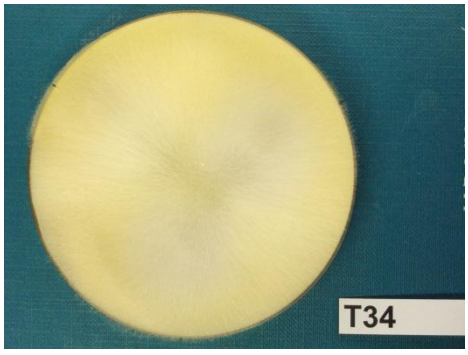

Figure 7-21. *Mucor* (from Mologic UK)

7.7 Phase 2 white wood pellets

Figure 7-22 and Figure 7-23 show the white wood pellets at the start of storage in November 2011 and the degraded pellets after six months in storage.

Figure 7-22. White wood pellets from the surface of indoor pile at the start of storage, November 2011

Figure 7-23. Degraded white wood pellets from the surface of indoor pile after six months in storage, May 2012

As the white wood pellets had degraded to such an extent to a powdered form (see Section 6.6.1), it was difficult to observe fungal presence through visual inspection.

Table 7-5 shows the full list of fungi and count for the Phase 2 white wood pellets

Table 7-5. Phase 2 white wood pellets fungal type and count (CFU/g)

Fungus type	Fresh	Month 3 IS	Month 3 IM	Month 6 IS	Month 6 IM
Cladosporium	Null	2.E+01	Null	Null	Null
Emericella	Null	Null	Null	Null	1.E+03
Paecilomyces	6.E+02	2.E+02	9.E+02	2.E+04	7.E+03
Penicillium	1.E+03	2.E+02	3.E+02	5.E+04	6.E+03

The month at which the sample was taken is shown in the top row and the samples are labelled as follows:

IS – Indoor 2.4x2.4x1.5m pile, surface sample

IM – Indoor 2.4x2.4x1.5m pile, middle sample

The main observations from Table 7-5 are as follows:

- Two fungi (*Paecilomes* and *Penicillium*) were present on the white wood pellets at the start of the storage trial. The count was low (10^2-10^3 CFU/g) and they are non-pathogenic. Prior to being used in the storage trials, the pellets were stored in an enclosed environment at Ironbridge power station. It is possible that the pellets could have come into contact with airborne fungi in storage or transport.
- As storage progressed, two more fungi were detected on the pellets but the count remained low
- Visible fungal presence on the white wood pellets was low

Figure 7-24 and Figure 7-25 show the *Emericella* and *Paecilomyces* fungi growing on agar plates in the laboratory

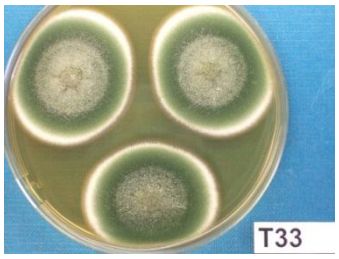

Figure 7-24. *Emericella* (from Mologic UK)

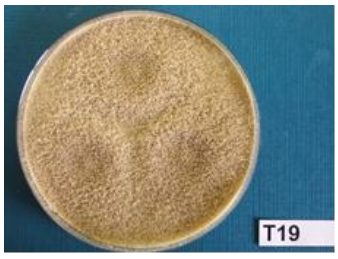

Figure 7-25. *Paecilomyces* (from Mologic UK)

7.8 Occupational health implications of storing Willow chips, thermally treated pellets and white wood pellets

In this section, the different fungi identified on the fuels with potential to harm workers on site will be highlighted.

The three commonly known pathogenic fungi present in the samples were Aspergillus, Rhizopus and Candida (Noll and Jirjis, 2012), all three reported on the Willow chips. Candida can cause a range of illnesses, such as thrush, arthritis, osteomyelitis, endocarditis, endolphthalmitis, meningitis and fungemia (Fridkin and Jarvis, 1996). Airborne Aspergillus pathogens can cause invasive and non-invasive pulmonary infections or allergic bronchopulmonary aspergillosis (Mccormick et al., 2010).

While Aspergillus was also identified on the degraded thermally treated wood pellets, the low count showed that the fungus was not growing actively on the pellets and could have just been a result of contamination from the adjacent Willow chip piles.

A range of other fungi were identified as seen in Table 7-1 to Table 7-5 but their pathogenicity is less well recognised. The main conclusion from (Doctor Fungus) was that even if the pathogenicity of a fungus or bacteria has not been fully researched and defined, they would be more likely to cause harm to immunocompromised patients (e.g. diabetes, HIV, leukaemia, lymphoma, transplantation).

The National Allergy Bureau, reporting the NAB SCALE (National Allergy Bureau) of mould and pollen counts, considers mould counts in outdoor air of 0-6499 spores per cubic meter of air as low, to 6500 to 12,999 spores per cubic meter of air as moderate, to 13,000 to 49,999 spores per cubic meter of air as high, and above 50,000 as very high. At "high" levels most individuals with any sensitivity will experience symptoms.

Acceptable levels for individual species vary since species toxicity varies widely as does spore size, weight, and other features which affect risk to building occupants. E.g. Aspergillus/Penicillium in a "clean" residential building study was at a mean of 230, in buildings known to have a moisture or flooding problem it was at 2235 and in mould contaminated buildings the figure was 36,037 (NAB). (Oppliger et al., 2005) carried out a study on bio-aerosols in sewage treatment plants in Switzerland and (Grisoli et al., 2009) did an assessment of airborne microorganism contamination in an industrial area characterised by an open compositing facility and a wastewater treatment plant. For composting and sewage treatment plants, the suggested limit for airborne fungal spores is 1000 CFU m^{-3}.

In order to fully appreciate the inhalation and ingestion potential of fungal spores as well as their deposition onto the skin and eyes of workers, the release mechanism of the spores from the wood fuels into the air needs to be understood and the resulting concentration of airborne spores (Grisoli et al., 2009). Airborne spores have a diameter of 2-10µm and easily reach the lower airways of the human respiratory tract (O'Gorman, 2011), causing diseases such as invasive pulmonary infection or contributing to allergic sinusitis and allergic broncho-pulmonary diseases.

The release of spores from the degraded wood materials and the resulting concentrations in the surrounding air was not carried out in the study and was outside the scope of the project due to time and resource constraints.

The occupational health hazards brought about by the storage of Willow chips, as studied in this project, can only be fully assessed through further work in which the airborne fungi is collected and measured in the proximity of Willow chip piles.

Barontini et al. (2014) carried out a study to determine the concentration of airborne fungi at a range of distances from Poplar chip piles which were being stored for a period of six months. The spore measurements (both active and passive) took place during pile handling.

In the active method, air samples were taken in a stationary air sampling device which sucked 8L of air per minute for 15 minutes. In the passive method, petri dishes were positioned at a height of 1.5m for an hour in proximity to the piles during handling. Worker exposure level was measured by epidermal (skin) and operator breathing sampling (dust and spores). However no spore measurements were carried out on the Poplar chips themselves.

The total amount of fungal spores measured in the storage area during movement operations was over the value of 1000 CFU per m^3 of air. No significant differences in total amount of spore were observed within the first 5m from the piles, while at a distance of 300m the level of fungal spore concentration declined to 614 CFU m^{-3}, due to atmospheric dispersion and dilution. The manual operators working on the pile were exposed to high levels of fungal spores (4864 ± 580 CFU m^{-3}). In terms of epidermal exposure of the skin close to the eyes, after 1h of manual work, a mean value of 7 CFU cm^{-2} was recorded.

14 main fungal types were identified in the bio-aerosol and on workers' skin, including Aspergillus, Cladosporium, Fusarium, Lichetmia and Trichoderma which were found on the degrading Willow chips in the storage trials. Penicillium, which was identified on both the white wood and thermally treated pellets, was also present in the Poplar chips storage area.

Similar work on airborne fungi types and concentrations should be encouraged in biomass storage studies. The results could then be translated into occupational health and safety guidelines for workers handling biomass.

8 Conclusions

This project has focused on the long term storage of different biomass fuels in outdoor and indoor stockpiles and was a joint study between the Efficient Fossil Energy Technologies engineering doctorate training centre at the University of Nottingham and E.ON Technologies at Ratcliffe.

The first part of this concluding chapter will discuss what this project adds to the existing literature domain. The main findings of this long term biomass storage project will then be presented followed by recommendations on the storage of biomass in the energy industry based on the findings of this study. The final section of this chapter will outline the remaining gaps which could be filled by further academic research.

8.1 What the project adds to the existing literature domain

The novelty which this project brings to the existing literature domain can be divided into the following areas:

- The scope of this study is novel in that it combined a range of different fuels, a range of storage scenarios, a range of stockpile sizes and a range of weather/seasonal patterns. Chapters 1 and 3 contain full details on the project testing matrix and methodology. Table 3-1 shows information on each of the different stockpiles investigated
- Another novelty which the project brings is that it investigated mechanical, biological and chemical degradation simultaneously, whereas other studies have only focused on one or two of these. For each type of degradation, a wide range of tests were performed. Furthermore, to fully understand the changes in properties, the results were processed and interpreted combined with the weather data and

fuel moisture content. This work therefore generated a uniquely wide and extensive data matrix.

- Most of the available papers on mechanical testing on wood pellets relate to the pellet quality tests and pellets comparison when manufactured. They are not directly focused on mechanical property changes as a result of storage. This study, on the other hand, had a strong mechanical degradation component during storage.
- From section 2.5.2 of the literature review, it is clear that a greater understanding and bank of data needs to be developed on the types and concentrations of fungi and bacteria growing on fuels during storage and then translated to occupational health implications and subsequently mitigation and control measures. In this work, biological activity on the different fuels has been closely monitored by performing a colony forming unit count and fungal species identification on a regular basis for the first six months of storage.

8.2 Project findings

This section will be split into the following sub sections:

- Heat generation in stockpiles during storage
- Chemical degradation
- Mechanical degradation
- Biological degradation

8.2.1 Heat generation in stockpiles during storage

8.2.1.1 Untreated white wood pellet pile

- The untreated white wood pellet pile saw very little change in temperature both near the surface and in the middle of the pile

8.2.1.2 Thermally treated wood pellet piles

- In both Phases 1 and 2 of the project, the temperatures in the thermally treated pellet piles showed a stable behaviour and the trends followed the ambient temperature. No signs of heat generation could be seen and this shows that the thermal treatment prior to pelletisation changed the wood properties so that it was no longer prone to biological activity which generates heat

8.2.1.3 Freshly harvested Willow chip piles

- For both Phases 1 and 2, the temperature in the middle of all four Willow chip piles (both outdoor and indoor) increased rapidly in the first two weeks of storage and then dropped again by the fourth week of storage and then stayed stable at a few degrees above ambient temperature for the rest of the storage period.
- In Phase 1 of the project which started in April 2011, the surface temperature of both the outdoor small and big Willow piles also spiked in the first two weeks of storage before dropping by week four. In Phase 2 which started in November 2011, the surface temperature of the indoor and outdoor Willow chip piles did not increase due to the cooling effect brought about by a much colder ambient temperature
- In Phase 1, the larger outdoor Willow pile reached 73°C in the middle and 32°C on the surface, while the smaller outdoor Willow pile reached a peak temperature of 62°C in the middle and 25°C on the surface.
- In Phase 2, the maximum temperature reached in the middle outdoor pile was 57°C. The middle of the indoor pile heated to a slightly higher temperature of 60°C as the pile was more sheltered from ambient conditions.

8.2.2 Chemical degradation

The main conclusions from the analysis of the chemical data were as follows:

- For the fresh Willow chips, untreated white wood pellets and thermally treated wood pellets, long term stockpile storage did not result in significant chemical degradation
- The dry ash, dry ash free (DAF) volatile content and DAF calorific value graphs showed no clear trends with time in storage. Any changes lie within the normal fuel variability range
- The same observations were made by (Jirjis, 2005), and (First Renewables Ltd., 2002) in their work on the storage of Willow chips
- Storing white wood pellets in an environment where the pellets are exposed to high humidity can result in the pellet's moisture content rising to as high as 13%. Section 6.6 fully describes the major resulting impacts on the pellets' mechanical strength. For the Willow chips, indoor storage with ventilation results in continuous drying of the chips on the surface but the chips in the middle of the pile undergo a lesser extent of drying. To ensure that all the chips are dried, the pile could be turned
- In outdoor storage, the moisture content of the Willow chips is influenced by the weather pattern, especially the rainfall. When rainfall is low, both the surface and middle of the pile dry continuously, the extent of drying being higher for the chips on the surface of the pile. Pile turning would help with achieving uniform drying throughout the pile. Drying is also faster in the summer months due to the higher ambient temperature. In both summer and winter, a period of high rainfall causes the chips to absorb moisture again.
- Storing thermally treated pellets in a covered but ventilated storage environment (open barn in this project) results in a gradual increase in moisture content over time due to exposure to humidity but after 20 months in storage, the moisture content was still < 10%. A step increase in humidity results in a step increase in moisture content.

- In outdoor storage, the moisture content is highly influenced by humidity and rainfall, but the effects of rainfall are more dramatic and significant. In the first six months of Phase 1, the humidity averaged at 75%, but rainfall was low. The outdoor pellets showed high resistance to moisture ingress with the moisture content of the pellets from both the surface and middle of the pile staying below 15%. From the seventh month onwards, both the humidity and rainfall increased and stayed continuously high and the outdoor pellets absorbed a lot of moisture.
- Thermally treated wood pellets decrease in net calorific value (net CV) during storage, the drop being more significant for the pellets stored outdoor as the increase in moisture content is higher
- For the white wood pellets, the drop in net CV is smaller (approximately 5%). These pellets were only stored indoors and the moisture intake was low
- Willow chips in indoor storage undergo gradual drying and increase in net CV. In outdoor storage, the moisture content and therefore net CV are influenced by the weather conditions, particularly rainfall.

8.2.3 Mechanical degradation

Mechanical testing constituted a significant part of this study and was carried out on the untreated white wood pellets and the thermally treated wood pellets throughout the storage period. The main conclusions from the mechanical data analysis were as follows:

- When comparing the fresh pellets at the start of storage, the Phase 1 thermally treated pellets had the highest durability, axial and diametrical compression strengths and shear modulus, with the Phase 2 white wood pellets having the lowest. The moisture content and diameter of the pellets followed the reverse sequence. These differences were to be expected because the pellets had different raw materials,

manufacturing and pelletisation processes and pre and post shipping storage as well as transport and handling.

- This shows that during initial handling and conveying upon delivery at the storage site/power station, the fresh Phase 1 pellets are likely to undergo the least breakage and dust formation, with the fresh Phase 2 white wood pellets having the greatest likelihood to break down to fragments and dust during the same operations
- Even though the fresh Phase 1 thermally treated pellets exhibited higher mechanical strength than the fresh Phase 2 pellets; throughout storage, the outdoor Phase 2 thermally treated pellets exhibited higher resistance to mechanical degradation than the outdoor Phase 1 pellets, especially the pellets on the surface of the piles.
- For both the Phase 1 and Phase 2 outdoor thermally treated pellets, there was a strong correlation between the increase in the moisture content of the pellets and the decrease in mechanical strength. In Phase 1, there was a larger difference in the moisture content of the surface and middle pellets from the outdoor pile. As a result the surface pellets exhibited lower mechanical strength than the middle pellets.
- In Phase 2, the moisture content of the pellets on the surface and middle of the outdoor pile matched more closely, also true for the durability, compression strength and shear modulus
- For the thermally treated wood pellets stored outdoor, both the humidity and rainfall contributed to an increase in the moisture content of the pellets which resulted in pellet swelling and a drop in mechanical strength. However, as expected, high rainfall had the most dramatic effect. While a step increase in humidity took place gradually and over time, high rainfall was more sudden, resulting in a large step change in the moisture content
- The drop in compression (axial and diametrical) strengths and shear modulus of both the indoor and outdoor pellets was larger than the drop in mechanical durability as storage progressed. In the durability test, the pellets are tumbled at high speed and although they experience forces as they rotate around and bounce against each other, the forces are not

continuous and of increasing magnitude. In the compression and three point shear test, a force of increasing magnitude is applied to the pellet continuously until the pellet fractures, providing a value which is checked across multiple pellets in a repeatable manner. Therefore it would be recommended to carry out compression and shear tests in addition to mechanical durability when characterising the mechanical properties of the pellets

- For the Phase 1 thermally treated wood pellets which were stored indoors, the extent of mechanical degradation was low. Therefore long term storage of these pellets in an open barn with covered storage would be a viable option
- The mechanical degradation seen in the indoor Phase 2 white wood pellet pile was severe on both the surface and in the middle of the pile with pellet disintegration starting as early as after one month in storage. This shows that exposure to humidity and changing temperatures (day-night cycle) causes the pellets to weaken. Therefore it would be advisable to store white wood pellets in a fully enclosed environment with no exposure to ambient temperature and humidity

8.2.4 Biological degradation

The main observations from the fungal testing on the fresh and degraded fuels were as follows:

8.2.4.1 Phase 1 Willow chips

- There were nine fungal species on the fresh Willow chips, none of which were pathogenic. The maximum count was in the order 10^5 CFU/g which is to be expected on fresh wood
- After three months in storage, all the fungi types seen on the fresh Willow chips were no longer present. This could be attributed to the heat generation in the piles which led to high temperatures and therefore the elimination of the mesophilic fungi.

- Four new fungi were present in the Willow piles after three months in storage namely *Aspergillus Fumigatus*, *Hypocrea*, *Rhizopus (Oryzae and Microsporus)* and *Trichoderma*.
- After six months in storage, there is still significant presence of *Aspergillus* and *Rhizopus*. The presence of the *Phanerochaete* fungus was also reported

8.2.4.2 Phase 2 Willow chips

- There were fewer fungi on the fresh Phase 2 Willow chips compared to fresh phase 1 chips.
- After three months in storage, all the fungi present on the fresh Phase 2 Willow except *Penicillium* had disappeared because of the heat generation and temperature rise in the Willow piles in the first few weeks in storage
- As for Phase 1, *Aspergillus Fumigatus* was present on the Phase 2 Willow chips after three months in storage. However, the fungus was only seen in the middle of the piles and not on the surface, with the count lower than what was seen in Phase 1
- There was still a significant presence of *Aspergillus* after six months of storage in Phase 2, in the middle of both the outdoor and indoor Willow chip piles
- The surface of the outdoor Willow pile was sustaining the growth *Aureobasidium*, *Cladosporium*, *Penicillium* and *Truncatella* while *Hypocrea*, *Endocymes* and *Penicillium* were found on the surface of the indoor Willow pile
- There was a close relationship between the ambient and pile temperatures and the number and count of fungi with both decreasing when temperatures got low

8.2.4.3 Phase 1 thermally treated wood pellets

- There was no fungal presence on the fresh pellets because of the thermal treatment at elevated temperatures
- As storage progressed, the pellets were exposed to airborne fungi and a few species were reported after three and six months in storage
- *Sporidiobolus*, *Cladosporium* and *Penicillium* were present along with *Aspergillus Fumigatus* and *Rhizopus Microsporus*. The count for all of the fungi was low (maximum 10^4 CFU/g). The low counts of the *Aspergillus* and *Rhizopus* fungi reflect that they were not actively growing on the pellet piles and that they were most likely present through contamination from the Willow chip piles

8.2.4.4 Phase 2 thermally treated wood pellets

- There was no fungal presence on the fresh pellets
- During outdoor storage, the pellets were exposed to airborne fungi and a few species were reported after three and six months in storage
- The count for all of the fungi was low (maximum 10^5 CFU/g) and this reflects that they were not actively growing on the pellet piles

8.2.4.5 Phase 2 untreated white wood pellets

- Two fungi were present on the white wood pellets at the start of the storage trial. The count was low (10^2-10^3 CFU/g). They could have landed on the pellets after production, through transport and storage
- As storage progressed, two more fungi were reported on the pellets but the count remained low

8.3 Recommendations to the energy industry

Based on the findings of this project, the following recommendations can be made on the storage of Willow chips, thermally treated wood pellets and white wood pellets.

8.3.1 Storage of Willow chips

- In both the indoor and outdoor storage of freshly harvested Willow chips, there is a rapid rise in pile temperature during the first few weeks of storage. Therefore continuous pile monitoring would be recommended during the initial period of storage. Also it would be advisable not to store the piles in close proximity to buildings and other structures to prevent damage in the unfortunate event of a spontaneous combustion scenario
- Furthermore, wherever practical, a conical shaped pile with sloped edges is better than a pile with a flat top, because sloped edges encourage flow of rain water down the pile sides to the ground as opposed to directly through the pile. A higher moisture content inside the pile contributes to a higher extent of self heating through fungal growth
- The storage of Willow chips in stockpiles results in fungal activity and the warm moist environments within the piles encourage the growth of the thermophilic fungi. Three thermophilic and pathogenic species (Aspergillus Fumigatus, Rhizopus and Candida) were identified on the Willow chips. Therefore workers should wear suitable respiratory and skin protection when handling stored Willow chips. Further work is needed in this area to better understand the concentration of airborne species, see Section 0
- In dry and warm weather conditions, outdoor storage of Willow chips results in gradual drying of the chips on both the surface and in the middle of the piles, with the extent of drying being larger on the surface. Pile turning would ensure uniform drying throughout the pile

- However significant exposure to rainfall results in a large step increase in moisture content following drying.

- In countries with long periods of low humidity and rainfall, outdoor storage of Willow chips would promote gradual drying and an increase in the net CV of the fuel and pile turning could be performed to promote uniform drying
- In the UK, the weather is not very predictable and there could be unexpected periods of continuously high rainfall. Therefore it is more risky to store Willow chips in outdoor stockpiles
- In the UK, indoor storage (or covered storage) would result in continuous drying of the piles but summer storage combined with pile turning would be advantageous over winter storage in promoting drying of the piles throughout. In this study, indoor storage was carried out in the winter months and drying in the middle of the pile was limited by the cold ambient temperatures.

8.3.2 Storage of thermally treated wood pellets

- Covered storage in an open barn is a viable option as moisture intake rate is low and mechanical integrity of pellets is preserved
- Indoor pile is also very thermally stable (follows ambient temperature) with low fungal activity due to low moisture content within pile
- For outdoor storage of thermally treated wood pellets, exposure to humidity but to a larger extent rainfall, results in moisture intake and a drop in mechanical integrity.

- As for the Willow chips, in countries with long periods of low humidity and rainfall, outdoor storage of thermally treated wood pellets would be viable
- In the UK, the weather is not very predictable and there could be unexpected periods of continuously high rainfall. Therefore it is more risky to store thermally treated wood pellets in outdoor stockpiles

- However, thermally treated wood pellets are more flexible than white wood pellets (Section 8.3.3 below). Exposure to humidity alone does not result in significant pellet degradation and fresh pellets do exhibit resistance to light rainfall. However after a period of heavy rainfall, degradation occurs and the resistance decreases subsequently. The resistance of the fresh pellets to low rainfall does provide flexibility to fuel users as short term outdoor storage during a dry period could be considered and also short exposure of the pellets at ports and on ships and on train wagons is less of an issue than when dealing with white wood pellets

8.3.3 Storage of white wood pellets

- Covered storage in an open barn results in moisture intake upon continuous exposure to ambient humidity, resulting in a decrease in net CV
- An increase in moisture content is totally detrimental to the pellets' mechanical integrity (significant drops in durability and compression and shear strengths)
- Pellets rapidly break down and crumble to dust which would pose an occupational health hazard
- Therefore it would be recommended to store white wood pellets in a totally enclosed environment for e.g totally enclosed warehouse or silo

8.4 Remaining gaps for academic research

- In order to fully appreciate the inhalation and ingestion potential of fungal spores as well as their deposition onto the skin and eyes of workers during the handling of stored biomass, the release mechanism of the spores from the wood fuels into the air needs to be understood

and the resulting concentration of airborne spores when the piles are disturbed. So similar pile storage scenarios could be repeated but including pile disturbances. Both passive (agar plates positioned in piles vicinity) and active (air sampling device) could then be carried out as in the work of (Barontini et al., 2014).

- The most impactful part of such a study would be to translate the counts and fungal concentrations in the air and on workers' skin into guidelines on PPE requirements and also optimal storage for the biomass and this would be a long term thorough study and might need to involve the input of medical professionals and health and safety experts
- Another interesting study would be to store piles of biomass but include pile turning so that the pattern of drying could be understood because in industrial settings, pile turning is a regular practice
- A key environmental consideration when storing biomass outdoor is the leachate potential of the fuel and a valuable study to energy users would be to design and install a leachate collection system so that any run off from outdoor piles could be analysed

9 References

ADAMS, J.D. & FROSTICK, L.E. (2009) Analysis of bacterial activity, biomass and diversity during windrow composting. *Waste management,* 29, 598-605

AL-SAHAWNEH, E.I. (2013) Size effect and strength correction factors for normal weight concrete specimens under uniaxial compression stress. *Contemporary Engineering Sciences,* 6(no.2), 57-68.

ANAHASHI, M. (1990). Characterisation and degradation mechanism of wood components by steam explosion and utilization of exploded wood. *Bulleting of the Wood Research Institute*, 49-117.

Anon, Biofuels and Peat — Fuel Pellets, Swedish Standards Institution, 1998 SS 18 71 20.

ARIAS, B., PEVIDA, C., FERMOSO, J., PLAZA, M. G., RUBIERA, F. & PIS, J. J. (2008) Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing Technology,* 89**,** 169-175.

ARSHADI M. & GREF R. (2005). Emissions of volatile organic compounds from softwood pellets during storage. *Forest products Journal* 55, 132-5.

ARSHADI, M., GREF, R., GELADI, P., DAHLQVIST, S.-A. & LESTANDER, T. R. (2008) The influence of raw material characteristics on the industrial pelletizing process and pellet quality. *Fuel Processing Technology,* 89**,** 1442-1447.

ASAE S269.4 Dec 96, Cubes, pellets and crumbles—definitions and methods for determining density, durability and moisture content

ASABE Standard S269.4, 2007. Cubes, pellets, and crumbles: definitions and methods for determining density, durability, and moisture content. ASAE. St. Joseph, MI.

ASHBY, M.F. & JONES, D.R.H. (2006) Engineering Materials 2 - An introduction to microstructures, processing and design. Butterworth-Heinemann, UK

ASTM Standard D143-09, "Standard test methods for small clear specimens of timber", ASTM International, West Conshohocken, PA, 2009, DOI: 10.1520/D0143-09, www.astm.org.

BARONTINI, M., CROGNALE, S., SCARFONE, A., GALLO, P., GALLUCCI, F., PETRUCCIOLI, M., PESCIAROLI, L. & PARI, L. (2014). Airborne fungi in biofuel wood chip storage sites. *International Biodeterioration and Biodegradation,* 90, 17-22.

BATTISTA JR, J. J., HUGHES, E. E. & TILLMAN, D. A. (2000) Biomass cofiring at Seward Station. *Biomass & bioenergy,* 19**,** 419-427.

BERGMAN, P.C.A & KIEL J.H.A. (2005). Torrefaction for biomass upgrading, Energy Research Centre of the Netherlands. *Publication number ECN-RX 05-180.*

BIAGINI, E., BARONTINI, F. & TOGNOTTI, L. (2006) Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. *Industrial and Engineering Chemistry Research,* 45**,** 4486-4493.

Biomass Energy Centre. Available at http://www.biomassenergycentre.org.uk

Biomass Energy Centre. UK plants cofiring biomass with coal. Available at http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,41175&_dad=portal&_schema=PORTAL

BISWAS, A. K., UMEKI, K., YANG, W. & BLASIAK, W. (2011) Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment. *Fuel Processing Technology,* 92**,** 1849-1854.

BOEHMER, T.K., JONES, T.S., GHOSH, T.S., MCCARNMON, C.S. & VOGT, R.L. (2009) Cluster of presumed organic dust toxic syndrome cases among urban landscape workers-Colorado, 2007. *American Journal of Industrial Medicine*, 52, 534 - 538.

Bomb calorimeter available at http://www.parrinst.com/products/oxygen-bomb- calorimeters/6100-compensated-jacket-calorimeter/

BREEZE, P.A. (2008). Coping with carbon: a near-term strategy to limit carbon dioxide emissions from power stations. *Philosophical Transactions of the Royal Society A* 366, 3891-3900.

BRIDGEMAN, T. G., JONES, J. M., SHIELD, I. & WILLIAMS, P. T. (2008) Torrefaction of reed canary grass, wheat straw and Willow to enhance solid fuel qualities and combustion properties. *Fuel,* 87**,** 844-856.

British Standard DD CEN/TS 15414-2:2010, "Solid recovered fuels – Determination of moisture content using the oven dry method part 2", www.bsigroup.com/standards

BS EN 14774-1:2009	Solid biofuels - Determination of moisture content - Oven dry method. Total moisture: Reference method
BS EN 14774-2:2009	Solid biofuels - Determination of moisture content - Oven dry method. Total moisture: Simplified method
BS EN 15148:2009	Solid biofuels. Determination of the content of volatile matter
BS EN 14775:2009	Solid biofuels. Method for the determination of ash content

BS EN 15210-1:2010 Solid biofuels. Determination of mechanical durability of pellets and briquettes

Campbell Scientific Ltd., available at http://www.campbellsci.co.uk/index.cfm?id=77

CARONE, M. T., PANTALEO, A. & PELLERANO, A. (2011) Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of Olea europaea L. *Biomass and Bioenergy,* 35**,** 402-410.

CARROLL, J. P. & FINNAN, J. (2012) Physical and chemical properties of pellets from energy crops and cereal straws. *Biosystems Engineering,* 112**,** 151-159.

CHEN, W.-H. & KUO, P.-C. (2010) A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy,* 35**,** 2580-2586.

CHP from DECC, CHP from DECC, available at http://chp.decc.gov.uk/cms/fuel-calorific-value/

CIBSE TM26 Hygienic Maintenance of Office Ventilation Ductwork available at http://www.cibse.org/Knowledge/CIBSE-TM-(1)/TM26-Hygienic-Maintenance of-Office-Ventilation-Du

CONRAD, R., KLOSE, M. & NOLL, M. (2009) Funtional and structural response of the methanogenic microbial community in rice field soil to temperature change. *Environmental microbiology,* 11**,** 1844-1853.

Coppice Resources Limited. Available at http://www.coppiceresources.co.uk/

CR10X data logger from Campbell Scientific Ltd., available at http://www.campbellsci.com/cr10x

DWR-205 ELE Environmental Ltd., available

at http://192.107.66.195/meteo_station/Meteo_Sensors-Wind_Speed.pdf

Department of Energy and Climate Change. Available at www.decc.gov.uk

Detailed information on Quanta 600 SEM from TAMU, available at http://microscopy.tamu.edu/instruments/scanning-electron-microscopy/fei-quanta-600-fe-sem.html

Doctor Fungus, available at http://www.doctorfungus.org.uk

Doosan Babcock Energy. Available at www.**doosanpower**systems.com

Drax. Biomass conversion. Available at
http://www.drax.com/biomass/biomass-data/

EDAX, available at http://www.edax.com/

FASINA O.O. & SOKHANSANJ S. (1996). Storage and handling characteristics of Alfalfa pellets. *Powder handling and processing* 8(4), 361-365.

FERRERO, F., MALOW, M. & NOLL, M. (2011). Temperature and gas evolution during large scale outside storage of wood chips. *European Journal of Wood and Wood Products,* 69, 587-595.

FILBAKK, T., JIRJIS, R., NURMI, J. & HIB, O. (2011) The effect of bark content on quality parameters of Scots pine (Pinus sylvestris L.) pellets. *Biomass and Bioenergy,* 35**,** 3342-3349.

FILBAKK, T., SKJEVRAK, G., HIB, O., DIBDIAKOVA, J. & JIRJIS, R. (2011) The influence of storage and drying methods for Scots pine raw material on mechanical pellet properties and production parameters. *Fuel Processing Technology,* 92**,** 871-878.

First Renewables Limited, (2002). Identification and characterisation of factors affecting losses in the large scale, non ventilated bulk storage of wood chips and development of best storage practices. FES B/W2/00716/REP, DTI/Pub URN 02/1535.

FULLER, W.S. (1985) Chip pile storage – a review of practices to avoid deterioration and economic losses. *Tappi Journal, The Journal of the Technical Association of the Pulp and Paper Industry,* 68 (8).

EN 15103:2009. Solid biofuels – determination of bulk density

EN 15210–1:2009. Solid biofuels – determination of mechanical durability of pellets and briquettes. Pellets.

First Renewables Ltd, Identification and Characterisation of factors affecting losses in the large-scale, non-ventilated bulk storage of wood chips and development of best storage practices, FES B/W2/00716/REP&DTI/Pub URN 02/1535, available at www.bioenergycemtre.org.uk

FRANKE M. & REY A. Pelleting quality. *World Grain May 2006,* 78–9.

FRIDKIN, S.K. & JARVIS, W.R. (1996) Epidemiology of nosocomial fungal infections. *Clinical Microbiology Reviews,* 9, 499-511.

GAUTHIER, S., GRASS, H., LORY, M., KRAMER, T., THALI, M. & BARTSCH, C. (2012) Lethal carbon monoxide poisoning in wood pellet storerooms - Two cases and a review of the literature. *Annals of Occupational Hygiene,* 56 (no.7), 755-763.

GELBRICH, J., MAI, C. & MILITZ, H. (2008) Chemical changes in wood degraded by bacteria. *International Biodeterioration & Biodegradation,* 61**,** 24-32.

GIGLER, J. K., VAN LOON, W. K. P., VAN DEN BERG, J. V., SONNEVELD, C. & MEERDINK, G. (2000a) Natural wind drying of Willow stems. *Biomass and Bioenergy,* 19**,** 153-163.

GIGLER, J. K., VAN LOON, W. K. P., VISSERS, M. M. & BOT, G. P. A. (2000b) Forced convective drying of Willow chips. *Biomass and Bioenergy,* 19**,** 259-270.

GIL, M. V., OULEGO, P., CASAL, M. D., PEVIDA, C., PIS, J. J. & RUBIERA, F. (2010) Mechanical durability and combustion characteristics of pellets from biomass blends. *Bioresource Technology,* 101**,** 8859-8867.

GLADDING, T. (2014) Biomass sampling approaches: Research updates and current findings. Bioaerosols Conference, Solihull, UK

GRAHAM, S., EASTWICK, C.N., SNAPE, C.E. & QUICK, W. (2012) Degradation of biomass fuels during artificial storage in a laboratory environment. *International Journal of Low Carbon Technologies*, 7(2): 113-9.

GRANSTROM K.M. (2010). Emissions of hexanal and terpenes during storage of solid wood fuels. *Forest Products Journal* 60(1), 27-32.

GRISOLI, P., RODOLFI, M., VILLANI, S., GRIGNANI, E., COTTICA, D., BERRI, A. , MARIA PICCO, A. & DACARRO, C. (2009) Assessment of airborne microorganism contamination in an industrial area characterised by an open composting facility and a wastewater treatment plant. *Environmental Research,* 109, 135-142.

JAMASB, T. NUTTALL, W.J. & POLLITT, M.G. (2006). Future electricity technologies and systems. *Cambridge University Press*.

JENKINS, B.M., BAXTER, L.L., MILES JR., T.R. & MILES, T.R. (1998) Combustion properties of biomass. *Fuel Processing Technology,* 54, 17-46.

JIRJIS, R. (1995) Storage and drying of wood fuel. *Biomass and Bioenergy,* 9**,** 181-190.

JIRJIS, R. (2005) Effects of particle size and pile height on storage and fuel quality of comminuted Salix viminalis. *Biomass and Bioenergy,* 28**,** 193-201.

JOHANSSON, L. S., LECKNER, B., GUSTAVSSON, L., COOPER, D., TULLIN, C. & POTTER, A. (2004) Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. *Atmospheric Environment,* 38**,** 4183-4195.

KALIYAN, N. & VANCE MOREY, R. (2009) Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy,* 33**,** 337-359.

KUANG, X., SHANKAR, T. J., BI, X. T., LIM, C. J., SOKHANSANJ, S. & MELIN, S. (2009a) Rate and peak concentrations of off-gas emissions in stored wood pellets - Sensitivities to temperature, relative humidity, and headspace volume. *Annals of Occupational Hygiene,* 53**,** 789-796.

KUANG, X., SHANKAR, T. J., BI, X. T., SOKHANSANJ, S., JIM LIM, C. & MELIN, S. (2008) Characterization and kinetics study of off-gas emissions from stored wood pellets. *Annals of Occupational Hygiene,* 52**,** 675-683.

KUANG, X., SHANKAR, T. J., SOKHANSANJ, S., LIM, C. J., BI, X. T. & MELIN, S. (2009b) Effects of Headspace and Oxygen Level on Off-gas Emissions from Wood Pellets in Storage. *Ann Occup Hyg,* 53**,** 807-813.

LARSSON, S. H., LESTANDER, T. A., CROMPTON, D., MELIN, S. & SOKHANSANJ, S. (2012) Temperature patterns in large scale wood pellet silo storage. *Applied Energy,* 92**,** 322-327.

LEHTIKANGAS, P. (2000) Storage effects on pelletised sawdust, logging residues and bark. *Biomass and Bioenergy,* 19**,** 287-293.

LESTER, E., GONG, M. & THOMPSON, A. (2007) A method for source approportionment in biomass/coal blends using thermogravimetric analysis, J Anal Appl Pyrolysis, 80: 111–7.

LOPEZ E., VILLEN D. et al. Storage and natural drying techniques as a way to adapt woody feedstocks to cofiring requirements in Mediterranean countries.

MANI, S., TABIL, L. G. & SOKHANSANJ, S. (2004) Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass and Bioenergy,* 27**,** 339-352.

MANI, S., TABIL, L. G. & SOKHANSANJ, S. (2006) Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. *Biomass and Bioenergy,* 30**,** 648-654.

MATTSSON, J. E. & KOFMAN, P. D. (2003) Influence of particle size and moisture content on tendency to bridge in biofuels made from Willow shoots. *Biomass and Bioenergy,* 24**,** 429-435.

MCCORMICK, A., LOEFLER, J. & EBEL, F. (2010) Aspergillus Fumigatus: contours of an opportunistic human pathogen. *Cellular Microbiology,* 12, 1535-1543.

MCILVEEN-WRIGHT, D. R., HUANG, Y., REZVANI, S. & WANG, Y. (2006) A technical and environmental analysis of co-combustion of coal and biomass in fluidised bed technologies. *6th European Meeting on Coal Research and Its Applications.* Canterbury, ENGLAND.

MITCHELL, C. P., STEVENS, E. A. & WATTERS, M. P. (1999) Short-rotation forestry - operations, productivity and costs based on experience gained in the UK. *Forest Ecology and Management,* 121**,** 123-136.

Mologic Ltd. UK, available at www.mologic.co.uk

MONTI, A., FAZIO, S. & VENTURI, G. (2009) The discrepancy between plot and field yields: Harvest and storage losses of switchgrass. *Biomass and Bioenergy,* 33**,** 841-847.

NEGRO, M. J., MANZANARES, P., OLIVA, J. M., BALLESTEROS, I. & BALLESTEROS, M. (2003) Changes in various physical/chemical parameters of Pinus pinaster wood after steam explosion pretreatment. *Biomass and Bioenergy,* 25**,** 301-308.

NIELSEN, N. P. K., NRGAARD, L., STROBEL, B. W. & FELBY, C. (2009) Effect of storage on extractives from particle surfaces of softwood and hardwood raw materials for wood pellets

NIELSEN N. P. K. , HOLM J. K. & FELBY C. (2009) Effect of fiber orientation on compression and frictional properties of sawdust particles in fuel pellet production. *Energy Fuels* 23, 32.

NILLSSON, T. (1965) Mikroorganismer I flisstackar. *Svensk Papperstidning*, 68(15), 495-499.

NIXON P. & BULLARD M. (2003) Optimisation of Miscanthus harvesting and storage strategies. *Energy Power Resources Ltd.* B/CR/00745/00/00 URN 03/1633.

Einfluss der Lagerung von Nadel- und laubholzmaterial zur Herstellung von Holzpellets auf die extraktstoffe an den partikeloberflachen. *European Journal of Wood and Wood Products,* 67**,** 19-26.

NOLAN, A., MC DONNELL, K., MC SIURTAIN, M., CARROLL, J. P., FINNAN, J. & RICE, B. (2009) Conservation of Miscanthus in bale form. *Biosystems Engineering,* 104**,** 345-352.

NOLL, M., KLOSE, M. & CONRAD, R. (2010A) Effect of temperature change on the composition of the bacterial and archaeal community potentially involved in the turnover of acetate and propionate in methanogenic rice field soil. *FEMS Microbiology Ecology,* 73, 215-225

NOLL, M. & JIRJIS, R. (2012) Microbial communities in large-scale wood piles and their effects on wood quality and the environment. *Applied Microbiology and Biotechnology,* 95, 551-563.

NOVINSCAK, A., DECOSTE, N.J., SURETTE. C. & FILION, M. (2009) Characterisation of bacterial and fungal communities in composted biosolids over a 2 year period using denaturing gradient gel electrophoresis. *Canadian Journal of Microbiology*, 55, 375-387

O'GORMAN, C.M. (2011) Airborne Aspergillus Fumigatus conidia: a risk factor for Aspergilliosis. *Fungal biology reviews,* 25, 151-157.

O¨ NORM M 7135, Pre*X*linge aus naturbelassenem Holz und naturbelassender Rinde—Pellets und Briketts -Anforderungen und Pru¨ fbestimmungen

OBERNBERGER, I. & THEK, G. (2004) Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass and Bioenergy,* 27**,** 653-669.

OPPLIGER, A., HILFIKER, S. & DUC, T.V. (2005) Influence of seasons and sampling strategy on assessment of bioaerosols in sewage treatment plants in Switzerland. *The Annals of Occupational Hygiene*, 49, 393-400

PARIKH, J., CHANNIWALA, S. A. & GHOSAL, G. K. (2005) A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel,* 84**,** 487-494.

PETTERSSON, M. & NORDFJELL, T. Fuel quality changes during seasonal storage of compacted logging residues and young trees. *Biomass and Bioenergy,* 31**,** 782-792.

Power Technology. Power plants using biomass. Available at http://www.power-technology.com/features/featurepower-from-waste---the-worlds-biggest-biomass-power-plants-4205990/

PRINS, M. J., PTASINSKI, K. J. & JANSSEN, F. J. J. G. (2006a) Torrefaction of wood: Part 1. Weight loss kinetics. *Journal of Analytical and Applied Pyrolysis,* 77**,** 28-34.

PRINS, M. J., PTASINSKI, K. J. & JANSSEN, F. J. J. G. (2006b) Torrefaction of wood: Part 2. Analysis of products. *Journal of Analytical and Applied Pyrolysis,* 77**,** 35-40.

Quanta Scanning Electron Microscope by FEI, available at http://www.fei.com/products/sem/quanta-sem/

RAMOS, L. P. (2003) The chemistry involved in the steam treatment of lignocellulosic materials. *QuÃ-mica Nova,* 26**,** 863-871.

REBHAN, E. (2009). Challenges for future energy usage. *European Physical Journal- Special Topics,* 176, 53-80.

Retsch cutting mills available at http://www.retsch.com/products/milling/cutting-mills/

Retsch rotor beater mills available at http://www.retsch.com/products/milling/rotor-mills/sr-200/

REUSS, R. & PRATT, S. (2000) Accumulation of carbon monoxide and carbon dioxide in stored canola. *Journal of stored products research,* 37**,** 23-34.

ROSE, E., GRAHAM, S. & EASTWICK, C.N. (2012) Investigating the effects of temperature, humidity and precipitation on the mechanical and chemical properties of thermally treated hardwood pellets. MEng Mechanical Engineering individual research paper. The University of Nottingham UK.

RUPAR, K. & SANATI, M. (2005) The release of terpenes during storage of biomass. *Biomass and Bioenergy,* 28**,** 29-34.

SS 18 71 71:1. 1984. Solids-Determination of ash content. Swedish Standards Institution. Stockholm:SIS

SAMUELSSON, R., LARSSON, S. H., THYREL, M. & LESTANDER, T. A. (2012) Moisture content and storage time influence the binding mechanisms in biofuel wood pellets. *Applied Energy,* 99**,** 109-115.

SAMUELSSON, R., THYREL, M., SJOSTROM, M. & LESTANDER, T. A. (2009) Effect of biomaterial characteristics on pelletizing properties and biofuel pellet quality. *Fuel Processing Technology,* 90**,** 1129-1134.

SANDERSON, M. A., EGG, R. P. & WISELOGEL, A. E. (1997) Biomass losses during harvest and storage of switchgrass. *Biomass and Bioenergy,* 12**,** 107-114.

SCHLUNSSEN, V., MADSEN, A. M., SKOV, S. & SIGSGAARD, T. (2004) Does the use of biofuels affect respiratory health among male Danish energy plant workers? *Occup Environ Med,* 68**,** 467-473.

SCHOLZ, V., ILDER, C., DARIES, W. & EGERT, J. (2005) Schimmelpilzentwicklung und Verluste bei der Lagerung von Holzhackschnitzeln. *Holz Roh Werkstoff,* 63, 449-455

SDT Q-600 TGA from Thermal Analysis Instruments. Available at http://www.tainstruments.com/

SHANMUKHARADHYA, K.S. & SUDHAKAR, K.G. (2006) Effect of fuel moisture on combustion in a bagasse-fired furnace. *Journal of Energy Resources Technology,* 129(3), 248-253.

SHENG, C. & AZEVEDO, J. L. T. (2005) Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass and Bioenergy,* 28**,** 499-507.

SHINNERS, K. J. & BINVERSIE, B. N. (2004) Harvest and storage of wet corn stover biomass. Ottawa, ON, Canada, American Society of Agricultural and Biological Engineers.

SHINNERS, K. J., BINVERSIE, B. N., MUCK, R. E. & WEIMER, P. J. (2007) Comparison of wet and dry corn stover harvest and storage. *Biomass and Bioenergy,* 31**,** 211-221.

STELTE, W., CLEMONS, C., HOLM, J. K., SANADI, A. R., AHRENFELDT, J., SHANG, L. & HENRIKSEN, U. B. (2011) Pelletizing properties of torrefied spruce. *Biomass and Bioenergy,* 35**,** 4690-4698.

STELTE, W., HOLM, J. K., SANADI, A. R., BARSBERG, S., AHRENFELDT, J. & HENRIKSEN, U. B. (2011) Fuel pellets from biomass: The importance of the pelletizing pressure and its dependency on the processing conditions. *Fuel,* 90**,** 3285-3290.

STELTE, W., HOLM, J. K., SANADI, A. R., BARSBERG, S., AHRENFELDT, J. & HENRIKSEN, U. B. (2011) A study of bonding and failure mechanisms in fuel pellets from different biomass resources. *Biomass and Bioenergy*, 35**,** 910-918.

STENBERG, K., TENGBORG, C., GALBE, M. & ZACCHI, G. (1998) Optimisation of steam pretreatment of SO2-impregnated mixed softwoods for ethanol production. *Journal of Chemical Technology & Biotechnology*, 71**,** 299-308.

STENSENG, M., JENSEN, A. & DAM-JOHANSEN, K. (2001) Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry. J Anal Applied Pyrolysis, 58–59: 65–80.

SULTANA, A. & KUMAR, A. (2012) Ranking of biomass pellets by integration of economic, environmental and technical factors. *Biomass and Bioenergy*, 39**,** 344-355.

SVEDBERG, U. R. A., HOGBERG, H.-E., HOGBERG, J. & GALLE, B. (2004) Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic health hazard. *Annals of Occupational Hygiene*, 48**,** 339-349.

SWAN, J.R.M., KELSEY, A., CROOK, B. & GILBERT, E.J. (2003) Occupational and Environmental Exposure to Bioaerosols from Composts and Potential Health Effects – a Critical Review of Published Data. Sudbury, UK: Health & Safety Executive. At: www.hse.gov.uk/research/rrpdf/rr130.pdf

TC Direct Ltd., available at www.tcdirect.co.uk/deptprod.asp?deptid=140/7

TABIL JR L. G. (1996) Binding and pelleting characteristics of alfalfa. Ph.D. dissertation. Saskatoon, Saskatchewan, CA: Department of Agricultural and Bioresource Engineering, University of Saskatchewan; 1996.

TEMMERMAN, M., RABIER, F., JENSEN, P. D., HARTMANN, H. & BOHM, T. (2006) Comparative study of durability test methods for pellets and briquettes. *Biomass and Bioenergy*, 30**,** 964-972.

THEERARATTANANOON, K., XU, F., WILSON, J., BALLARD, R., MCKINNEY, L., STAGGENBORG, S., VADLANI, P., PEI, Z. J. & WANG, D. (2011) Physical properties of pellets made from sorghum stalk, corn stover, wheat straw, and big bluestem. *Industrial Crops and Products*, 33**,** 325-332.

Thermal Analysis Instruments. Available at www.tainst.com

THOMAS M. & VAN DER POEL A. F. B. (1996) Physical quality of pelleted animal feed. 1. Criteria for pellet quality. *Animal Feed Science and Technology* 1996, 61, 89–112.

TUMULURU, J. S., KUANG, X., SOKHANSANJ, S., LIM, J., BI, T., MANI, S. & MELIN, S. (2007) Studies on off-gassing During storage of wood pellets. Minneapolis, MN, United states, American Society of Agricultural and Biological Engineers.

TUMULURU, J. S., KUANG, X., SOKHANSANJ, S., LIM, J., BI, T. & MELIN, S. A. (2008) Effect of storage temperature on off-gassing and physical properties of wood pellets. Providence, RI, United states, American Society of Agricultural and Biological Engineers.

UNI. UNI CEN/TS 15210-1:2006. Solid biofuels. Methods for the determination of mechanical durability of pellets and briquettes. Part 1: pellets. Milan, Italy: UNI; 2006.

UK Met Office, Available at http://www.metoffice.gov.uk/weather/uk/em/waddington_latest_weather.html

VANE C.H., DRAGE T.C. & SNAPE C.E. (2006). Bark Decay By The White-Rot Fungus Lentinula Edodes: Polysaccharide Loss, Lignin Resistance And The Unmasking Of Suberin. *International Biodeterioration & Biodegradation* 57(1), 14-23.

VANE C. H., DRAGE T. C., SNAPE C. E., STEPHENSON, M. H. and FOSTER, C. (2005). Decay of cultivated apricot wood (Prunus armeniaca) by the ascomycete Hypocrea sulphurea, using solid state C-13 NMR and off-line TMAH thermochemolysis with GC-MS: International Biodeterioration & Biodegradation. *International Biodeterioration & Biodegradation* 55(3), 175-185.

WALDRON, D.J. (2007). Options for co-firing of biomass and coal. *Alstom Annual Conference on Asset Optimisation.*

World Coal Institute Ecoal Resources, issue March 2010. Available at http://www.worldcoal.org/resources/ecoal/ecoal-current-issue/co-firing-coal-biomass

WU, M. R., SCHOTT, D. L. & LODEWIJKS, G. (2011) Physical properties of solid biomass. *Biomass and Bioenergy,* 35**,** 2093-2105.

YAZDANPANAH, F., SOKHANSANJ, S., LIM, J., LAU, A., BI, X., LAM, P.K. & MELIN, S. (2013) Potential for flammability of gases emitted from stored wood pellets. *The Canadian Journal of Chemical Engineering,* 9999

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Appendix A

Methodology Chapter

This section provides more detailed information on some of the tests described in Chapter 3

A.1. SEM sample preparation

A.1.1. Epoxy setting

The first stage of sample preparation involves setting the sample into an epoxy resin in a sample mould. However because biomass is a relatively light material, it tends to float in the resin. Therefore the first step is to position a sample at the right orientation into a mould, so that it lies flat at the base of the mould. A small amount of epoxy resin/epoxy hardener mixture is then poured into the mould, to just cover the base. This is allowed to set for a minimum of 8 hours, by which time the sample would be glued to the bottom of the mould. More resin/hardener mixture is then poured into the mould until the sample is completely covered (approximately two thirds of the sample mould). The mixture is allowed to set for 24 hours.

A.1.2. Grinding and polishing

After allowing the epoxy resin to set for 24 hours, the sample is taken out of the mould using specialist equipment. A uniquely allocated sample number is engraved onto each sample before a series of grinding and polishing steps are carried out. A 600 MD piano diamond plate is first used to grind the samples until they cut through the resin. This is followed by a couple of minutes on a 1200 MD Piano diamond plate. The next step involves a 2400 (grit size of SiC on paper) paper followed by a 4000 paper. In each of the above stages, IPA solvent is used as a lubricant. The last two steps involve final polishing, first using a 3 micron diamond suspension on an MD Dac plate followed by a 1 micron diamond suspension on an MD Dur plate.

After the grinding and polishing stages, samples are washed and dried. Carbon coating of the sample is then carried out by the laboratory technician.

A.1.3. Microscopy

After carbon coating, the samples were all mounted on sample holders into the SEM. A high vacuum mode was used to carry out the microscopy.

A.2. Thermogravimetric analysis

Before any test is carried out, the following steps were necessary

- Ensure the required gases (in this case air and nitrogen) are connected to the instrument and check which is gas 1 and gas 2 as these would need to be entered in programme
- Enter test name and sample name in programme
- Select file name for data file and specify where it will be stored
- Write a procedure for the test and save it in procedures folder
- Load the procedure
- Open furnace
- Move safety tray across (The tray always needs to be positioned under the crucible when it is being moved)
- Remove crucible from beam
- Close furnace to minimise air ingress
- Clean crucible with water and dry
- Burn off any residual samples to ensure crucible is totally clean
- Open furnace and carefully position crucible on holder on horizontal beam
- Ensure reference crucible is also in place
- Close furnace
- Tare crucible so that the reference weight and sample weight are the same
- Open furnace and carefully remove crucible. Fill it with up to 5mg (weight can be read on screen) of sample using a spatula
- Position crucible carefully on sample beam. If any sample spills, move tray to the front (away from crucible area) and clean
- Close furnace
- Check everything that has been entered on programme is correct

- Start the run
- Once the run starts, the live screen will come up showing weight/weight % change with time/temperature
- The screen will also show the ‘estimated time left’
- At the end of the run, enter details for the next sample into programme and repeat the above steps

Appendix B - Chemical degradation chapter graphs

B.1 Dry ash, DAF volatile content and DAF CV

B.1.1. Phase 1 Willow chips

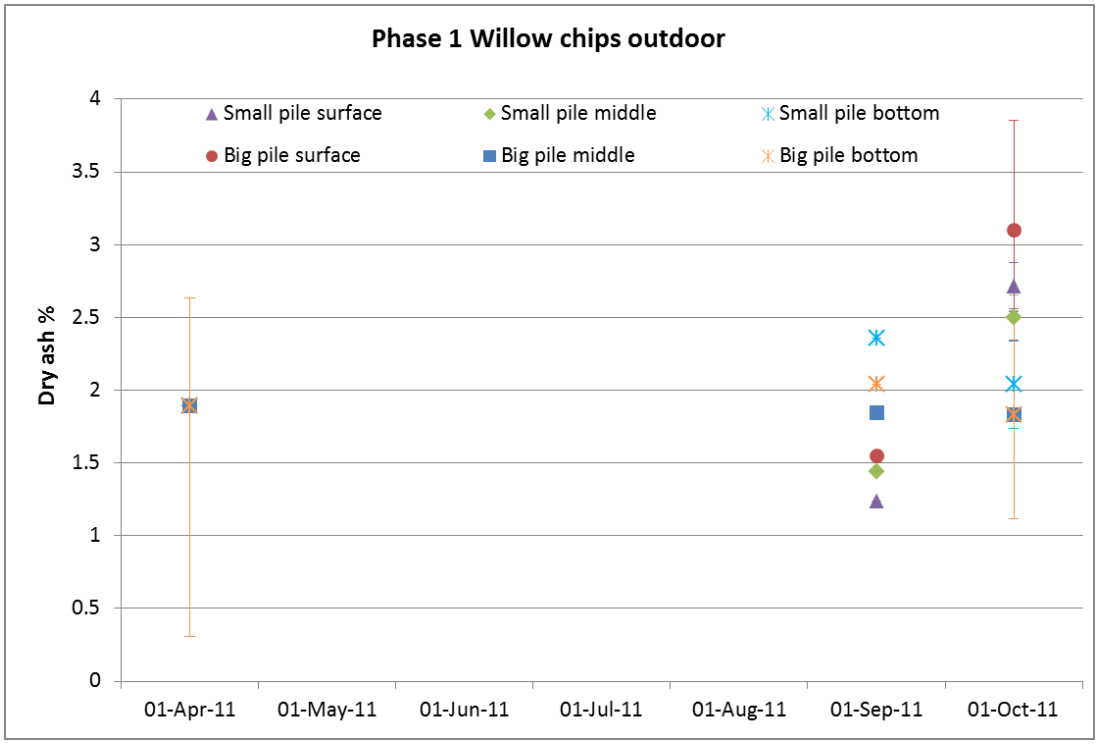

Figure B1

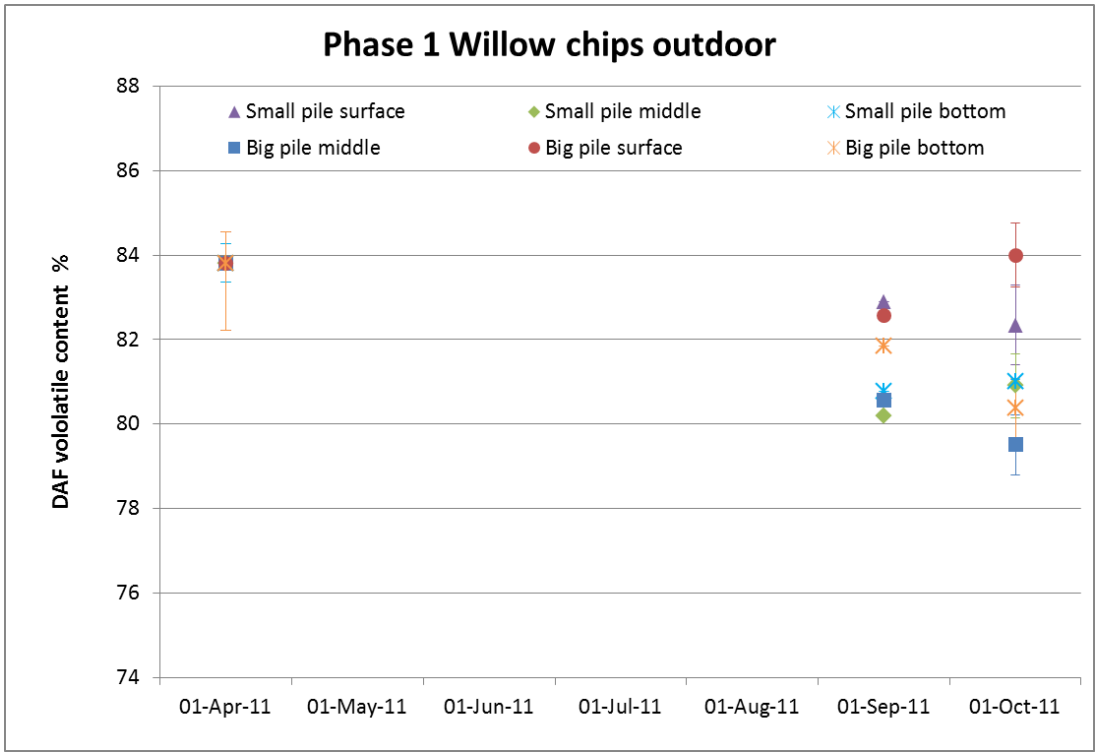

Figure B2

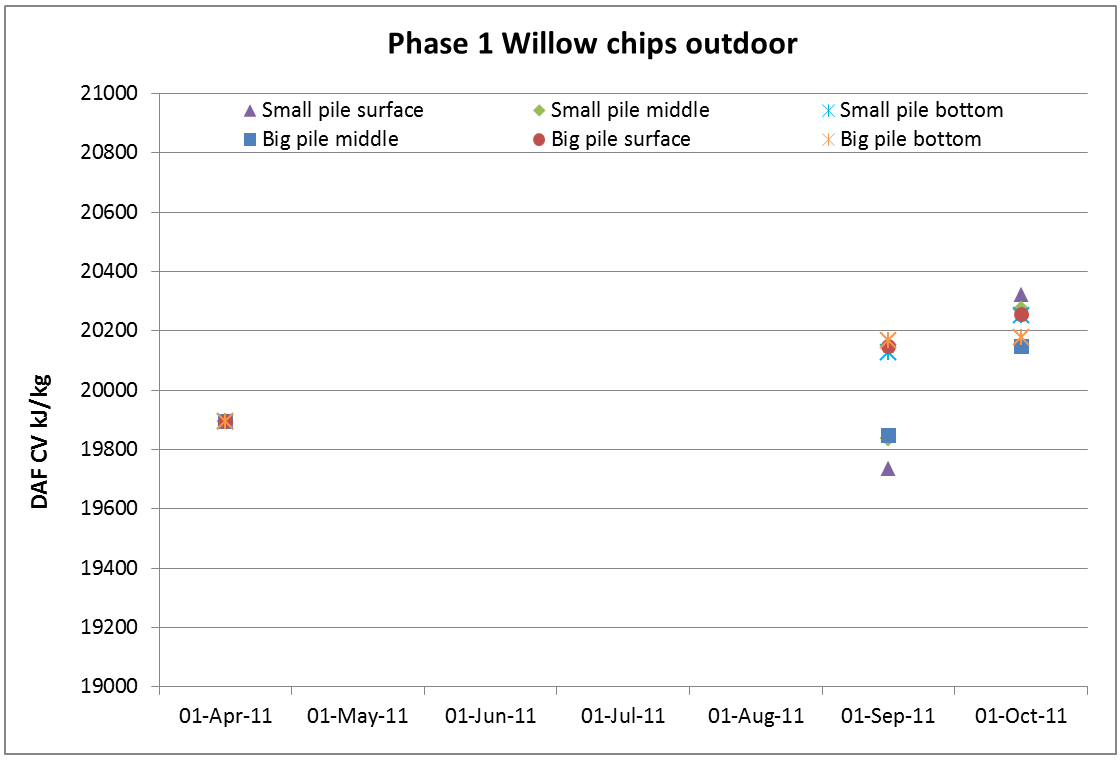

Figure B3

B.1.2. Phase 2 thermally treated wood pellets

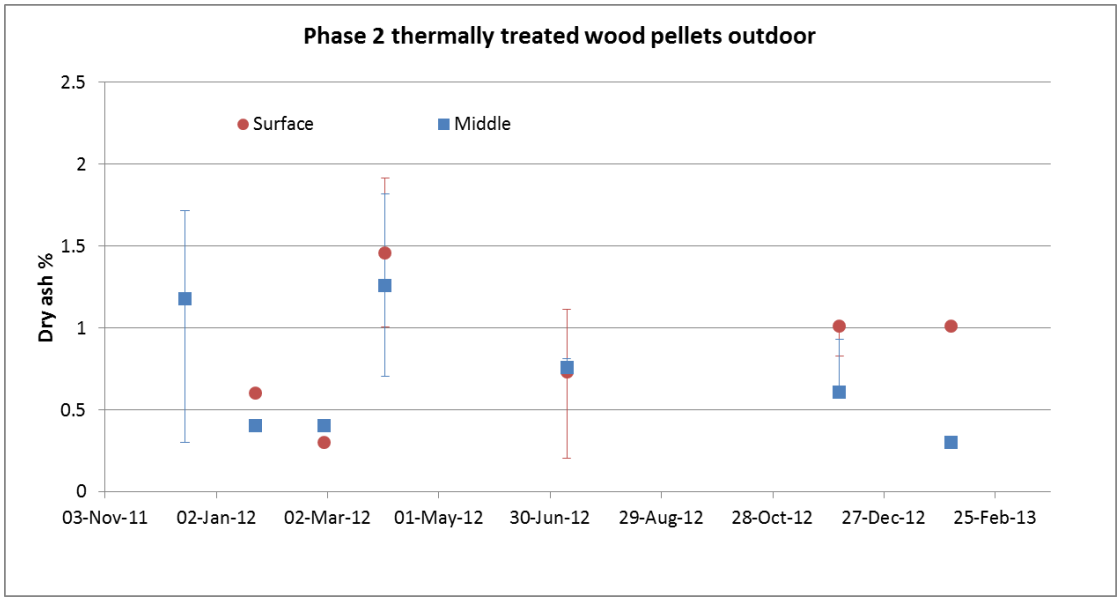

Figure B4

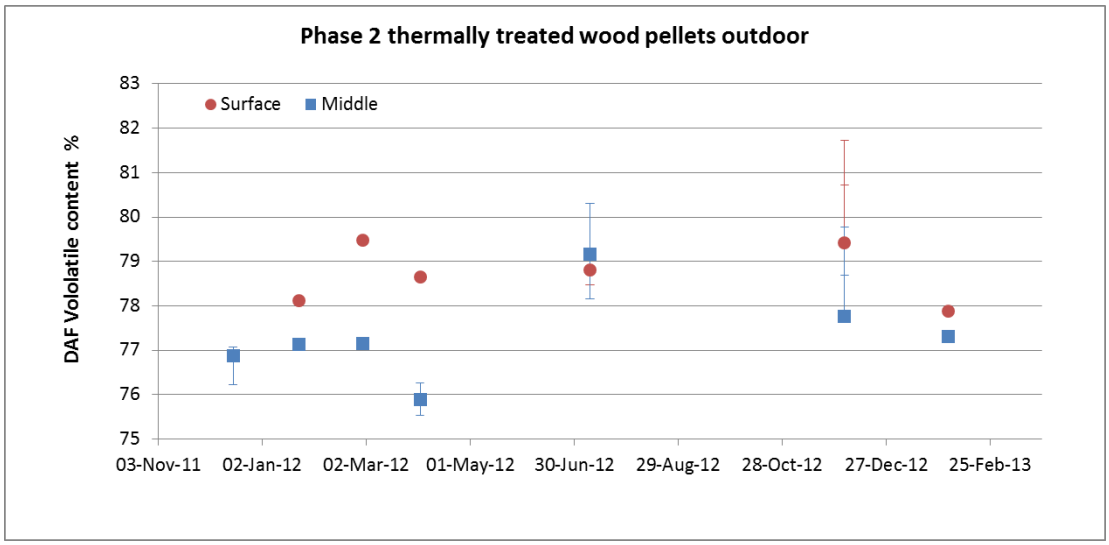

Figure B5

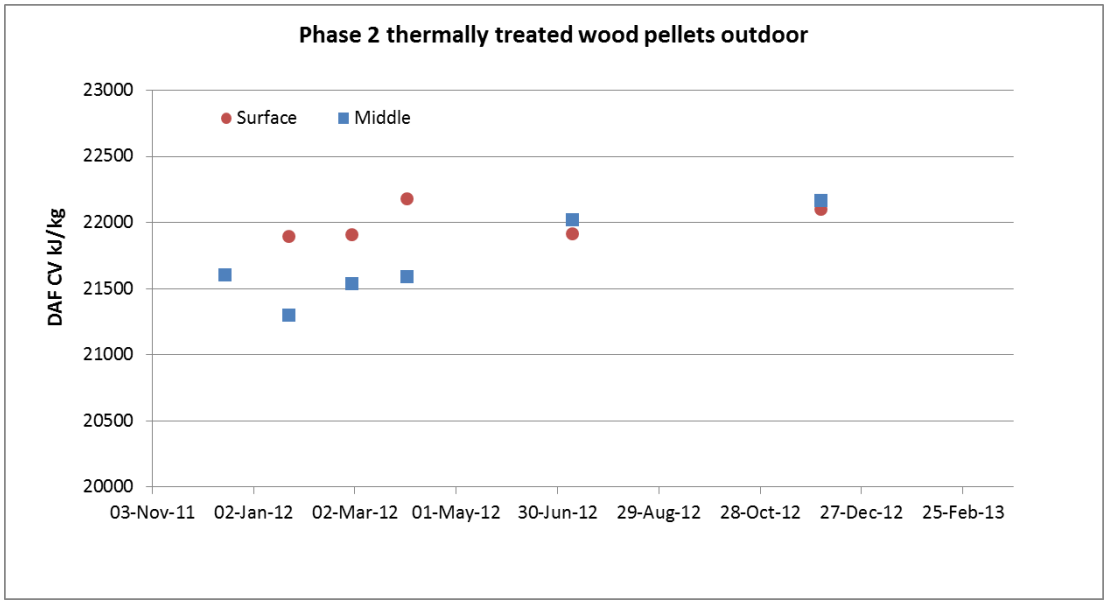

Figure B6

B.1.3. Phase 2 white wood pellets

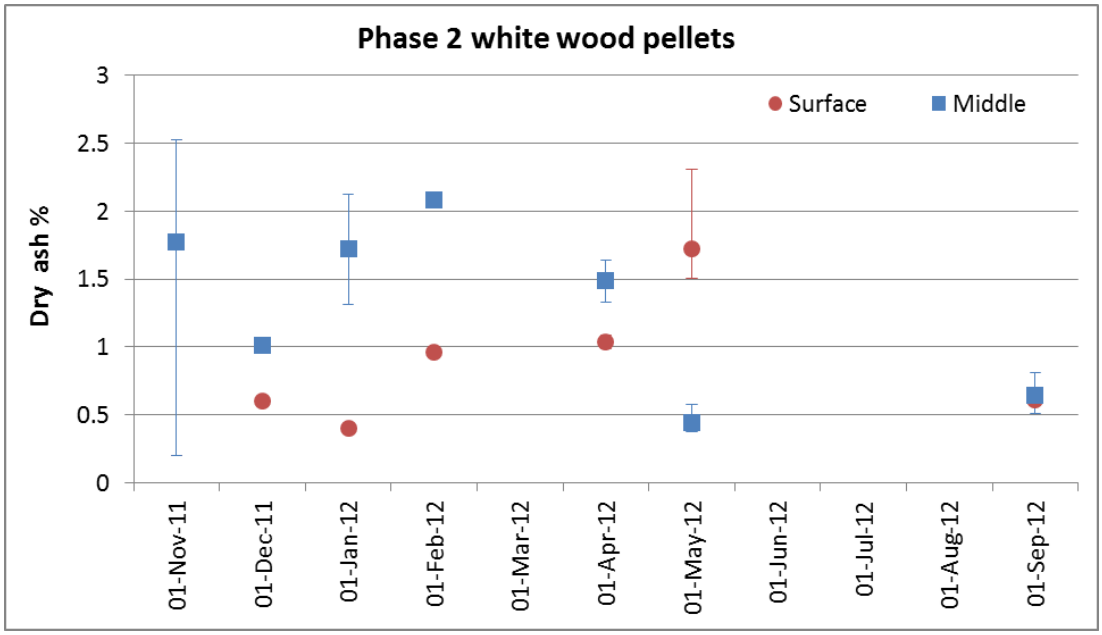

Figure B7

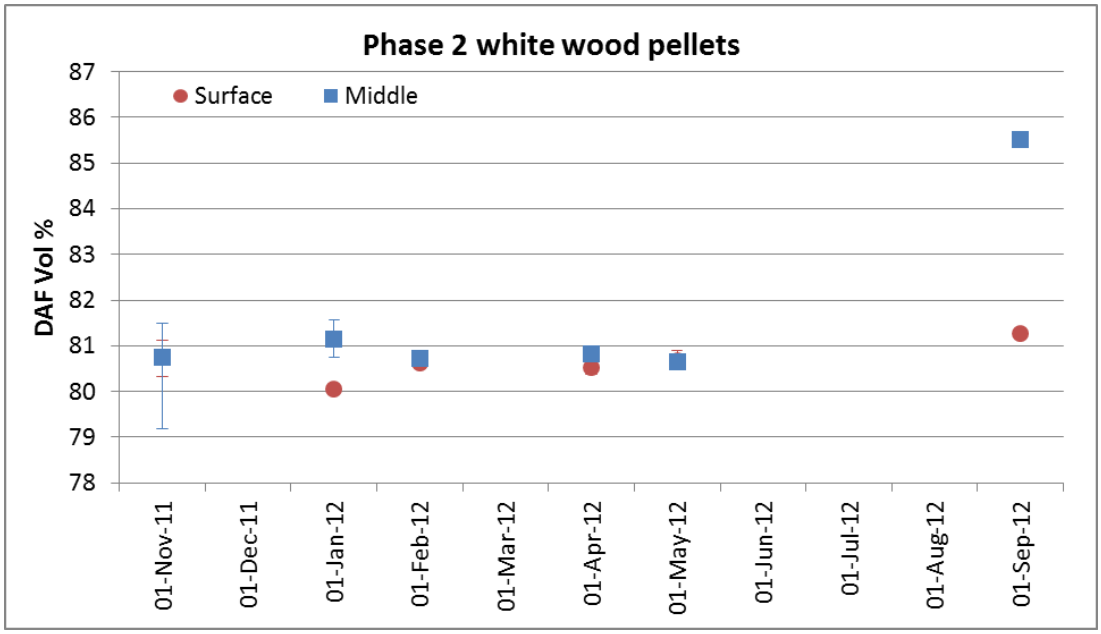

Figure B8

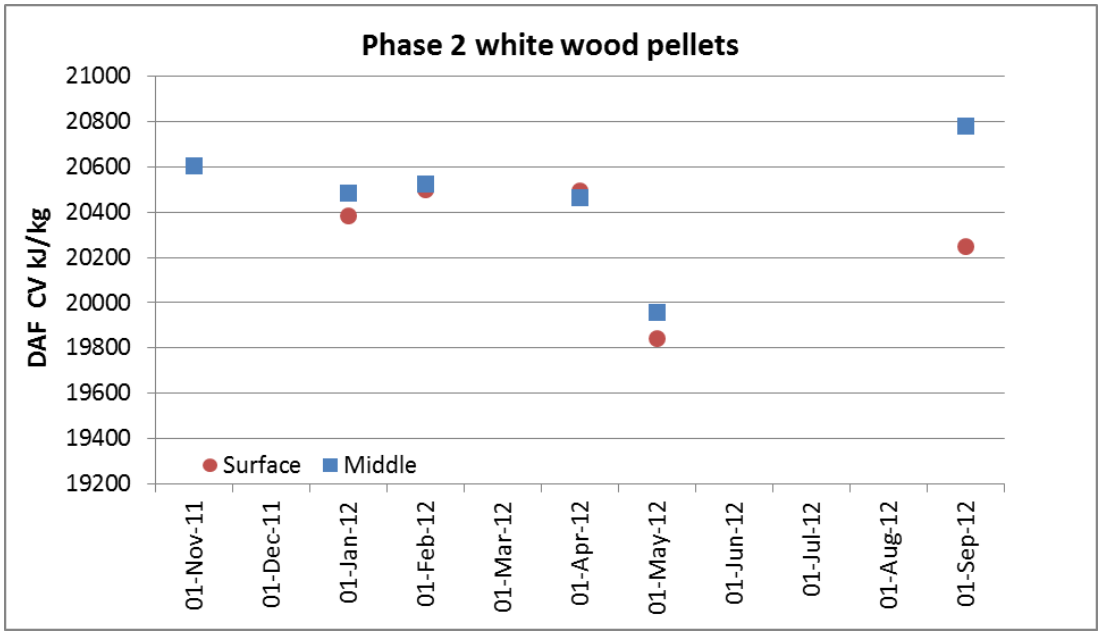

Figure B9

B.2. Free moisture content of fuels alongside weather parameter

B.2.1. Phase 1 Willow chips

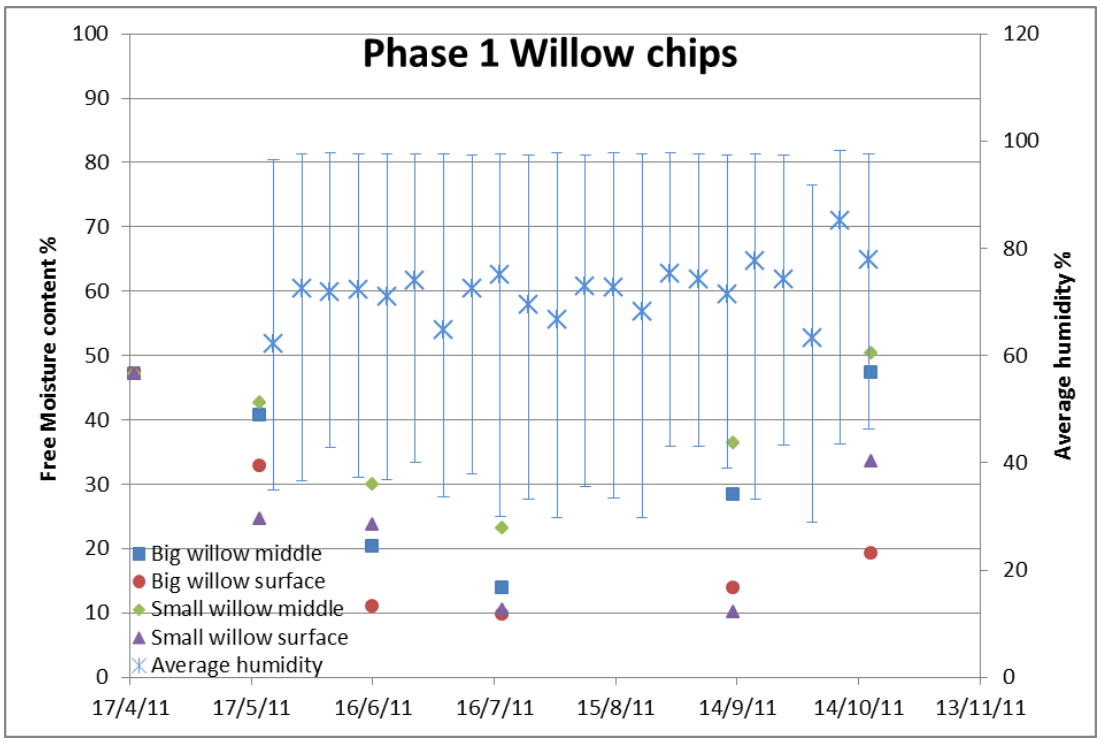

Figure B10

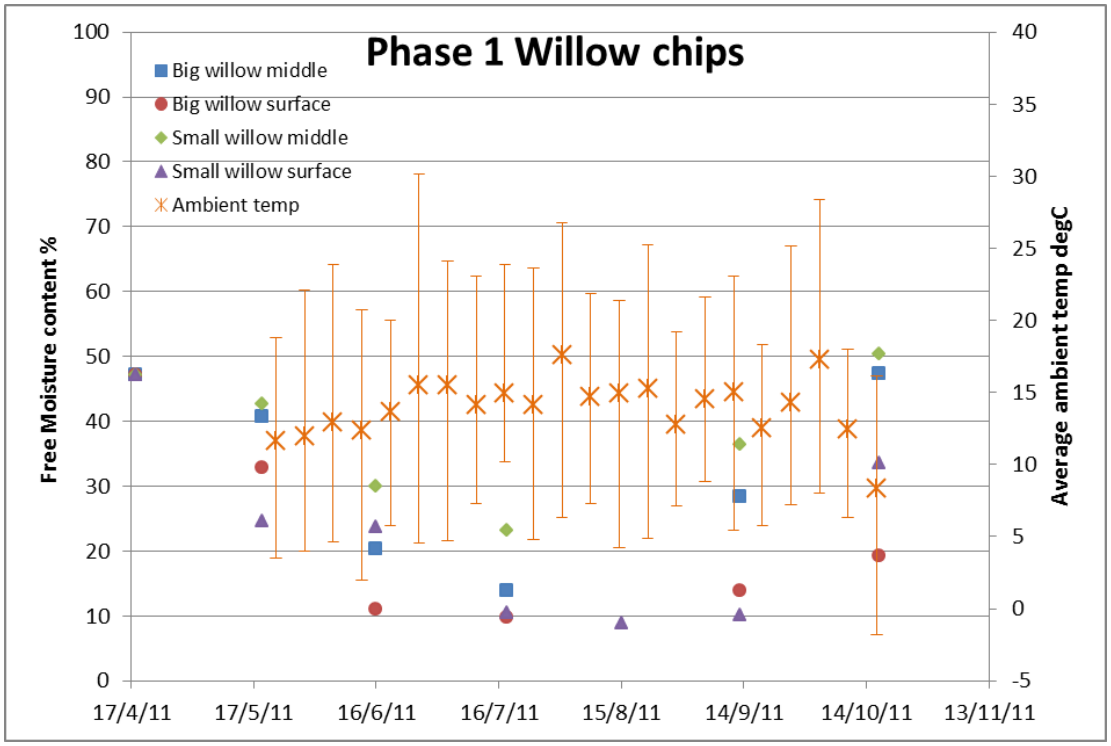

Figure B11

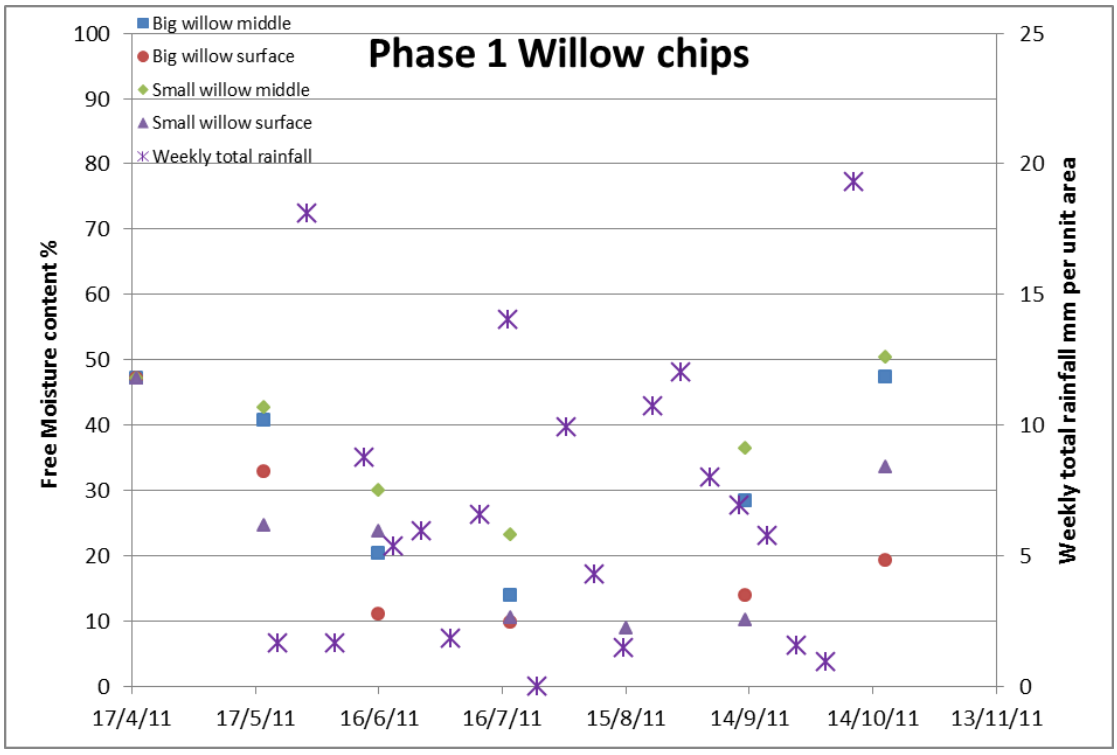

Figure B12

B.2.2. Phase 1 thermally treated wood pellets

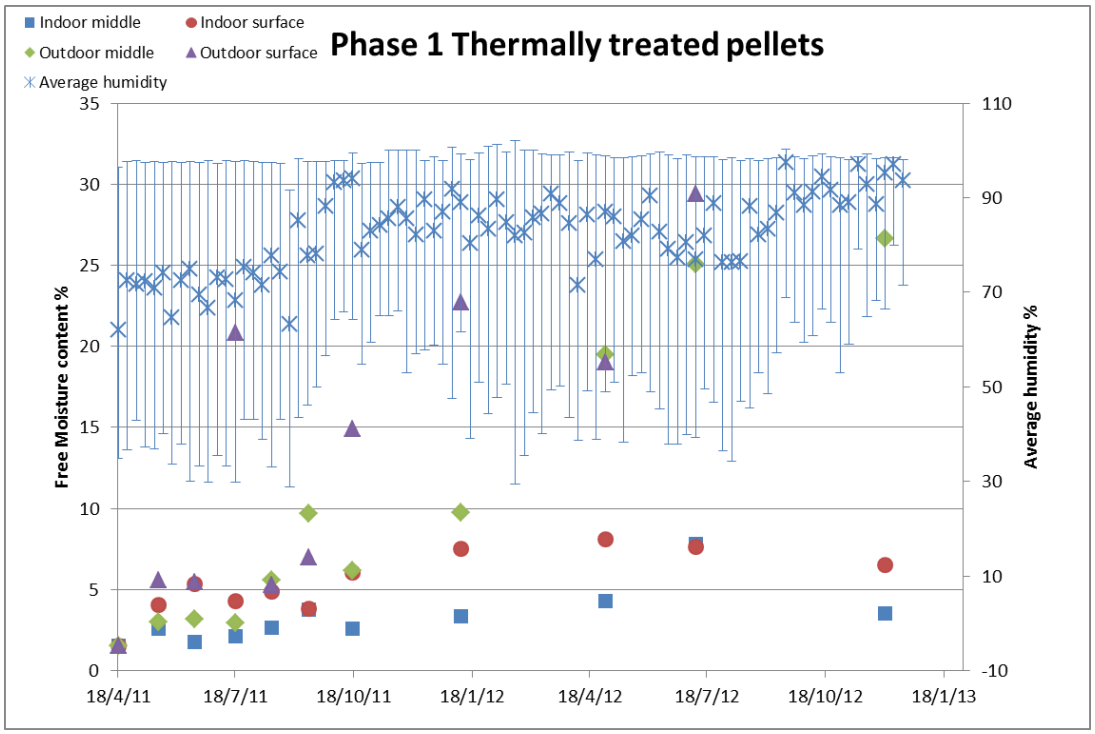

Figure B13

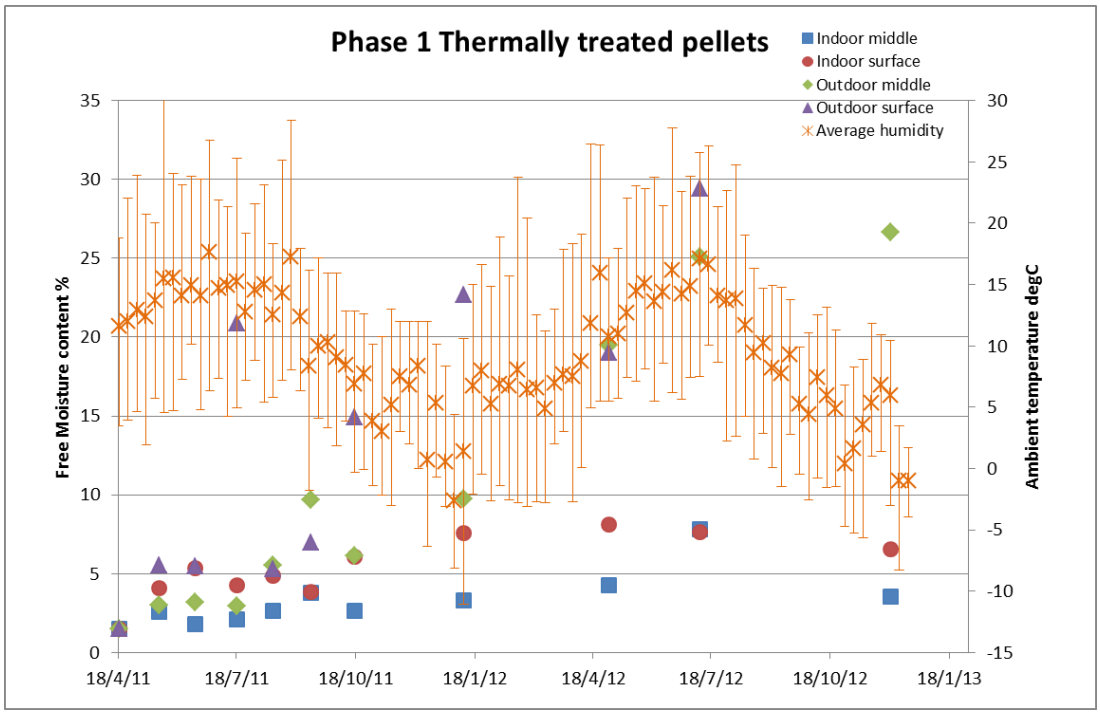

Figure B14

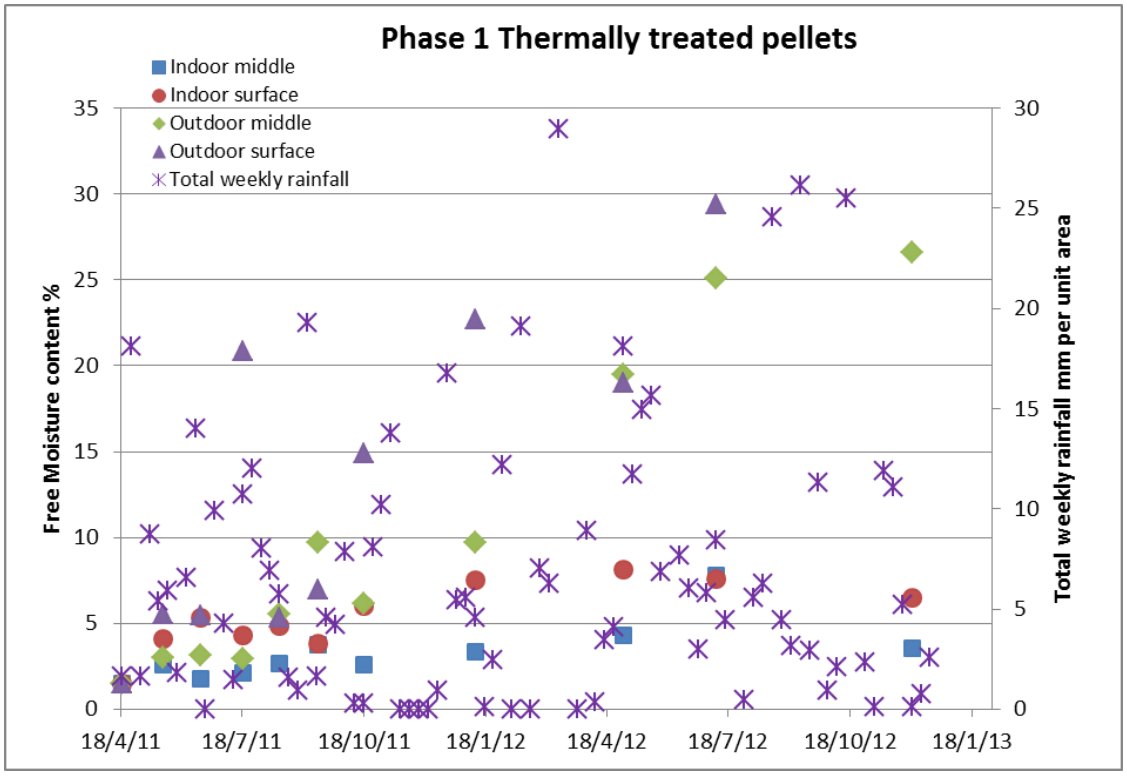

Figure B15

B.2.3. Phase 2 Willow chip piles

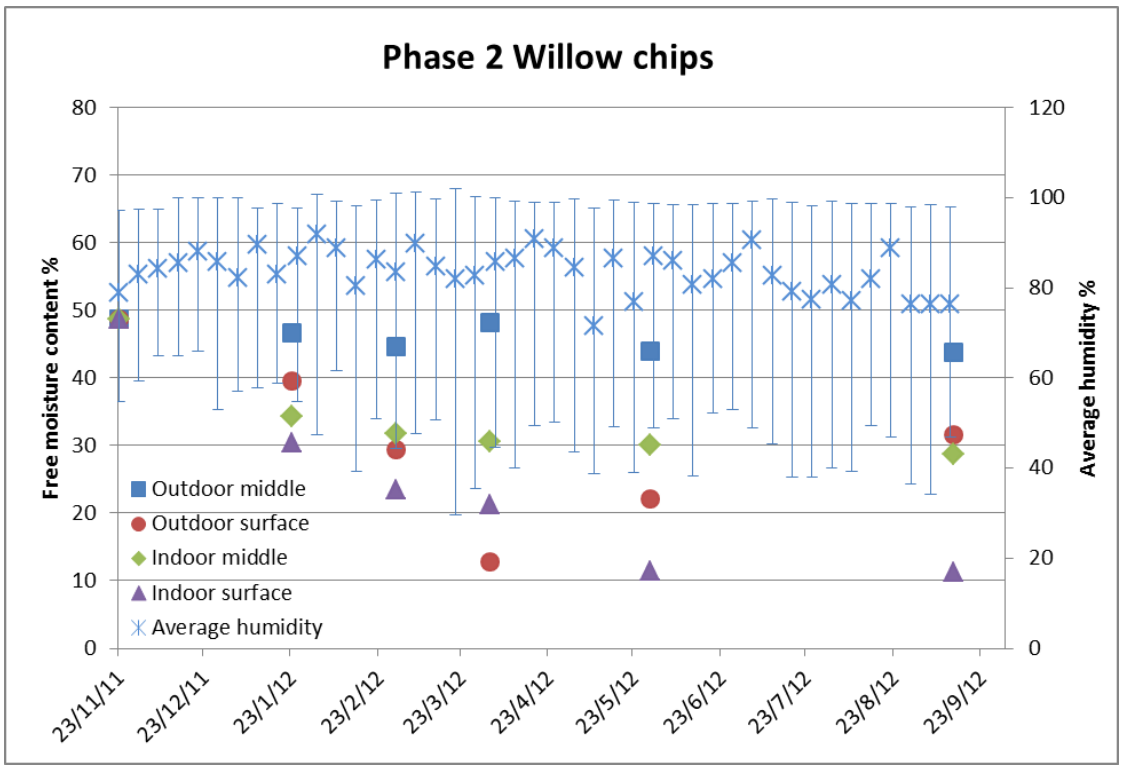

Figure B16

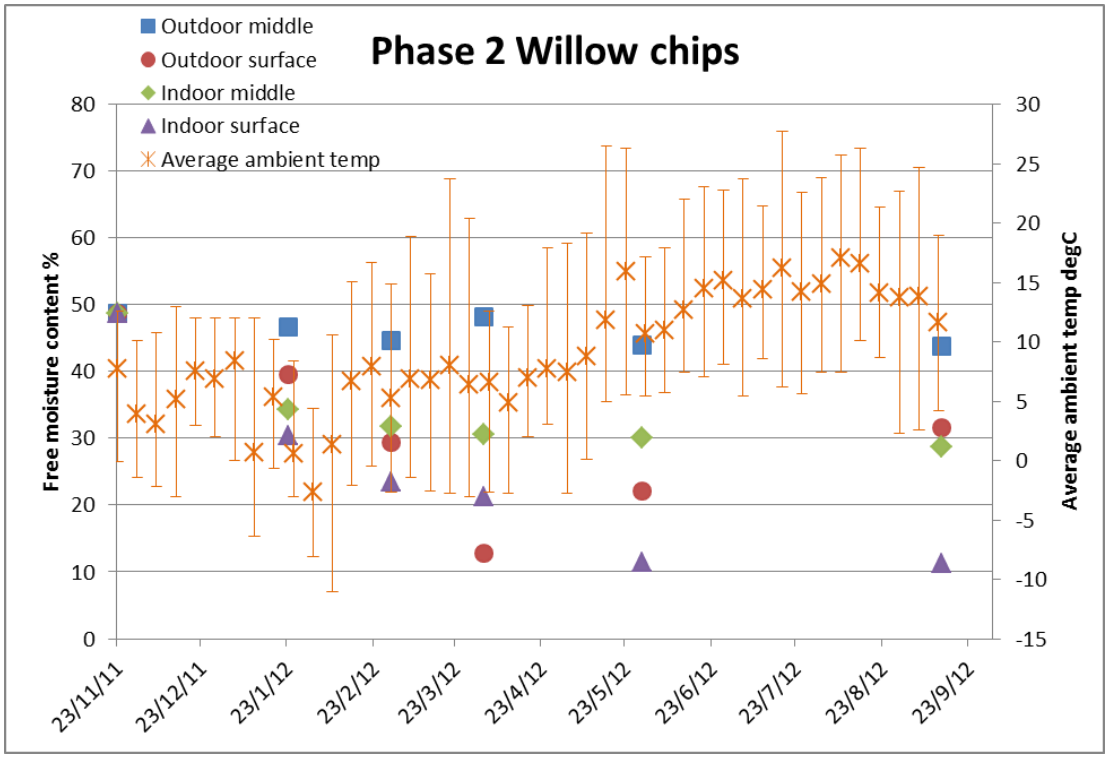

Figure B17

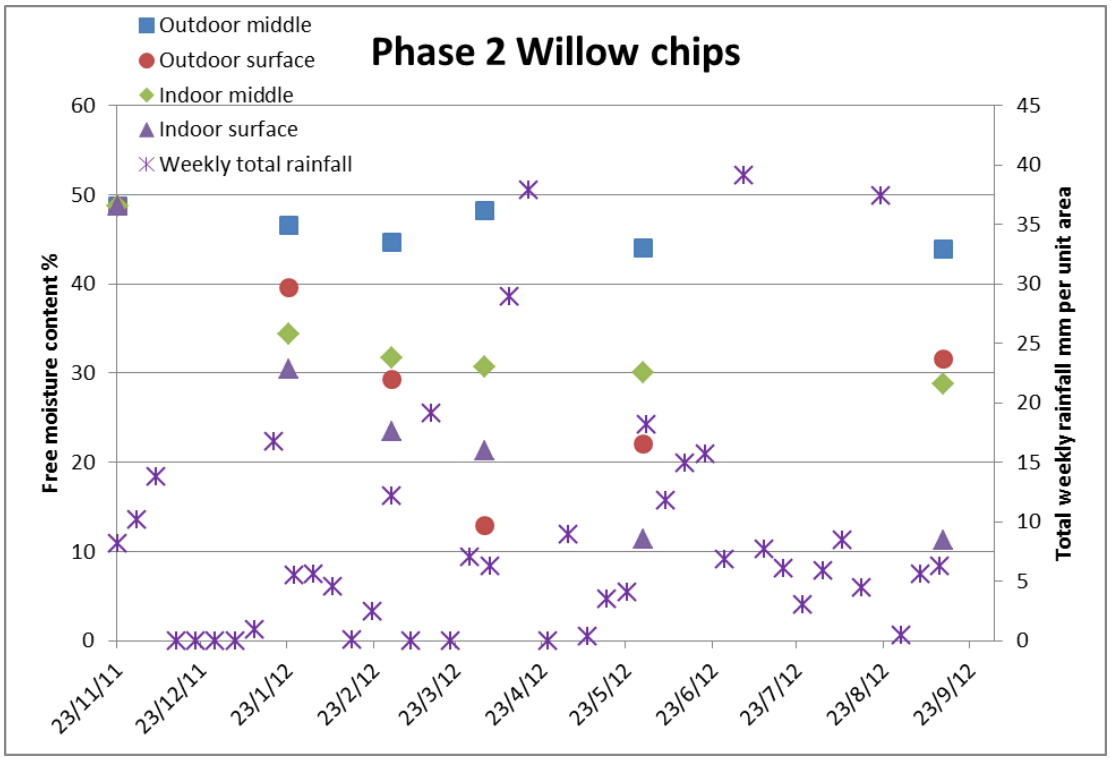

Figure B18

B.2.4. Phase 2 thermally treated wood pellets

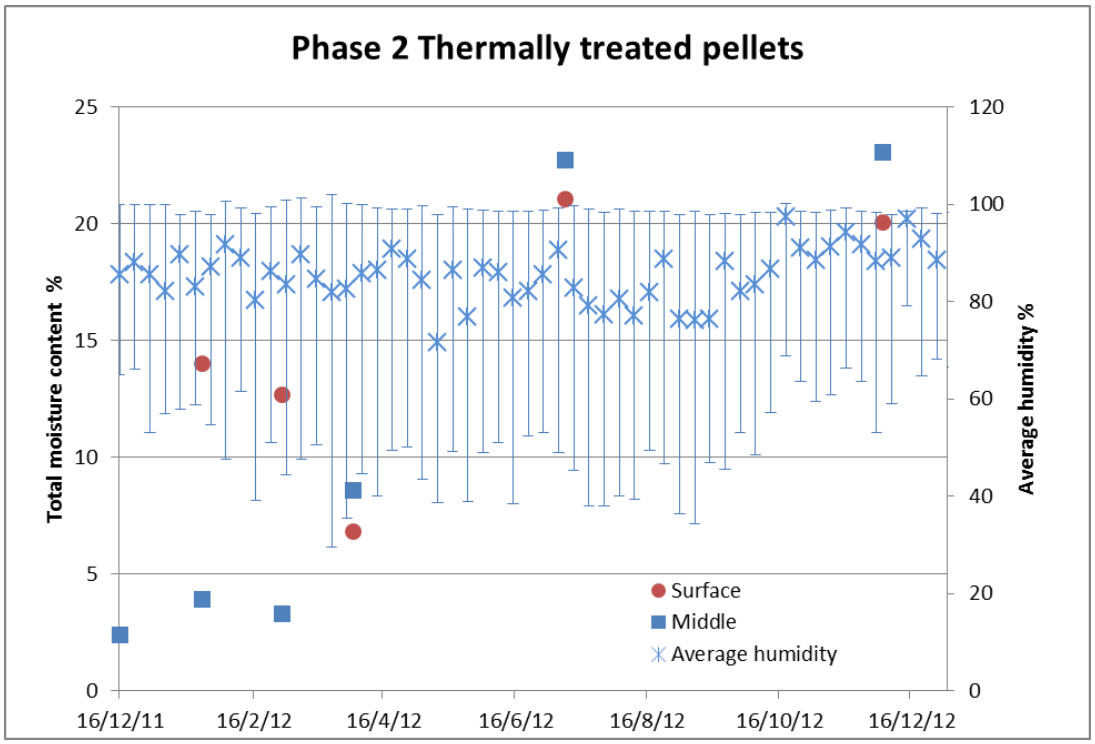

Figure B19

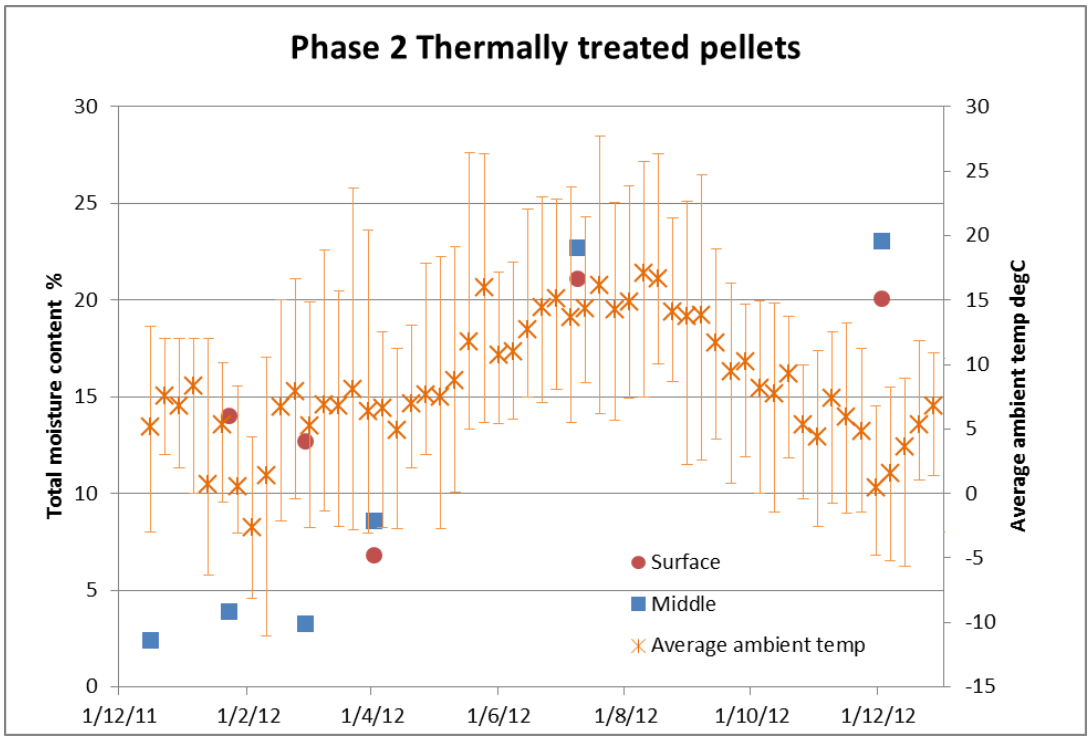

Figure B20

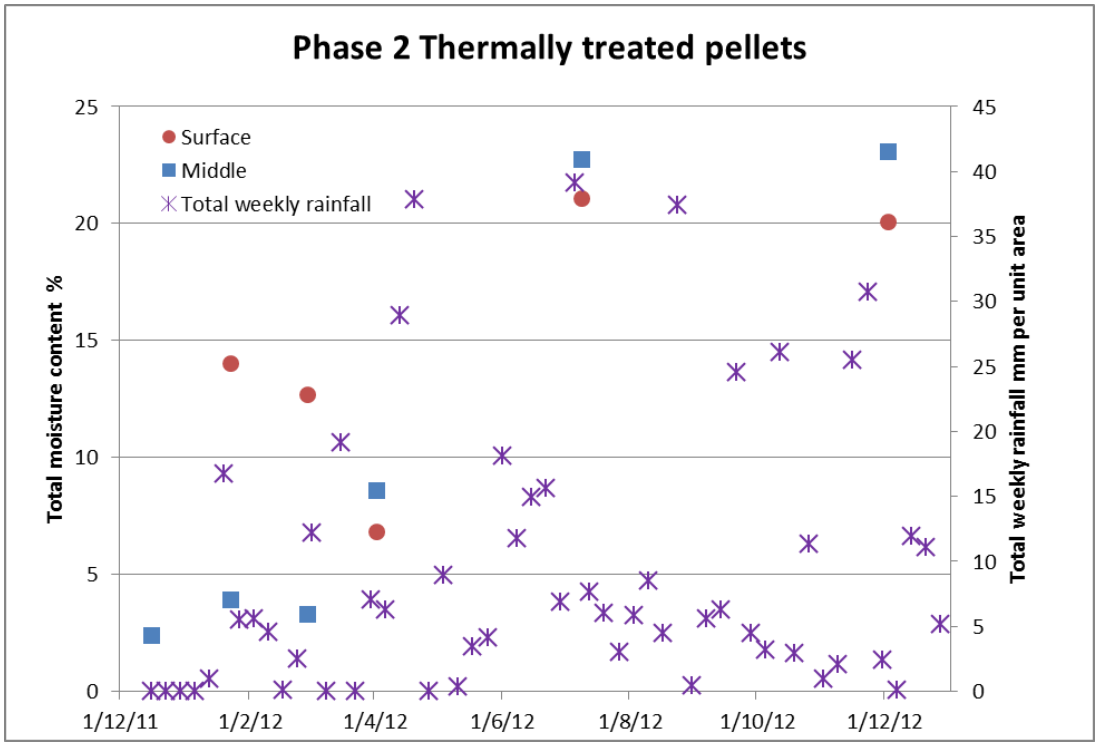

Figure B21

B.2.5. Phase 2 white wood pellets

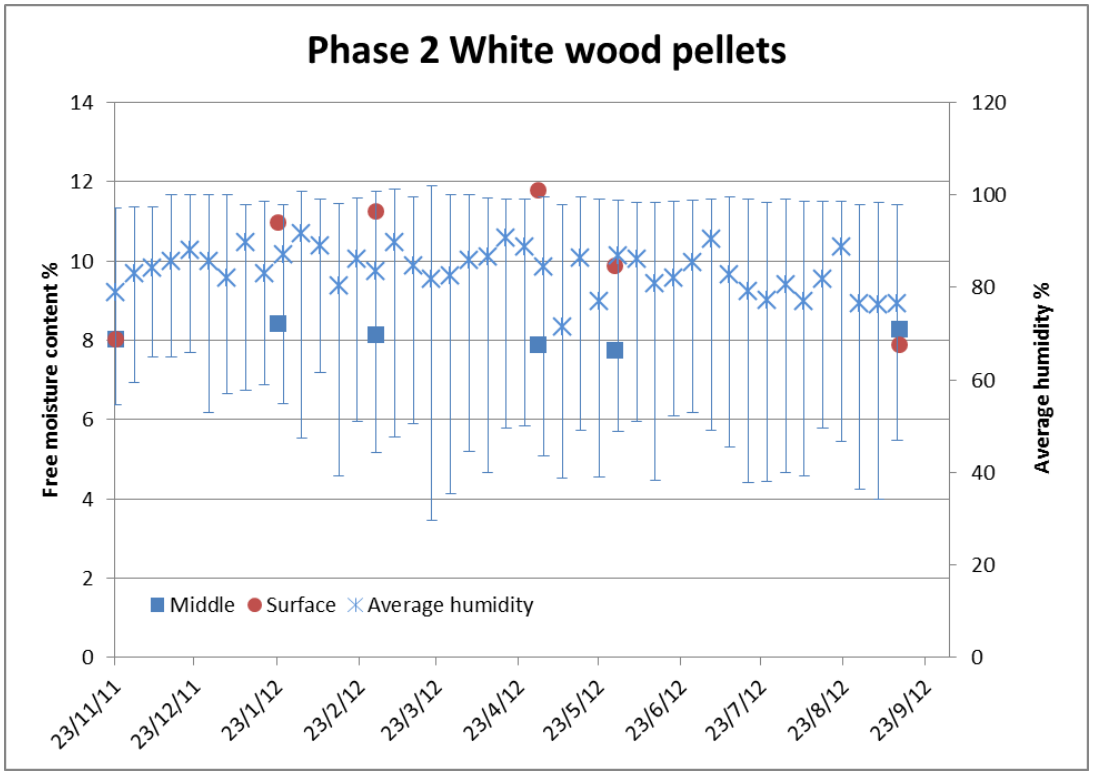

Figure B22

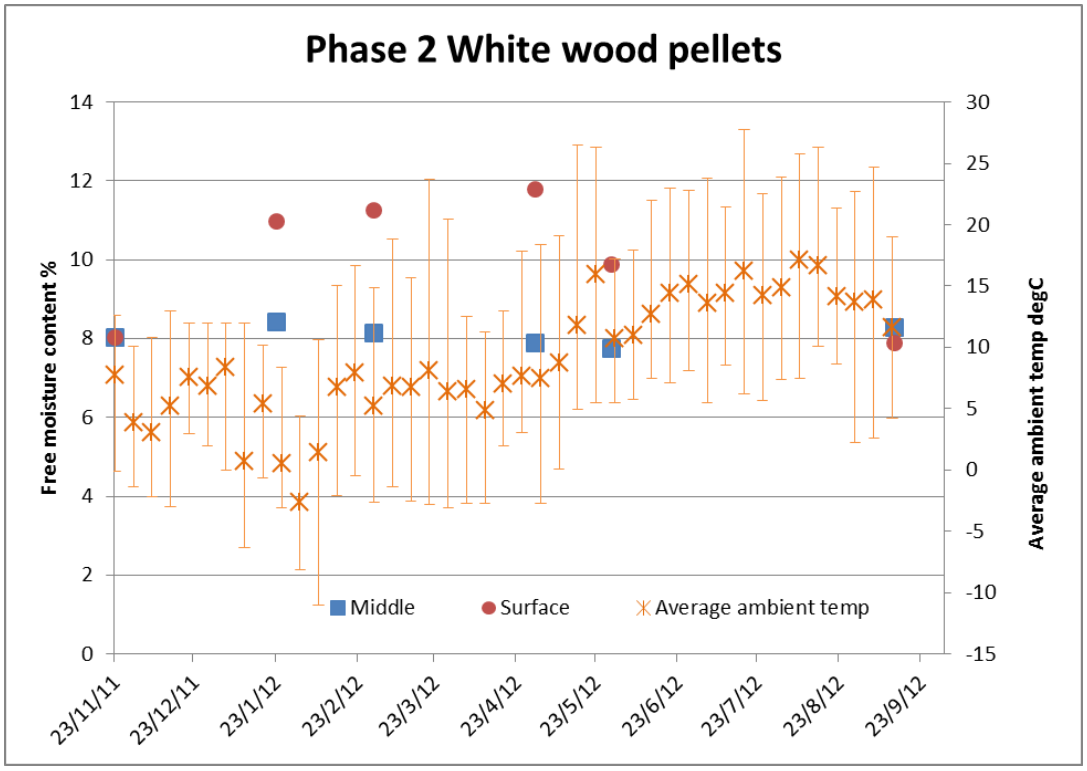

Figure B23

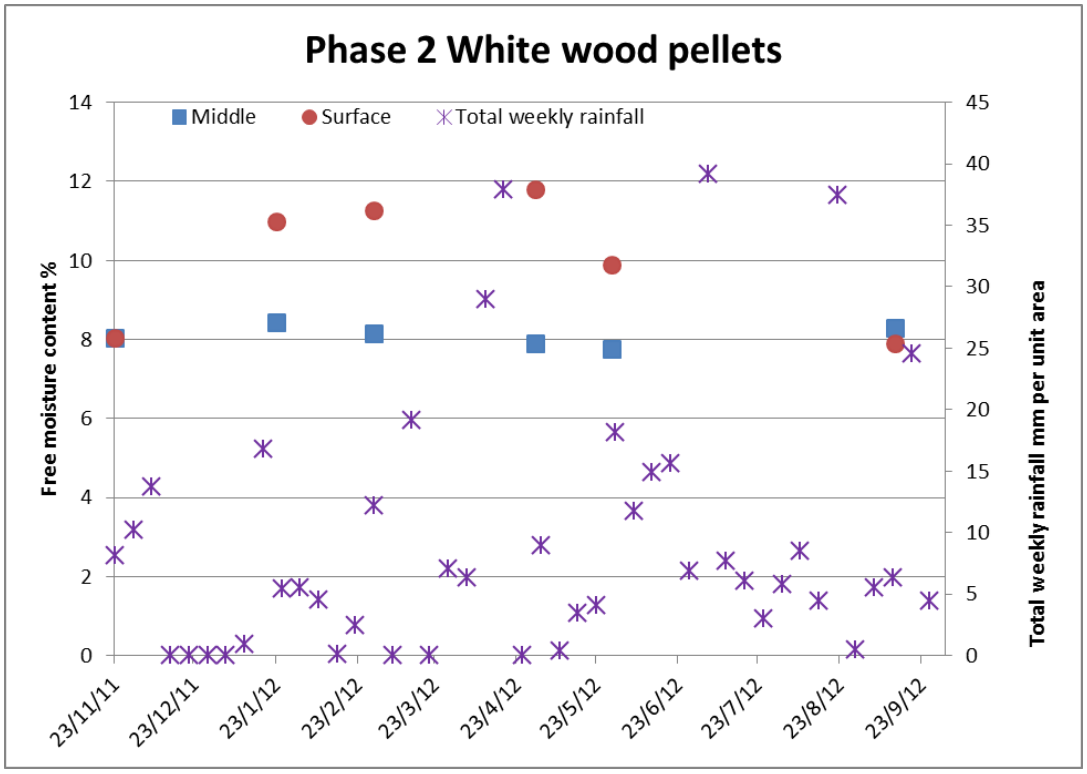

Figure B24

B.3. Net calorific value of fuels

B.3.1. Phase 1 Willow chips

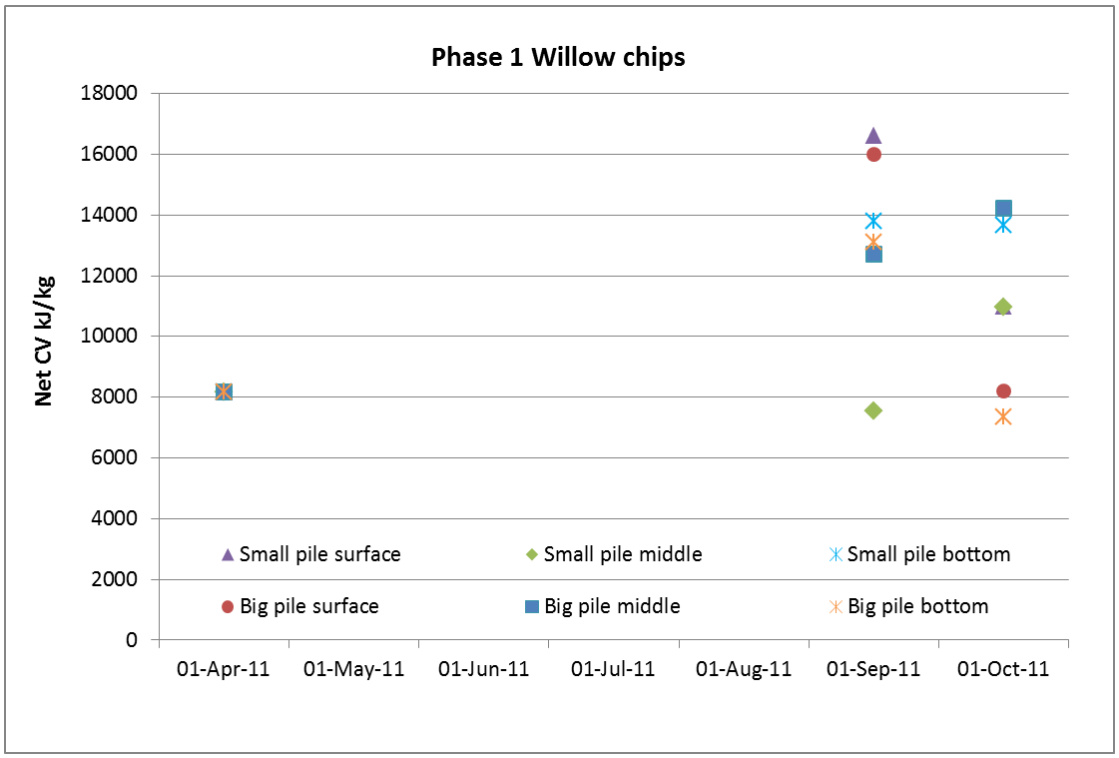

Figure B25

B.3.2. Phase 2 thermally treated wood pellets

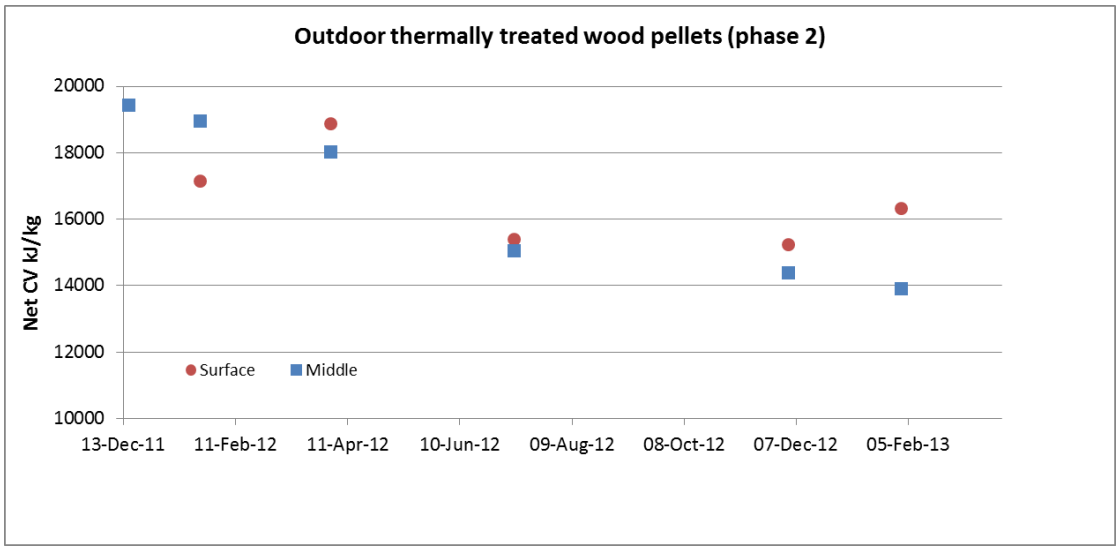

Figure B26

B.3.3. Phase 2 white wood pellets

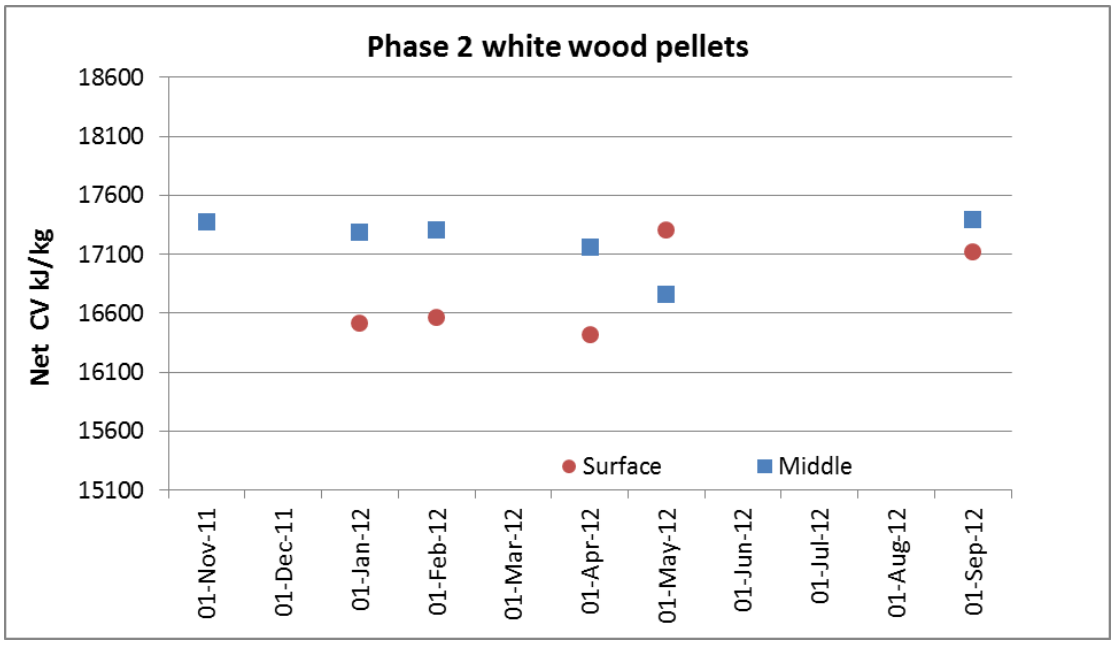

Figure B27

Appendix C - Mechanical degradation chapter graphs

C.1. Phase 1 thermally treated wood pellets

C.1.1. Durability

Figure C1

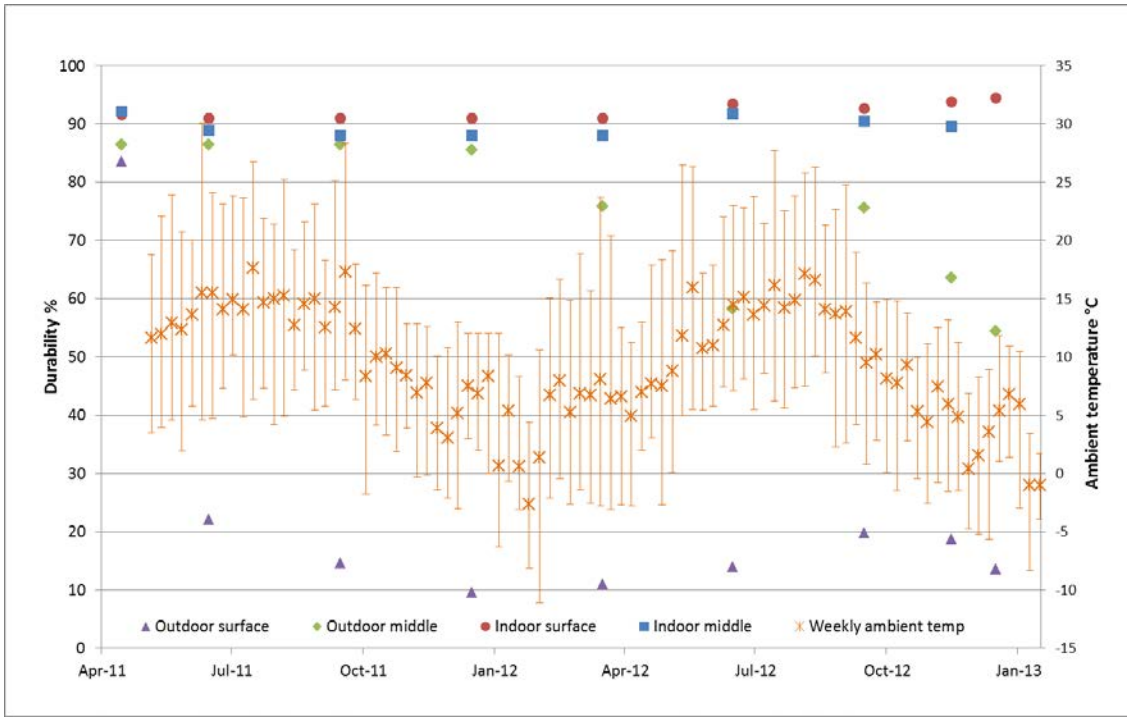

Figure C2

C.1.2. Pellet diameter

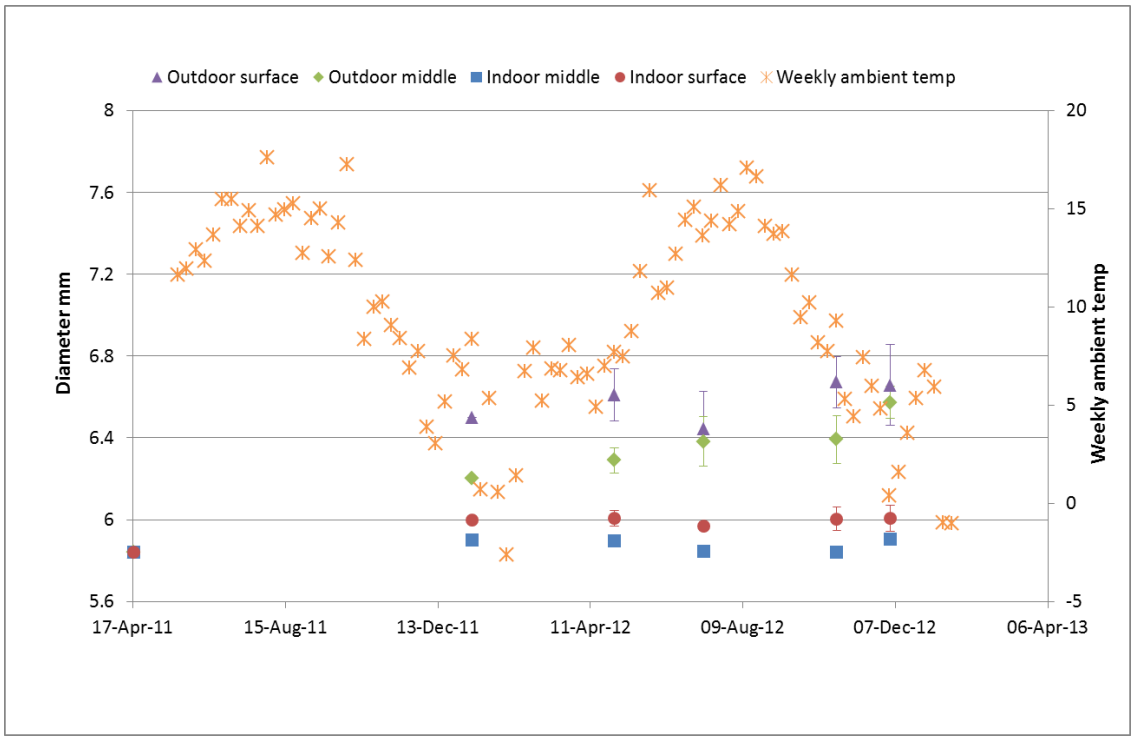

Figure C3

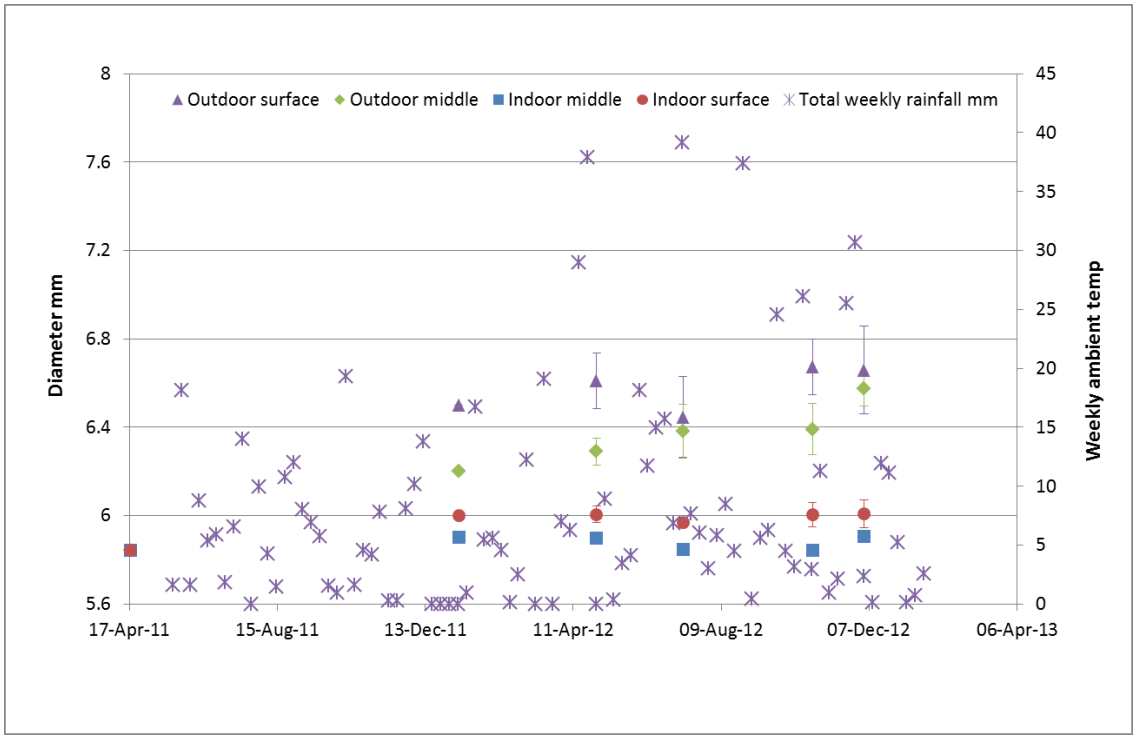

Figure C4

C.1.3. Axial compression strength

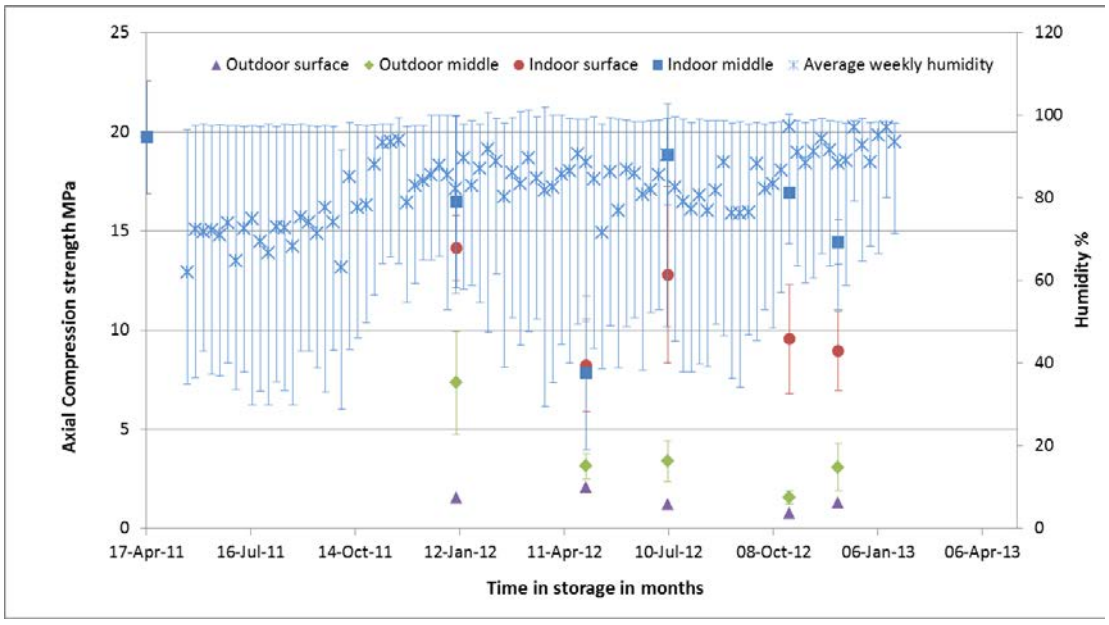

Figure C5

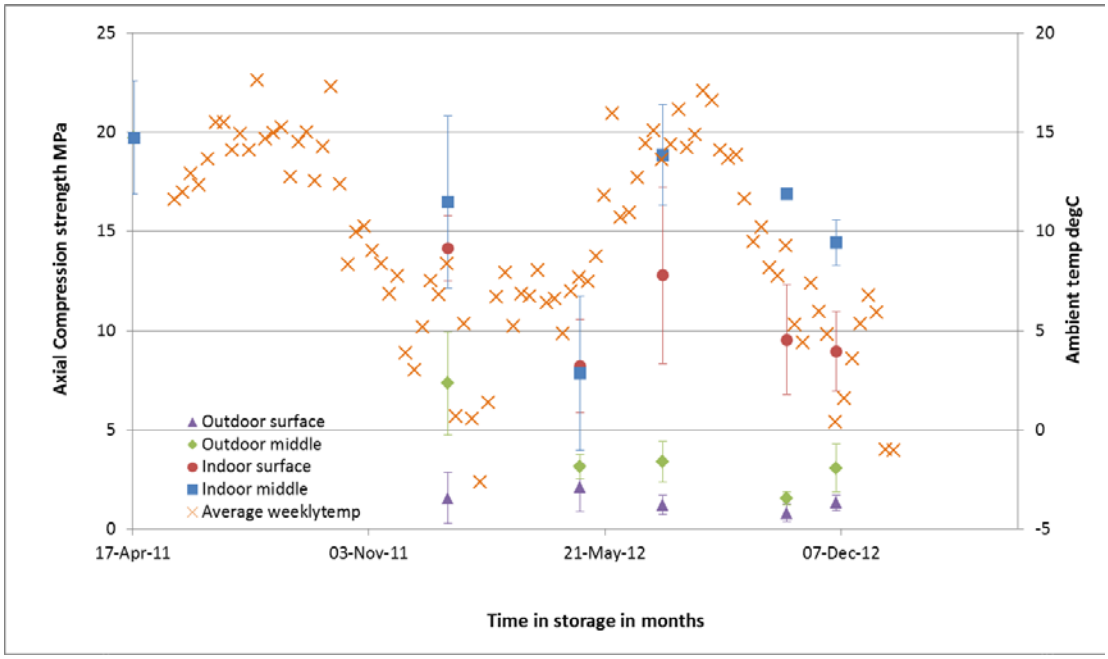

Figure C6

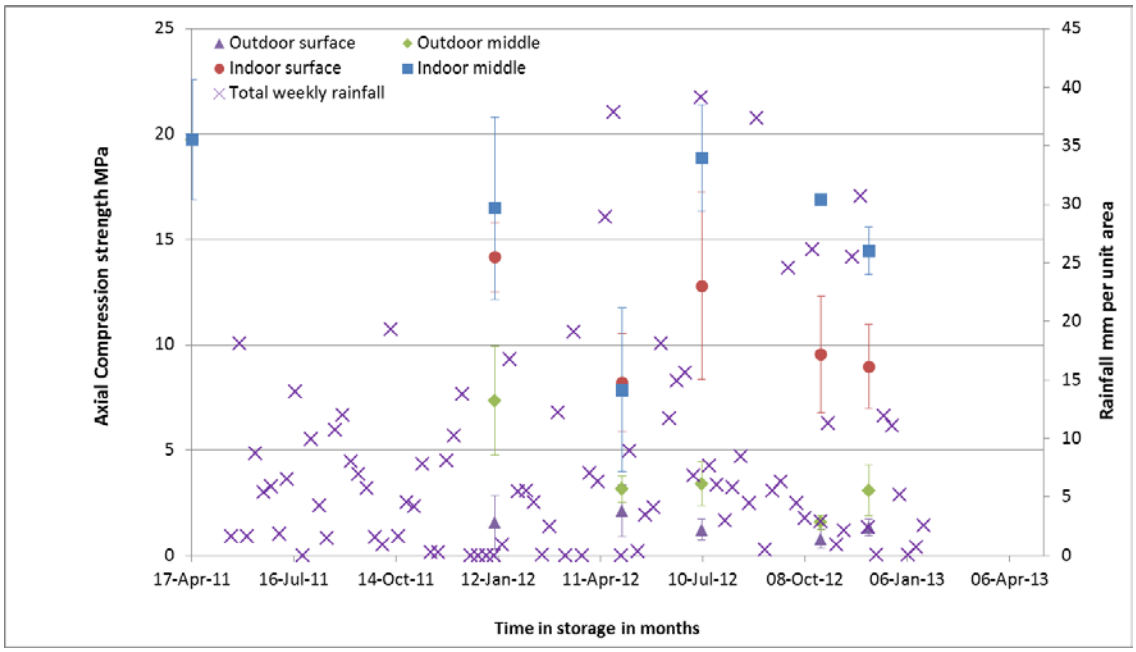

Figure C7

C.1.4. Diametrical compression strength

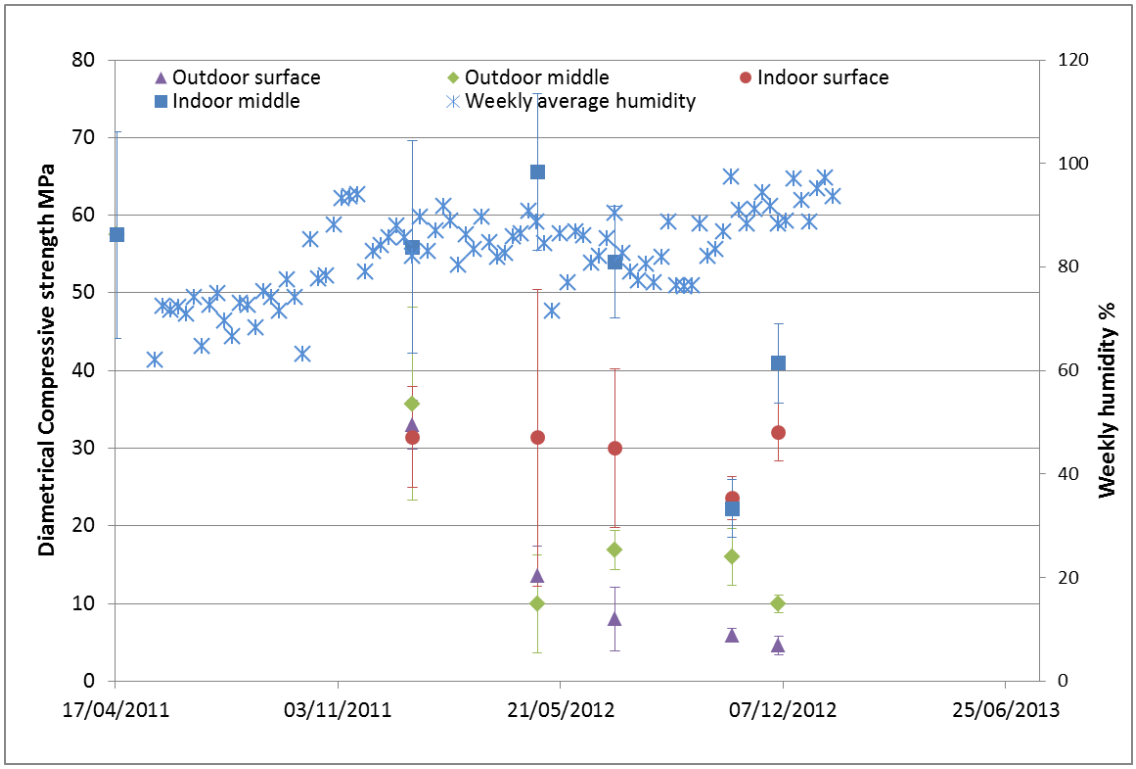

Figure C8

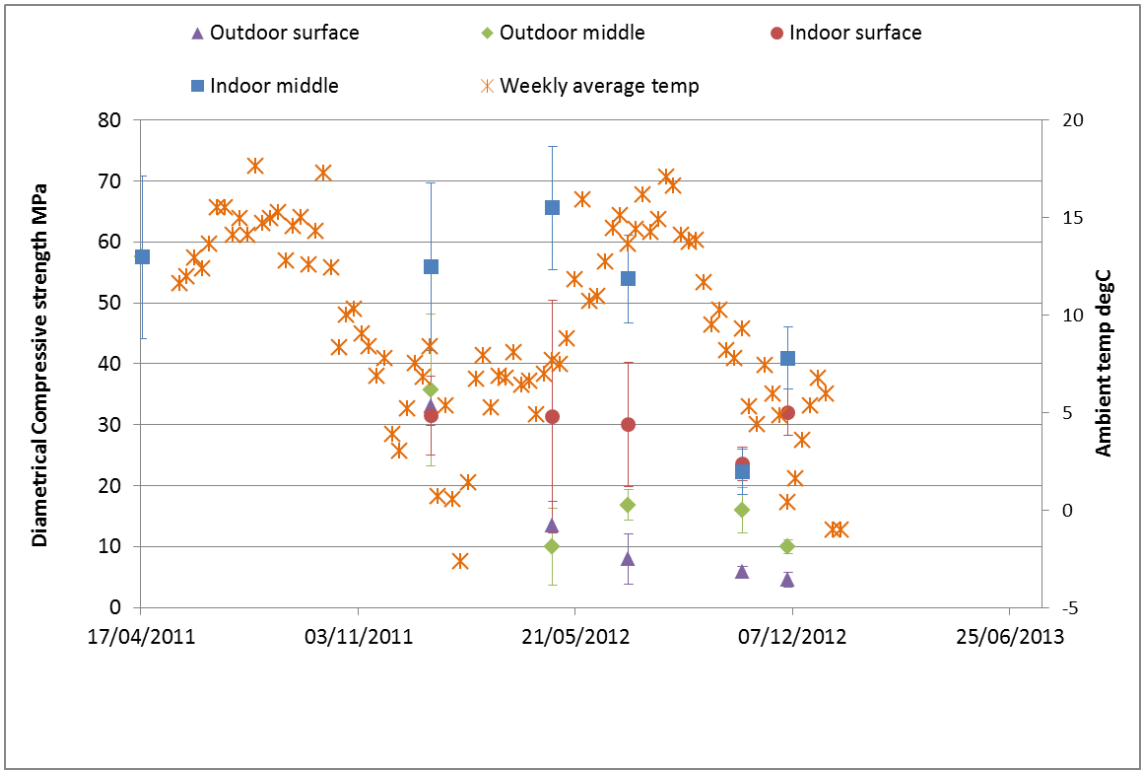

Figure C9

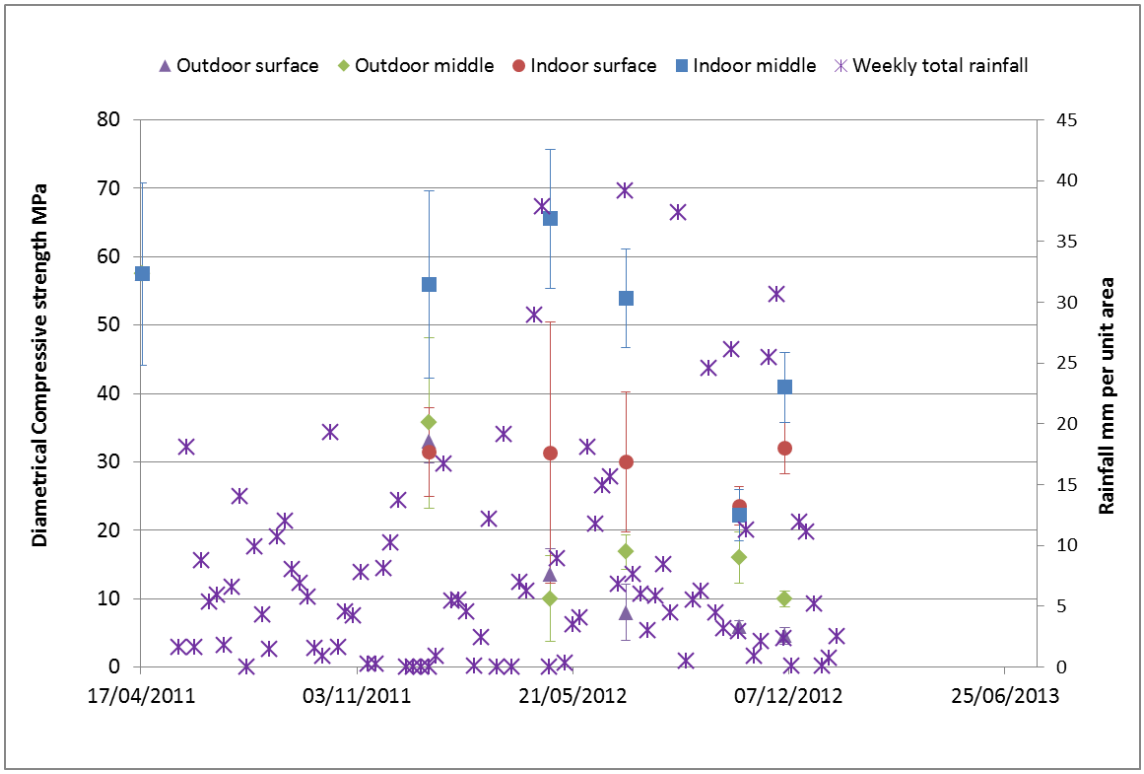

Figure C10

C.1.6. Inter-laminar shear modulus

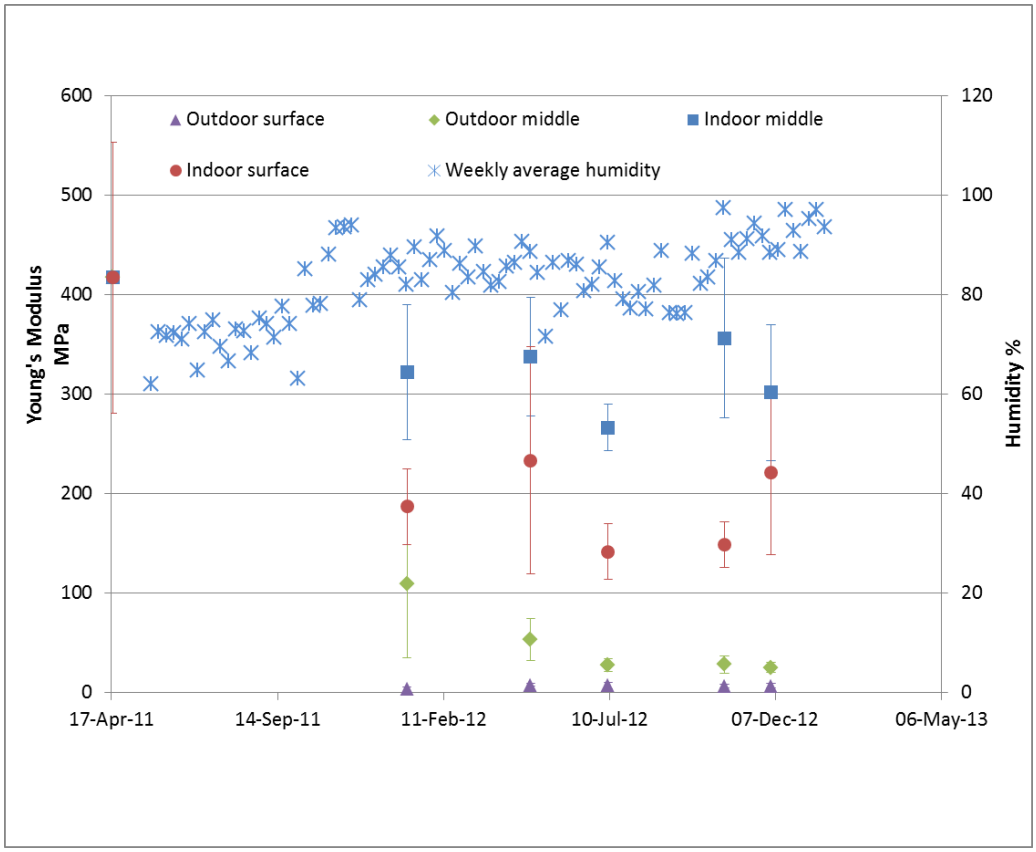

Figure C11

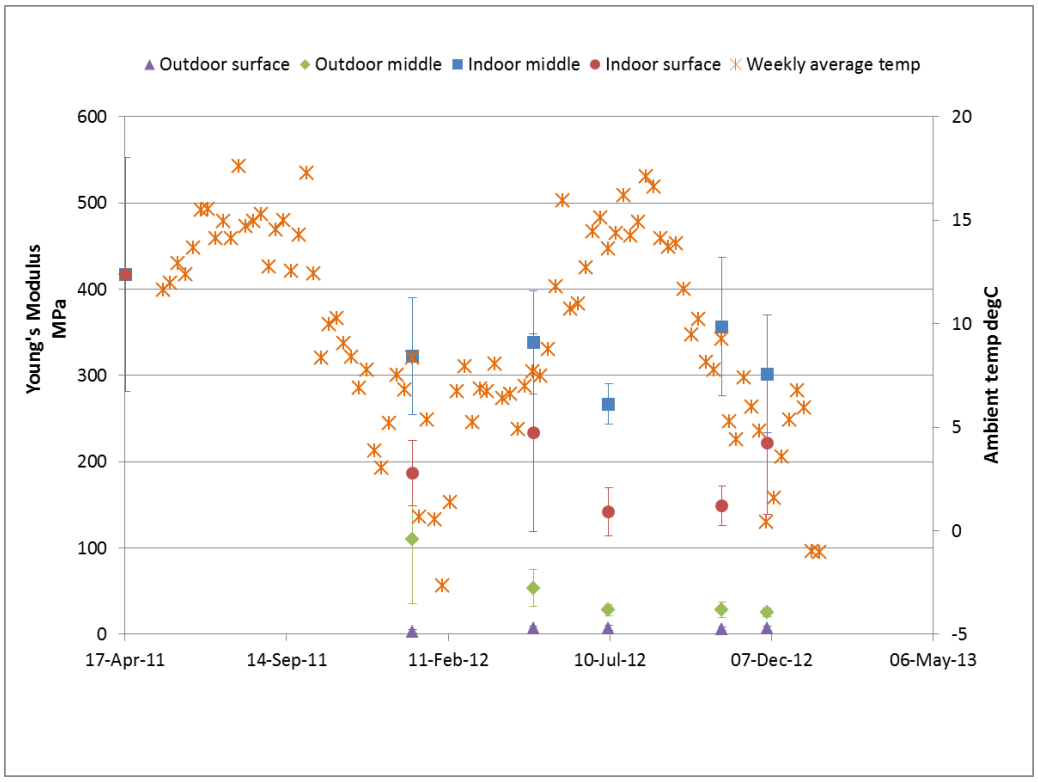

Figure C12

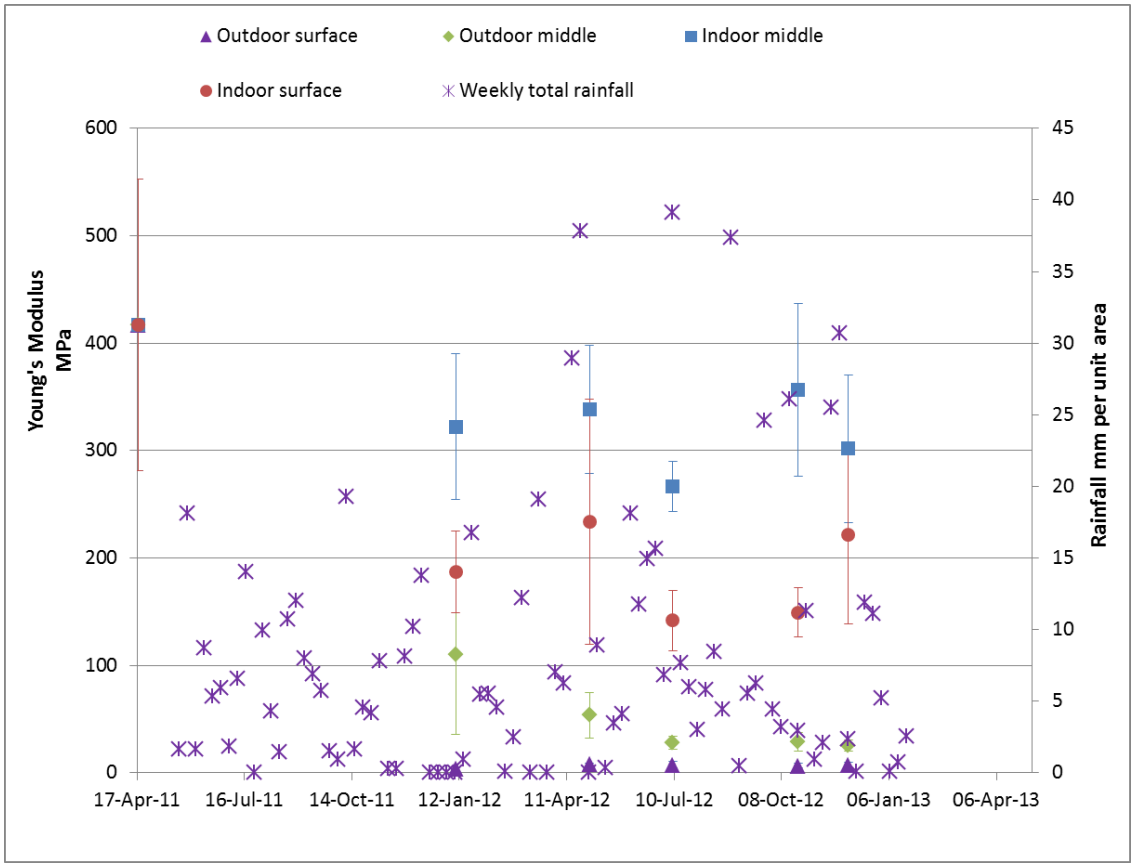

Figure C13

C.2. Phase 2 thermally treated wood pellets

C.2.1. Durability

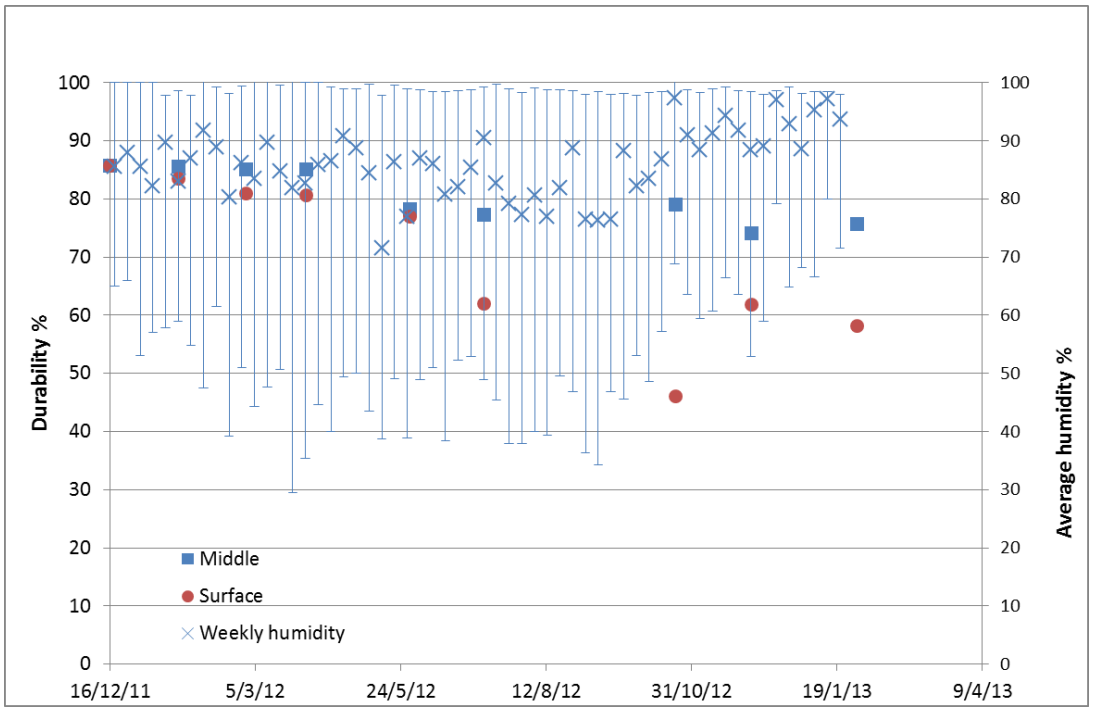

Figure C14

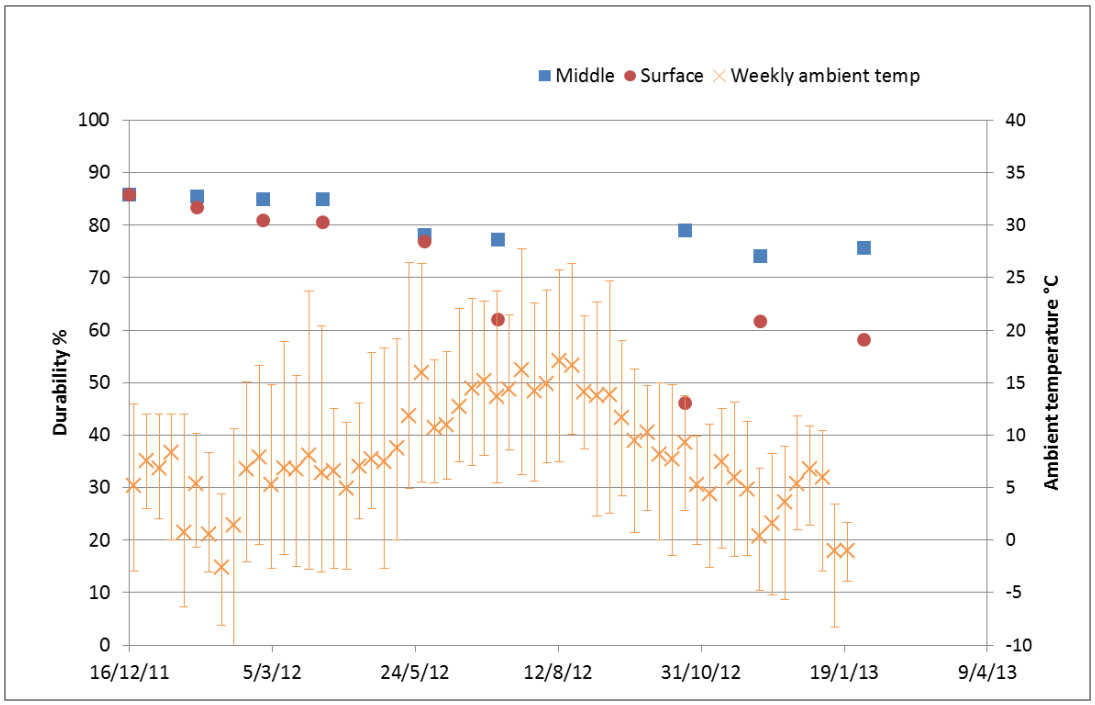

Figure C15

C.2.2. Pellet diameter

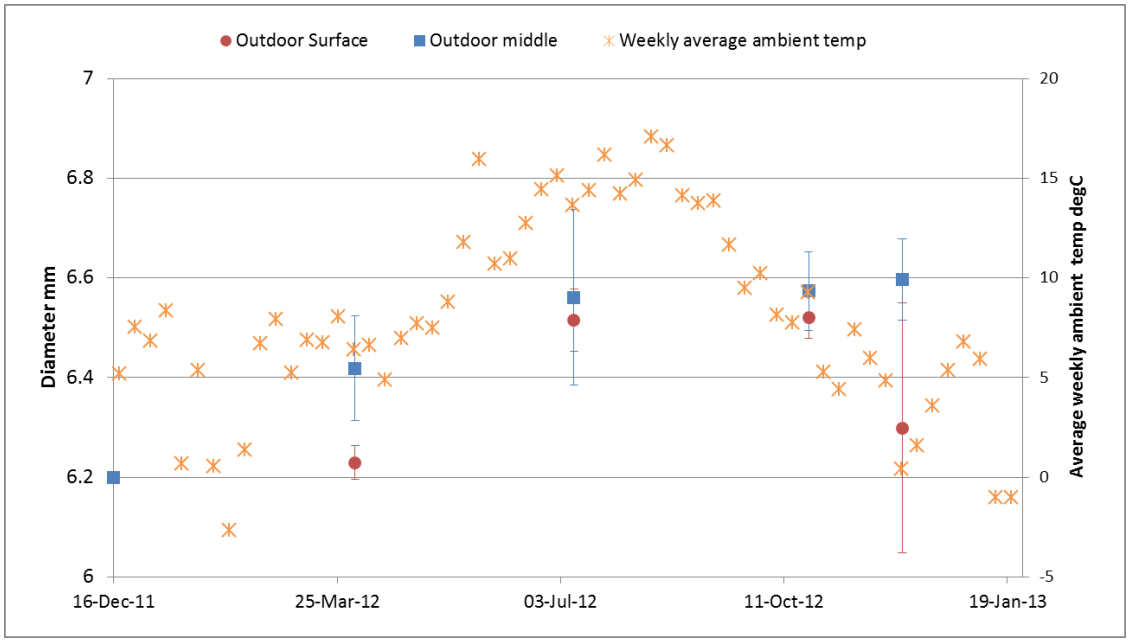

Figure C16

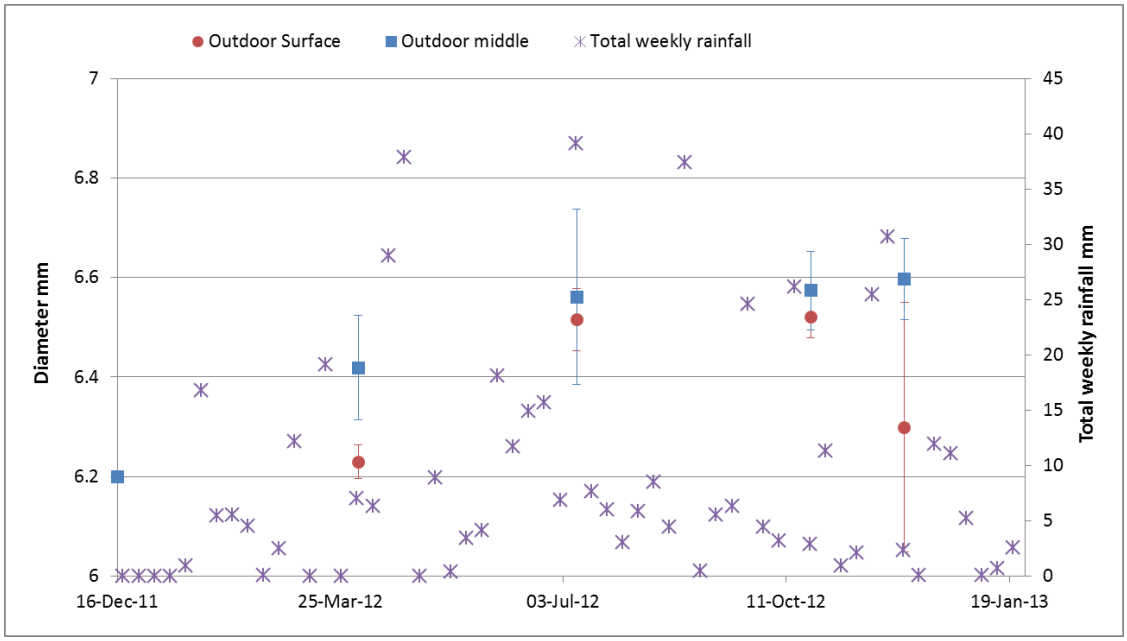

Figure C17

C.2.3. Axial compression strength

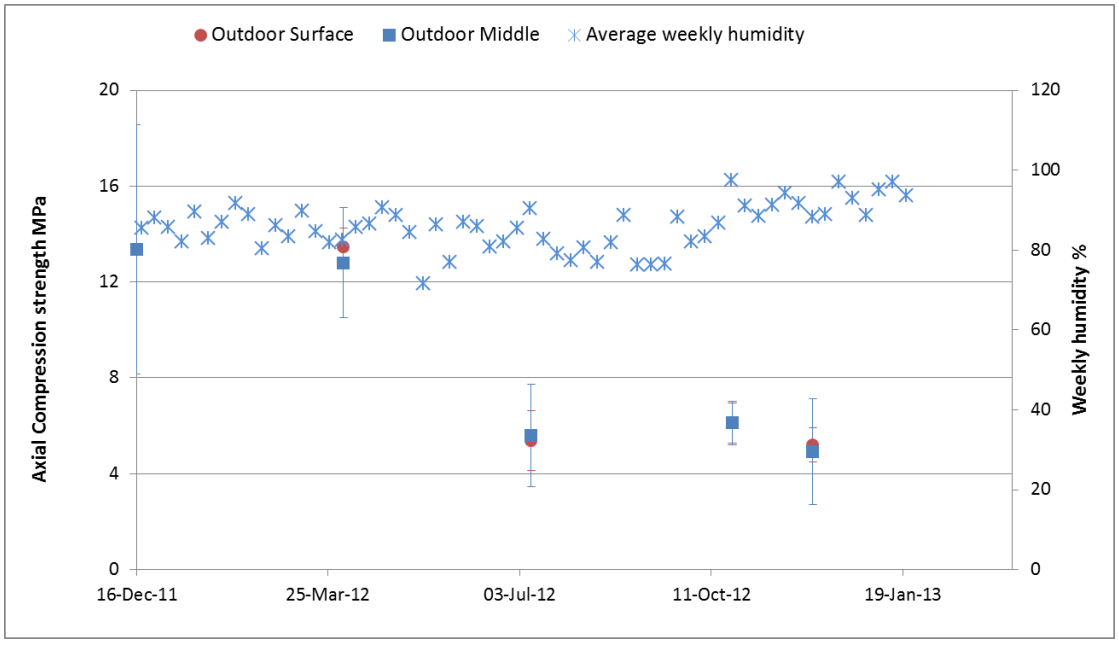

Figure C18

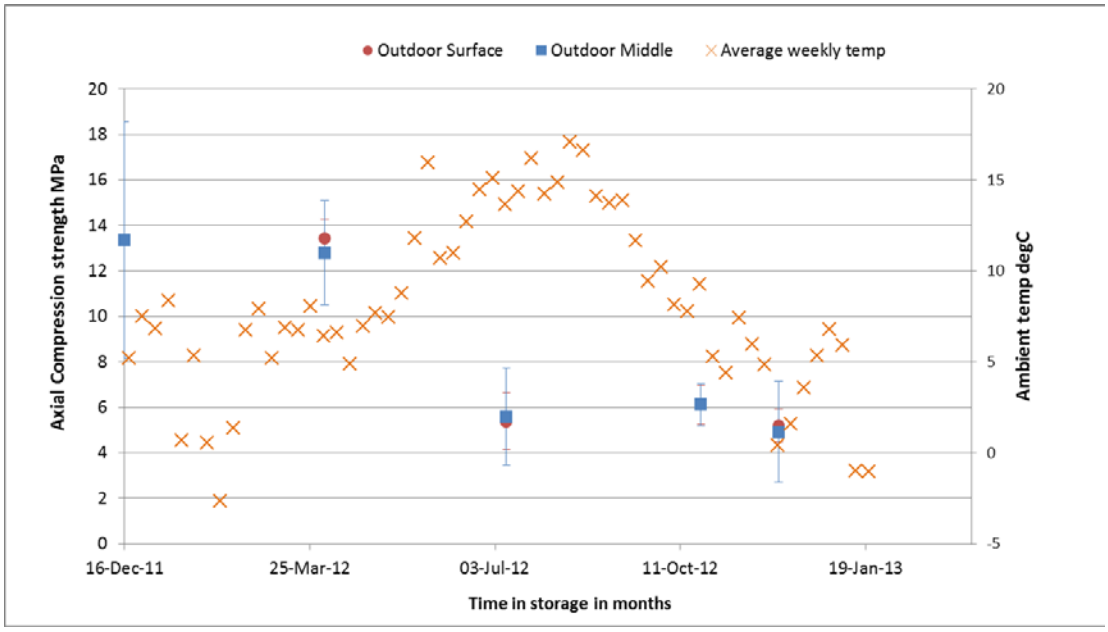

Figure C19

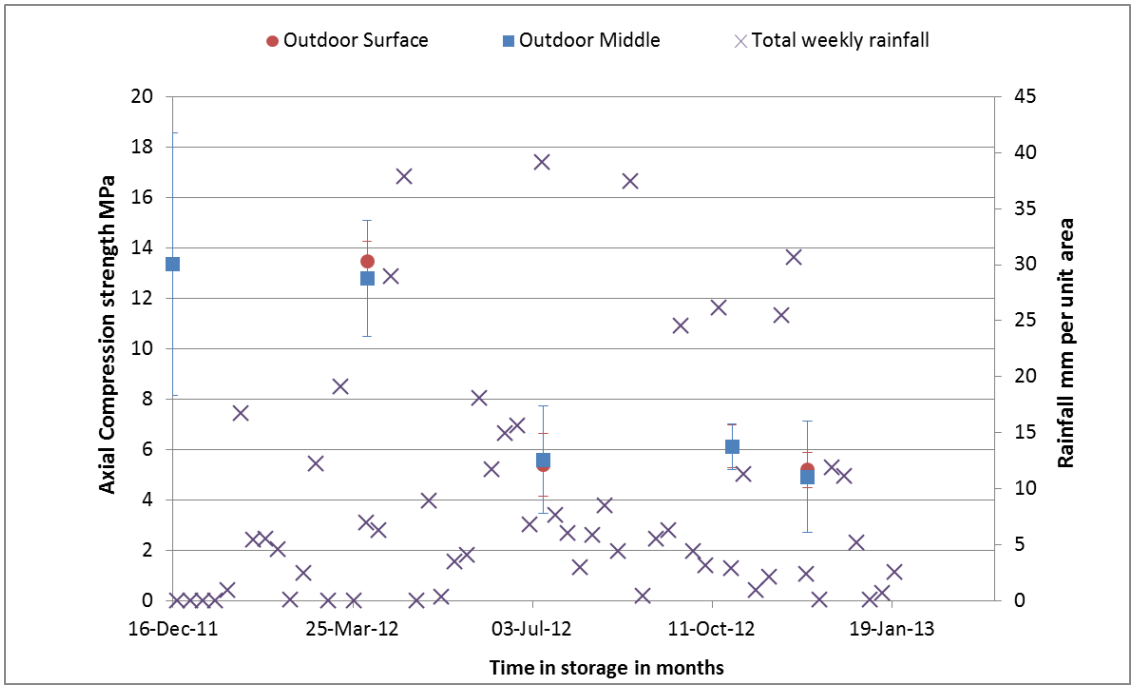

Figure C20

C.2.4. Diametrical compression strength

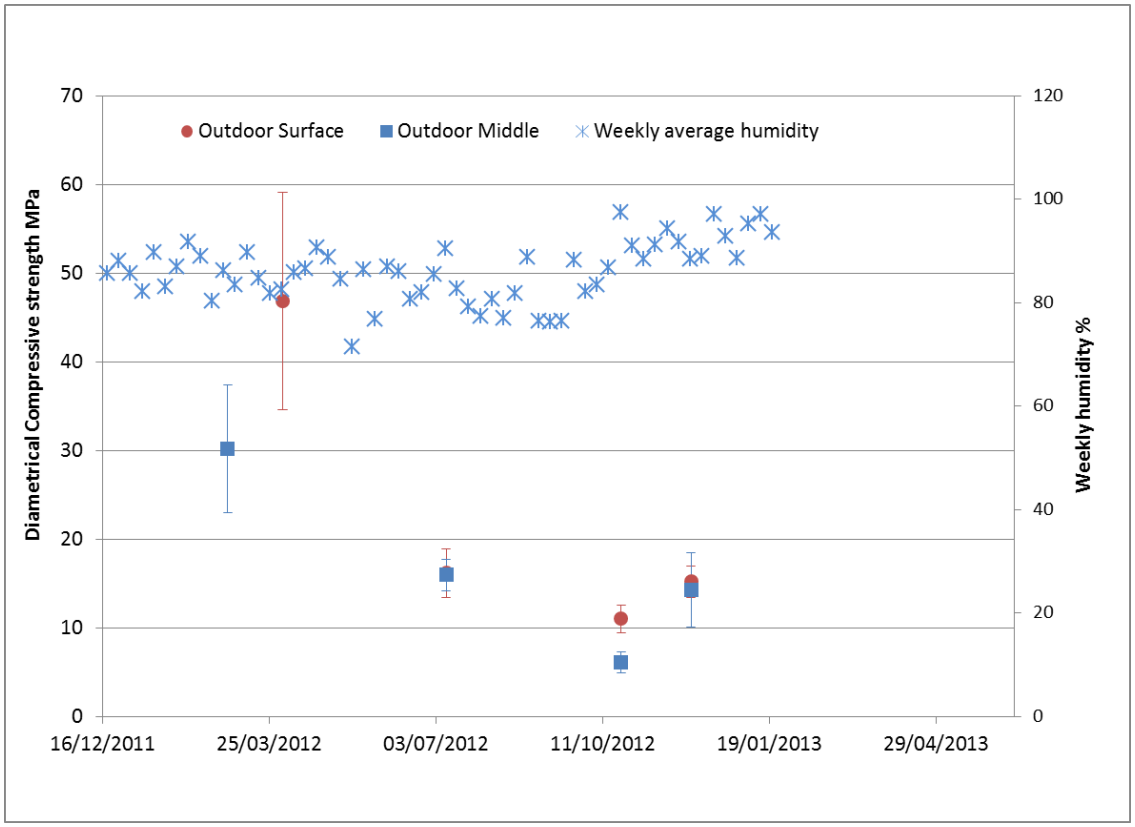

Figure C21

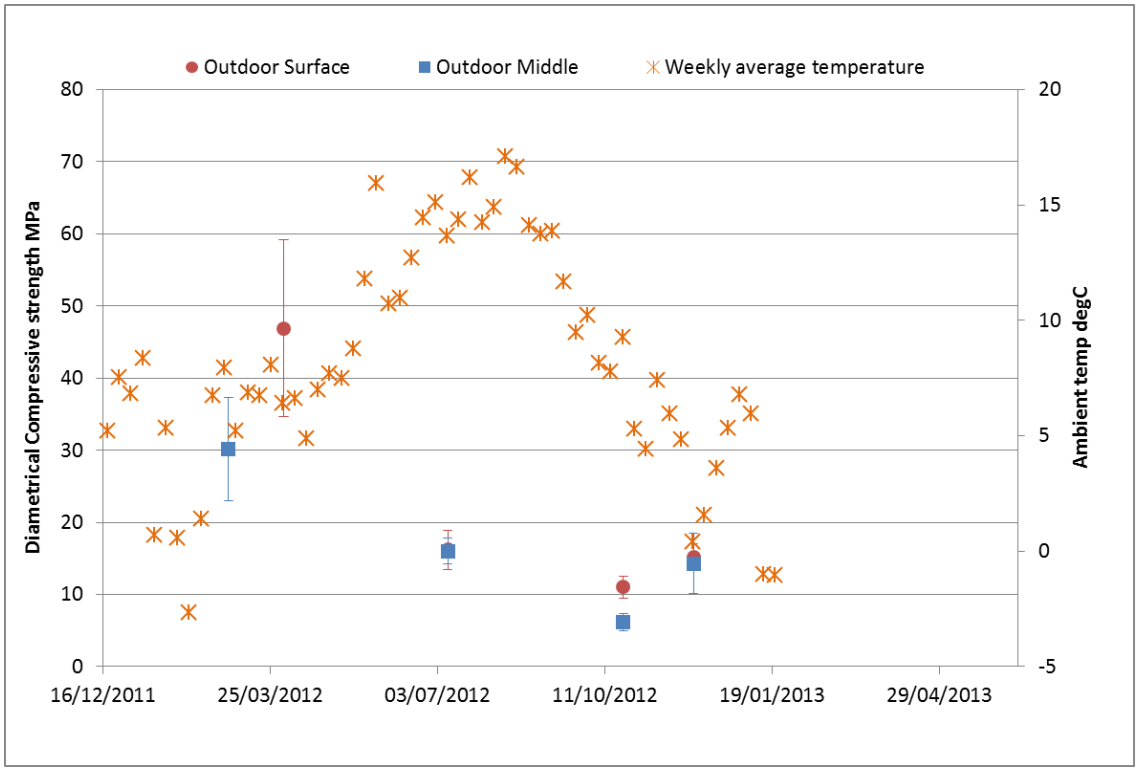

Figure C22

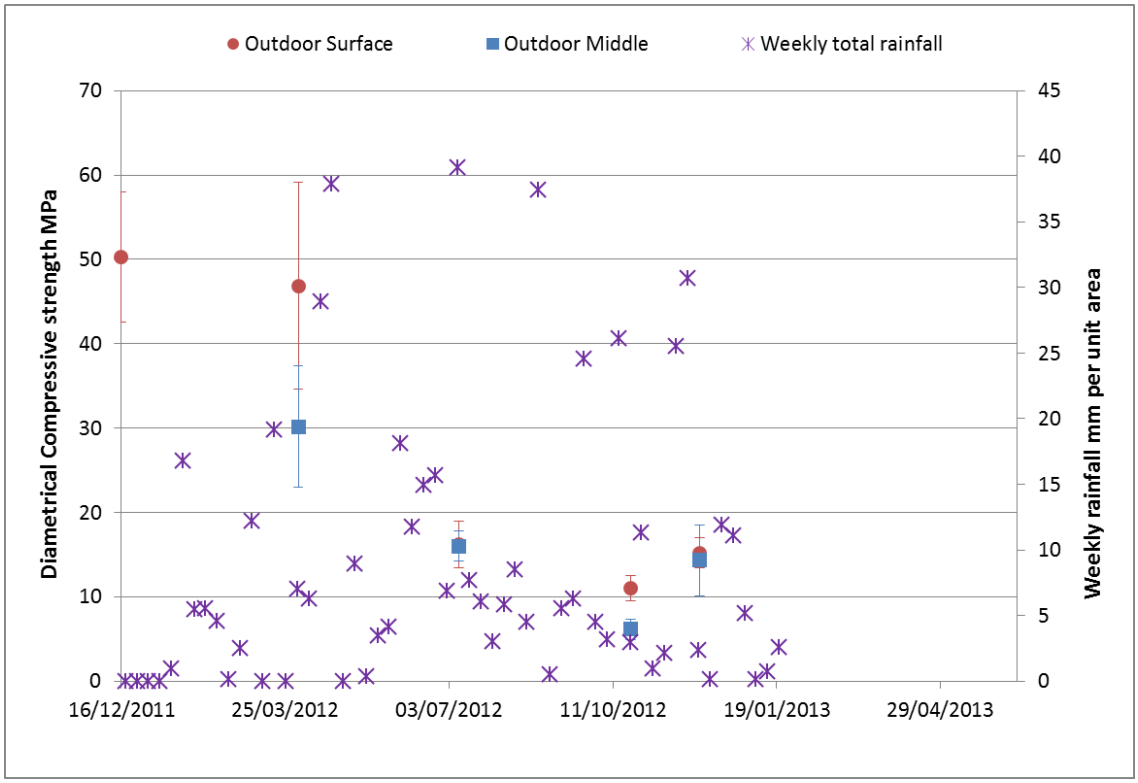

Figure C23

C.2.5. Inter-laminar shear modulus

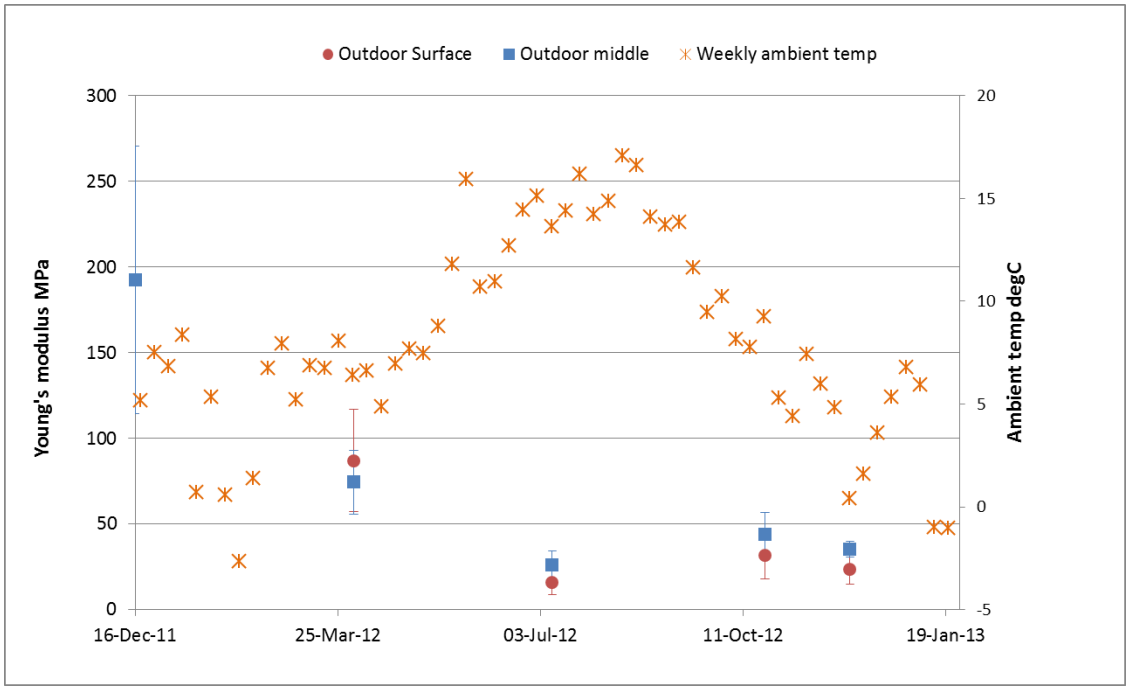

Figure C24

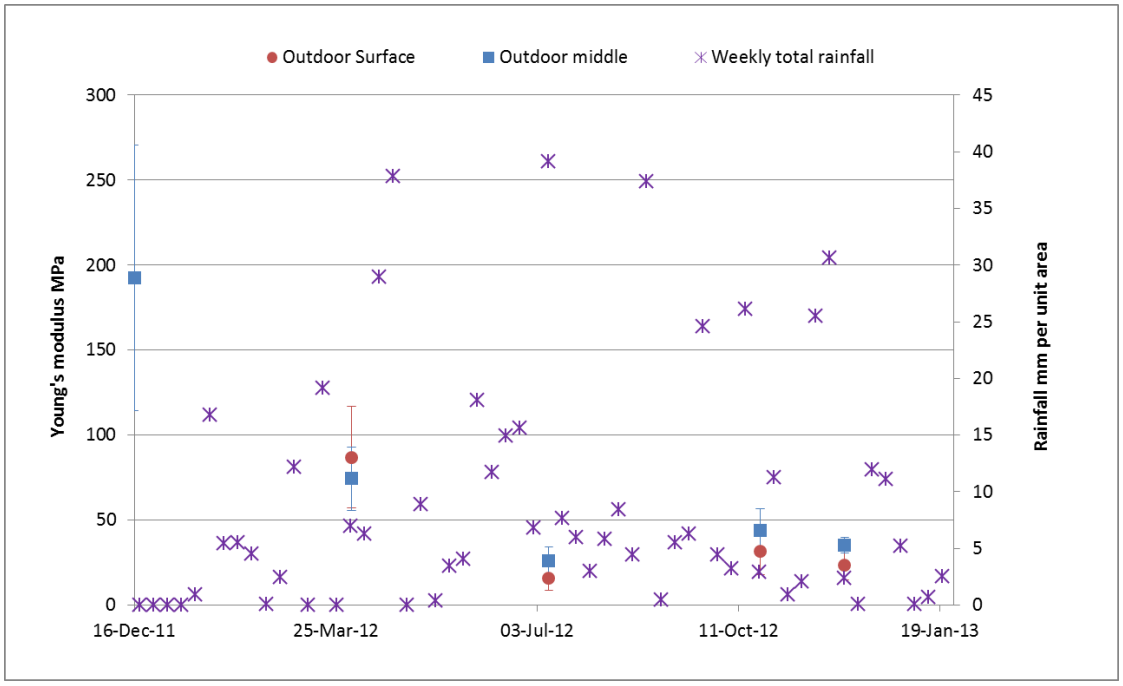

Figure C25

C.3. Phase 2 white wood pellets

C.3.1. Durability

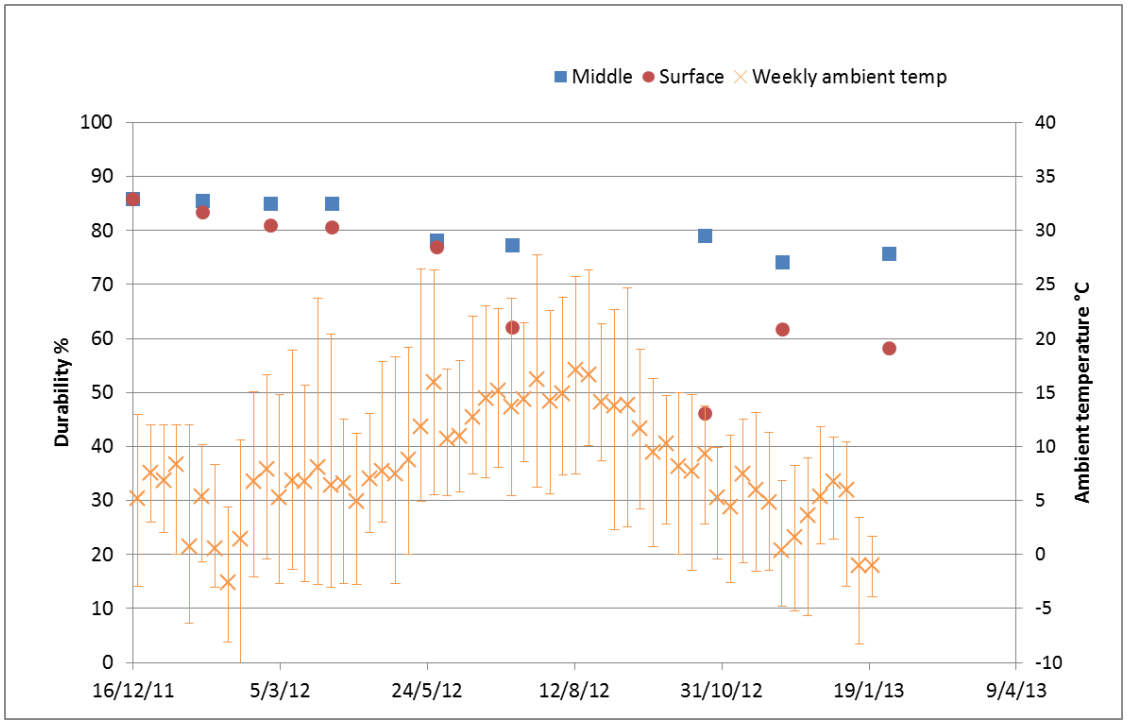

Figure C26

C.3.2. Pellet diameter

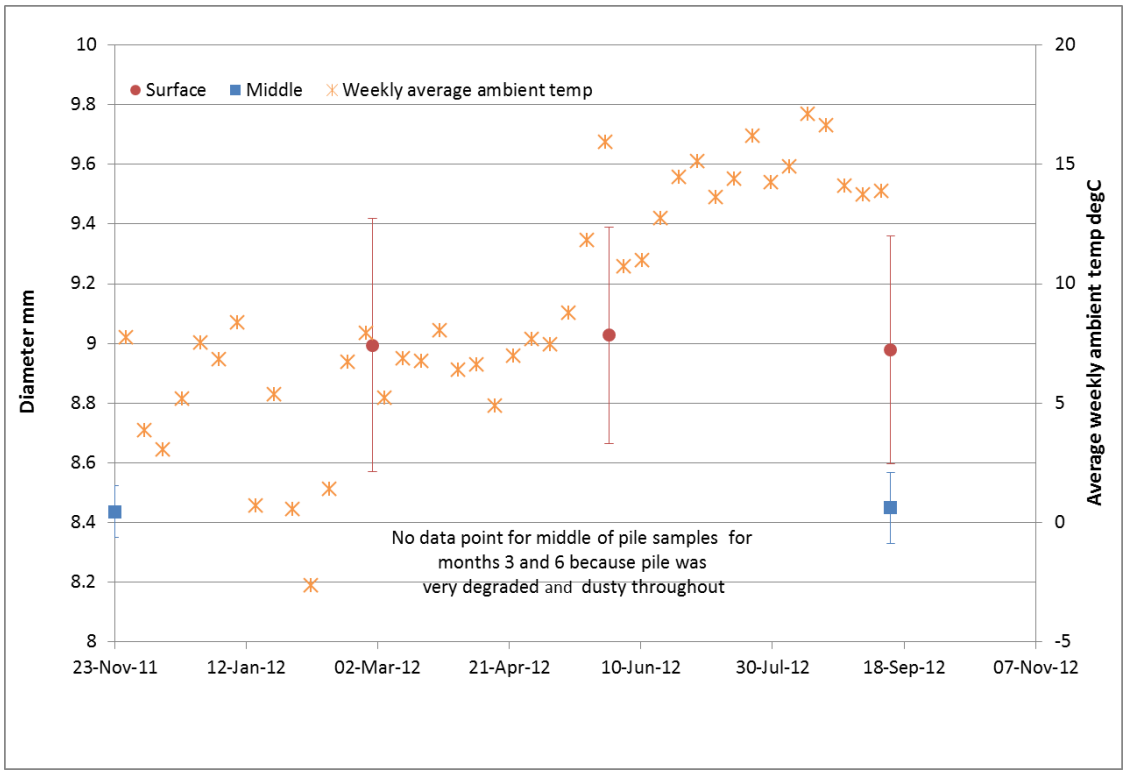

Figure C27

C.3.3. Axial compression strength

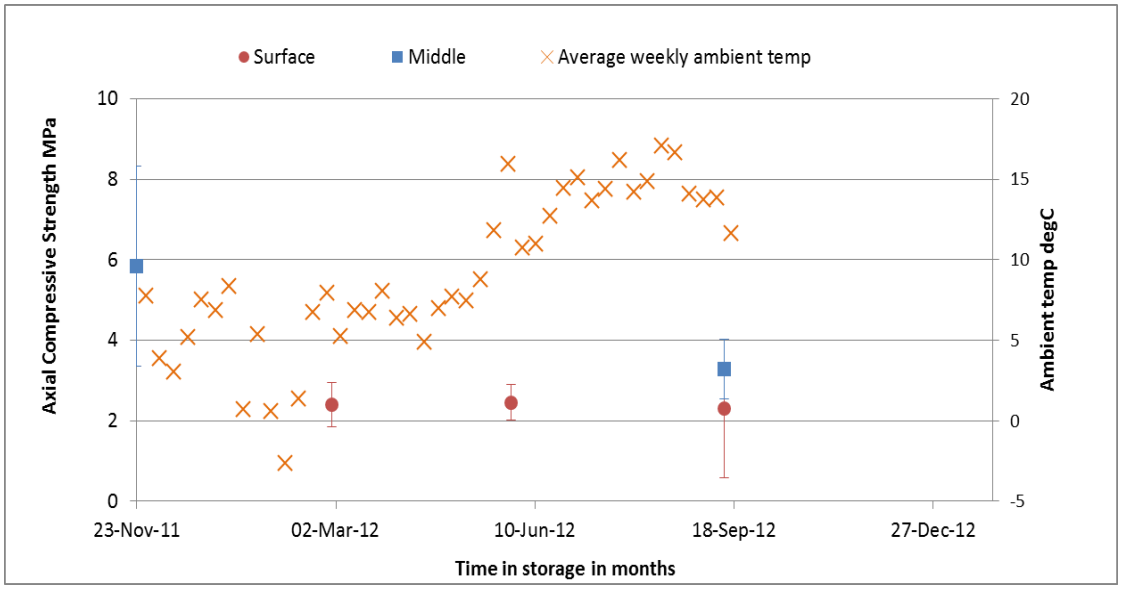

Figure C28

C.3.4. Diametrical compression strength

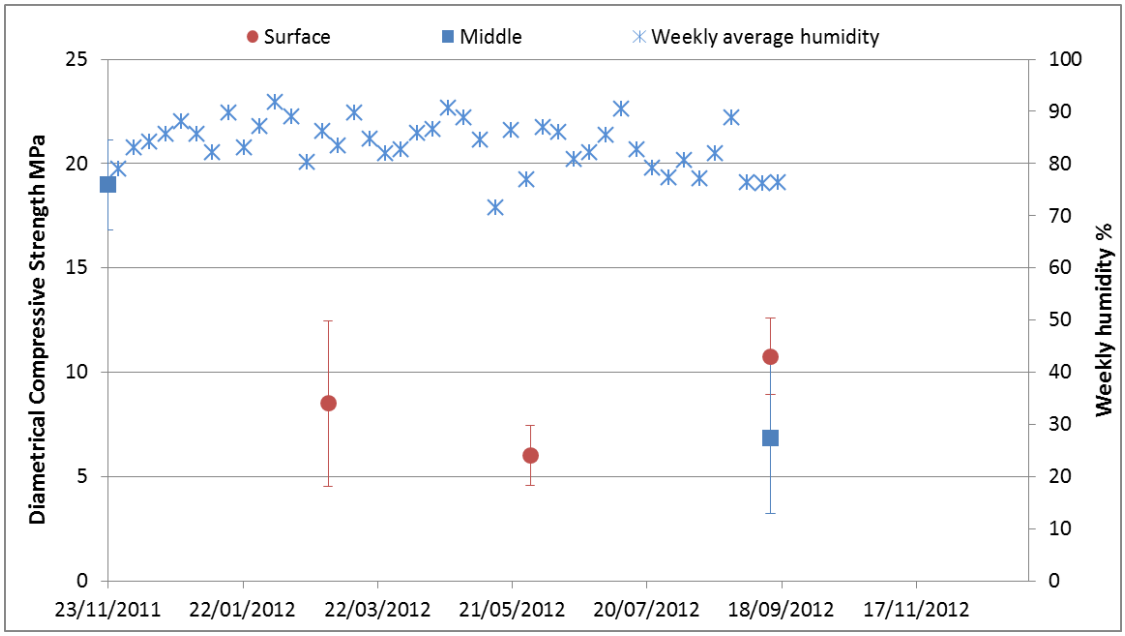

Figure C29

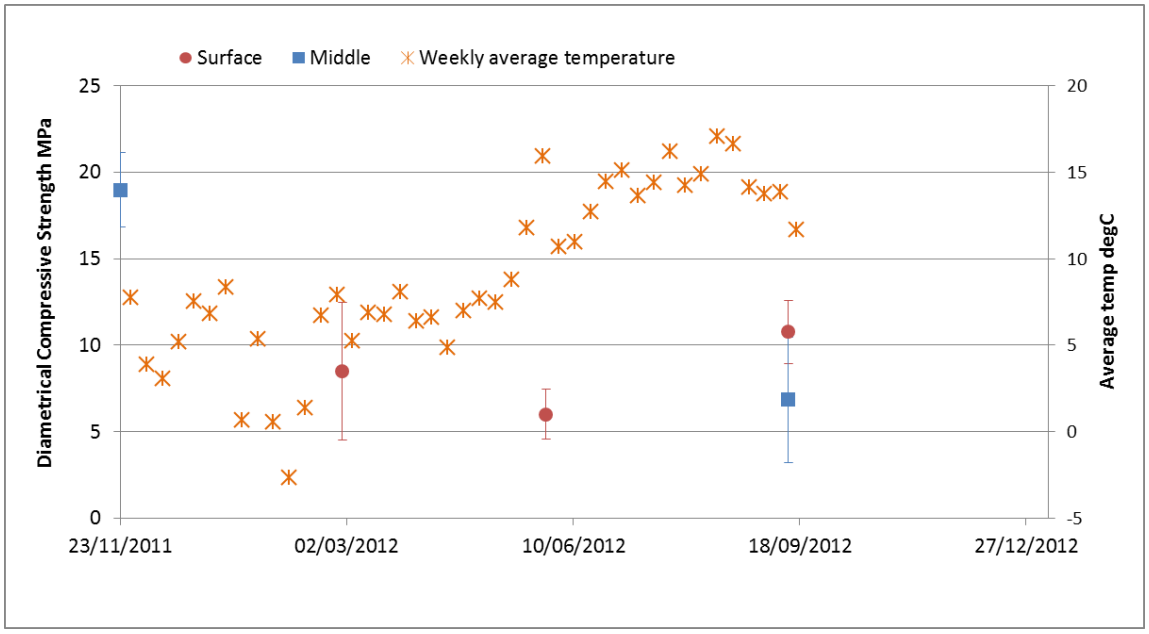

Figure C30

C.3.5. Inter-laminar shear modulus

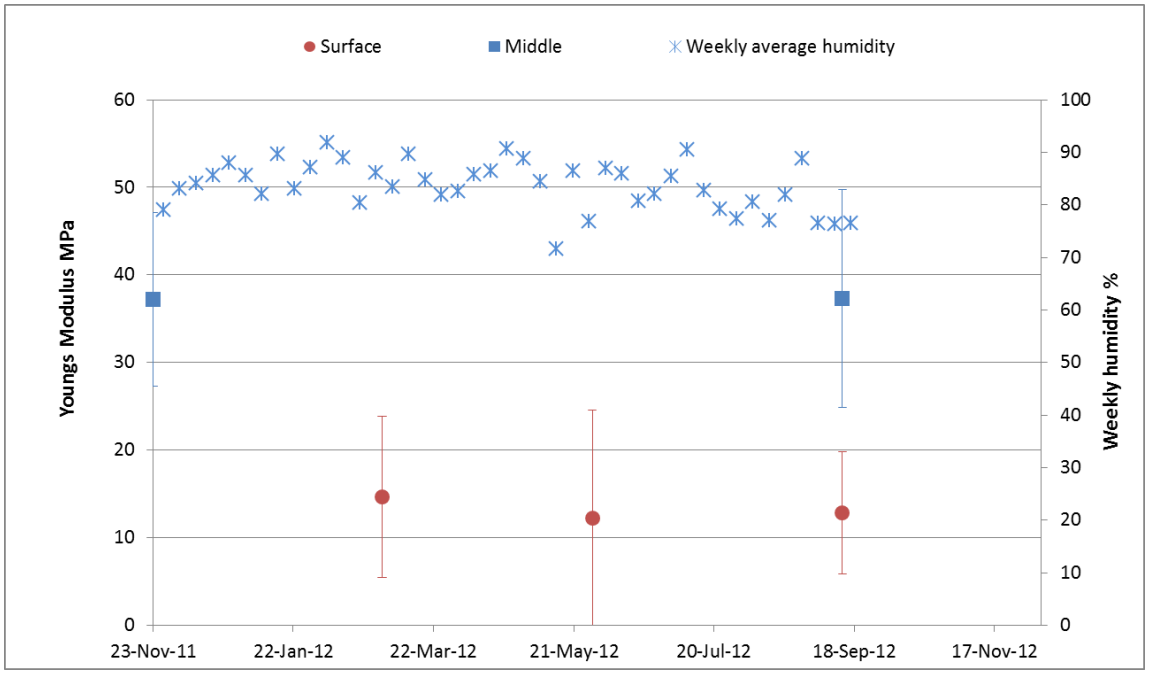

Figure C31

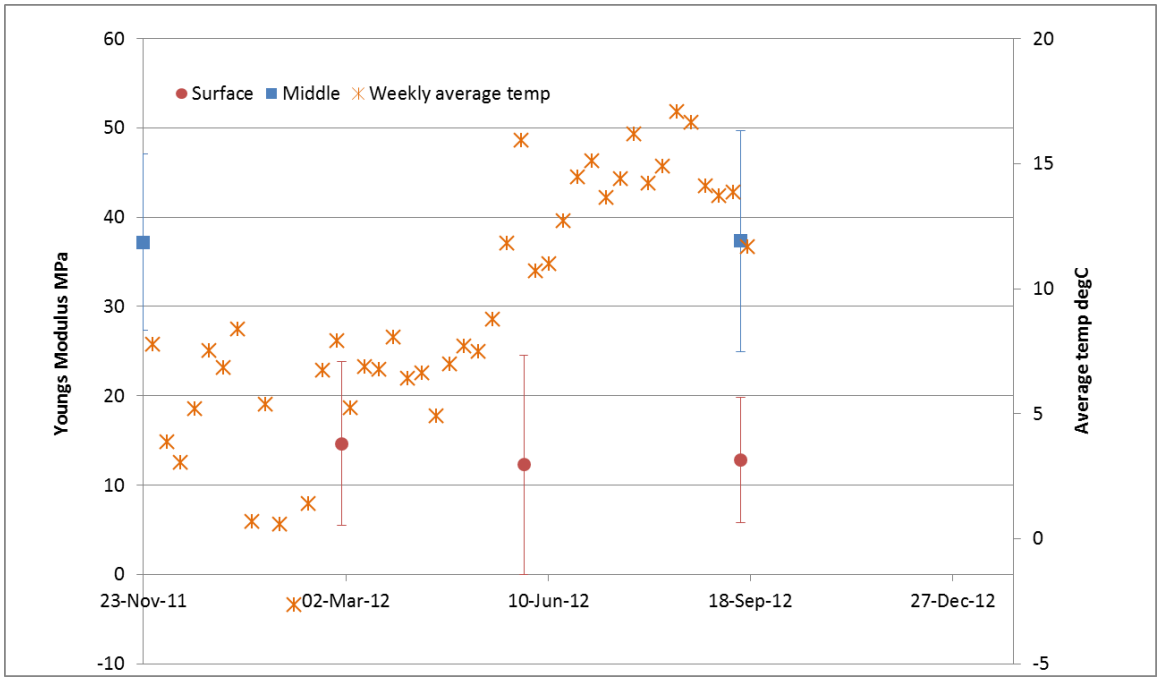

Figure C32

Appendix D

Masters student summer project on mechanical degradation of wood pellets during artificial degradation in a laboratory environment – paper to be submitted to 'Bioresource Technology' journal

CHANGES IN PROPERTIES OF WOOD PELLETS DURING ARTIFICIAL DEGRADATION IN A LABORATORY ENVIRONMENT

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ABSTRACT: This study is linked to a long term project on indoor and outdoor storage of biomass fuels. In order to fully understand the influence of environmental factors on the mechanical properties of woody biomass pellets three biomass pellets were artificially degraded in a laboratory environment under exposure to high humidity and heat. The fuels investigated included a white wood pellet, a torrefied pellet and a steam exploded pellet. Artificial degradation was achieved via two methods, in an enclosed environment where biomass pellets were sealed into a container and exposed to humidity and heat; and storage of biomass pellets in an environmental chamber where temperature and humidity were tightly controlled and monitored. During the degradation process, daily sampling and mechanical testing were conducted to compare extent of mechanical degradation of the different pellets. Durability testing and oven drying of the degraded biomass pellets were also performed at the end of the period over which the humidity (with and without heat) tests were carried out. The exposure of all three pellets to high humidity levels resulted in a drop in mechanical strength with time, as reflected by the shear and compression tests. The steam exploded pellets retained the highest strength when exposed to humidity. Exposing the pellets to heat combined with high humidity accelerated the drop in mechanical strength of all three pellet types. From the results obtained, conclusions and recommendations can be made on the best method of storing each type of biomass pellets to enhance efficient and effective handling and transportation with minimal occupational health hazards.

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Keywords: biomass, pellet, storage, torrefied, steam exploded, weather

1 INTRODUCTION

As generators continue their search for alternative energy sources, biomass remains a promising carbon-based renewable fuel [1]. Biomass fuel dedicated combustion and co-firing with coal are being utilised and optimised to improve fuel flexibility in power-plants and reduce greenhouse gas (GHG) emissions. Densified pelletized forms of biomass fuel are preferred because they have higher energy density and hence provide better economic viability in the areas of transport, storage and handling [2]. For biomass pellets as well as other forms of biomass such as chips and logs, a wide variety of research work is being carried out in each of the areas of sourcing and procurement, transport, storage and handling, conveying, milling, combustion, emissions and ash control. This paper however only focuses on the storage of biomass pellets.

The storage of biomass can result in fuel degradation, which can in turn result in handling, milling and combustion issues. A number of research projects have been carried out to characterise wood pellet degradation during storage. [3] carried out an extensive research on the changes in the properties of pelletized fuel during storage. Nine pellet assortments manufactured on a large scale from fresh and stored sawdust, bark and logging residues, were stored for five months in 1.3m^3 plastic bags in an unheated barn. The bags were tied at the top but not airtight. The wide range of property measurements carried out on pellet samples included: moisture content, ash content, calorific value, bulk density, pellet length and durability. The temperature in the middle of each bag was measured continuously. The main trends observed in the results are summarized below:

- The different types of pellets all showed a tendency to equilibrate to a moisture content of about 11%
- No significant changes were observed in the bulk density, individual pellet density, ash content and calorific value of the different pellets. The differences observed could be attributed to sample variations.
- No temperature surges were observed in the middle of the bags with the average temperature being a few degrees C above ambient in most cases
- Storage resulted in breaking up of the pellets, as reflected in the reduced pellet length. Furthermore the pellet durability was reduced during storage

[4] carried out a study on the effect of storage temperature on off-gassing and the physical properties of wood pellets. The storage temperatures investigated ranged between 30-50°C. The properties measured were % fines, pellet density, bulk density and durability index. The reactors were filled with pellets leaving a headspace of about 25 % and were insulated to mimimise loss of heat during heating. The off- gases were collected using air tight gas syringes and analyzed using gas chromatography. The emissions of CO (5000 ppm) and CO2 (10000 ppm) were relatively high at room temperature, but these values increased exponentially when the storage temperature was >30°C. At a storage temperature of 50°C a maximum concentration of CO2 of about 60000 ppm and CH4 3000 ppm was observed, whereas in the case of CO the maximum concentration of 18000 ppm was observed at a storage temperature of 40°C. The pellet % fines had significantly increased after exposure to elevated temperature where a maximum of 0.96 % was observed and whereas the loss of durability index has decreased by 32 % at 50°C. There were only marginal changes in other pellet properties like moisture content, pellet density and bulk density.

A similar study was carried out by [5] but at ambient temperature only. An added variable was the moisture content of the pellets. The gases were collected every 15 days using gas sampling bags. The gases were identified using gas chromatography. Results showed that the emission of CO was considerable and reached 800-900 ppm, CO2 around 1800 ppm and CH4 was around 25 ppm. The temperature of the pellets during the storage period was around 19±1°C. Increasing the moisture content of the wood pellets from 3.6 to 10% by adding water resulted in an increase in the temperature of the wood pellets by 3-4°C. At the end of the 150 day storage period, the pellets were very soft and around 70% of them were significantly disintegrated.

A long term indoor and outdoor storage trial on white wood but also thermally treated pellets is being carried out by [6] with monthly sampling and testing to determine the extent of chemical, mechanical and biological degradation and consequently the impacts on handling, milling and combustion. The occupational health and safety implications are also being considered. The results so far revealed that the investigated pellets show no significant chemical change during storage, but the extent mechanical degradation is significant.

In order to determine the environmental conditions which affect the mechanical properties of wood pellets the most throughout storage, a series of laboratory scale storage tests have been carried-out and they are reported in this paper. Three types of wood pellet have been tested and compared, including a white wood pellet, a torrefied pellet and a steam exploded pellet. They were

subjected to environmental variables such as humidity and heat in an enclosed environment and tested on a regular basis for changes in mechanical properties.

2 METHODOLOGY

Two storage environments were used in this work; in the first biomass pellets were enclosed in sealed buckets and subjected to environmental conditions of high humidity and temperature, and in the second pellets were tested in an environmental chamber at controlled temperatures and levels of humidity. For both storage methods, mechanical tests (flexural, compression) were carried out at regular intervals to check the fuel integrity as storage progressed. Pellet durability was carried out on fresh pellets and on degraded pellets at the end of the storage experiments.

Details of the two different storage setups used during this work are given below.

2.1 Artificial degradation experiments in an enclosed bucket environment

Buckets of 5 litre volumetric capacity were placed in a room with an average monitored ambient relative humidity and temperature of approximately 68% and 20^0C respectively. Two separate cases were studied, high humidity at ambient temperature and high humidity at elevated temperature as described below. The reason for using a sealed environment with high humidity and ambient temperature was that this replicated, at a small scale, what may be happening on storage sites.

2.1.1. High humidity (ambient temperature)

The high humidity (ambient temperature) experiment was conducted by filling a bucket with 1 litre of tap water at 22.3^0C (ambient). The pellets were placed, clear of the water, on a metallic mesh inside the bucket, typically the water surface being 100-150mm below the mesh. A type-T thermocouple probe (silicone type) connected to a temperature data logger was fitted into the small pellet pile to measure in-situ temperature. In addition, a Lascar EL-USB-2+ humidity datalogger was taped to the inside of the bucket lid (Figure 1) to monitor relative humidity levels. The bucket was sealed (air-tight) during the trial to increase in-situ humidity. The temperature data logger was calibrated and pre-set to record the in-situ bucket temperatures of the pellets at a frequency of 30 seconds, while the humidity data logger was pre-set to log in-situ relative humidity readings every 10 seconds with readings being downloaded every 24 hours, tests typically lasting three weeks. The temperature in each of the buckets stayed constant at about 20 ± 2°C.

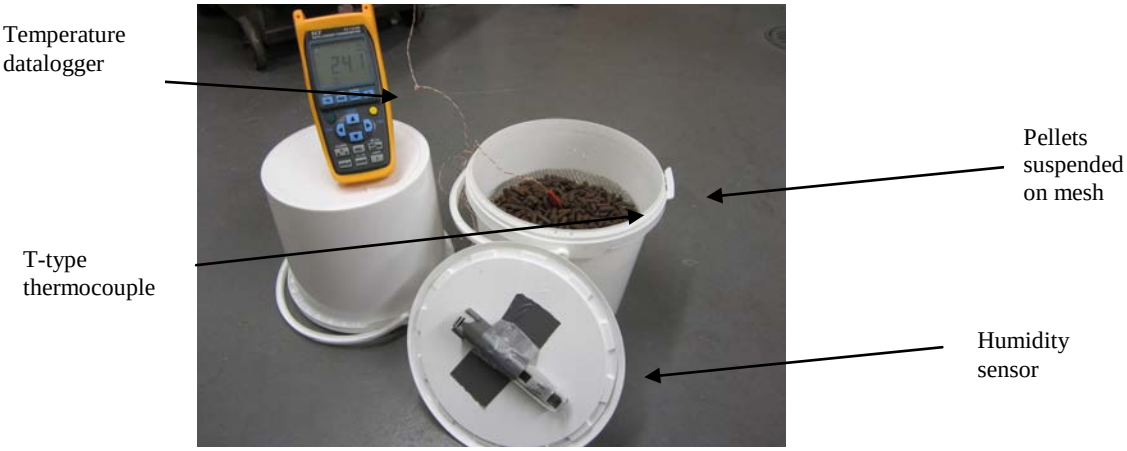


Figure 1: Instrumentation set up for enclosed high humidity trials, before sealing.

2.1.2. High humidity (elevated temperature)

A similar setup as in 2.1.1 was used in these trials. However the 1 litre of water in the bucket was introduced at an elevated temperature of 60^0C. Each morning, the cooled water in the bucket was replaced by fresh water at 60°C. This was to simulate a daily temperature regime whereby the temperature increases during a hot sunny afternoon and then decreases during the night and morning. The buckets were then sealed and submerged in an insulating box containing shredded bits of polyurethane and bubble nylon, to maintain the elevated temperature. Within the insulation box data loggers were used to measure background temperature and relative humidity values, and readings were extracted every 24 hours. Testing at elevated temperatures only lasted a week due to the increased degradation rate seen by the pellets. Figure 2 below shows the temperature time plot for the first three days of the test.

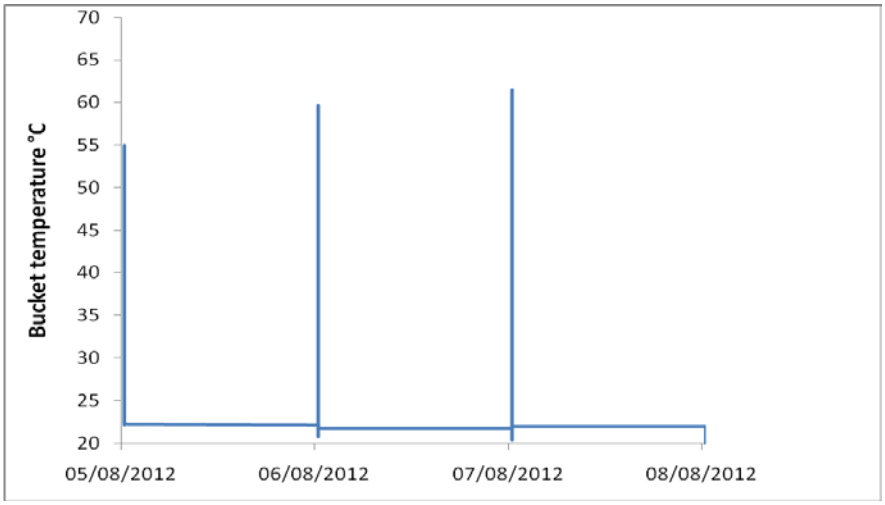


Figure 2: Temperature time plot

2.2 Environmental chamber experiments

In the enclosed bucket experiments described in section 2.1 above, pellets were exposed to uncontrolled temperature and humidity variations, which were

dependent on the laboratory ambient conditions. Whilst this replicates to some extent conditions that may be found on site, the variations in both temperature and humidity make it difficult to extract specific information about the impact of each separately. Therefore, a climate cabinet (TAS LT CL 600 Series 3) was utilised to enable the temperature and relative humidity to be set and controlled throughout the testing period. The chamber could be configured to keep temperature and relative humidity constant for a specified period of time or for a cyclic environmental condition to be programmed varying both the temperature and humidity as a function of time.

Approximately 100-150 g of each pellet sample were evenly placed in one layer on small-sized trays (280mm×220mm) and placed into the climate chamber compartment. The required temperature-humidity combination was entered manually via the digital interface on the chamber.

The following parameter combinations were used in the environmental climate chamber experiments (Table 1):

Table 1. Relative Humidity and Temperature settings for Environmental Chamber Tests

Parameter Combination	**Relative Humidity (rH)**	**Temperature ^{0}C**	**Exposure Duration**
High Humidity – Low Temperature	90%	20	3 days
High Humidity – High Temperature	90%	30	3 days
Low Humidity – Low Temperature	10%	20	4 days
High Humidity – Low Temperature	90%	10	24 hours
Low Humidity–High Temperature	10%	30	24 hours

3. PELLET TESTING TO MEASURE EXTENT OF DEGRADATION

3.1 Pellet sampling

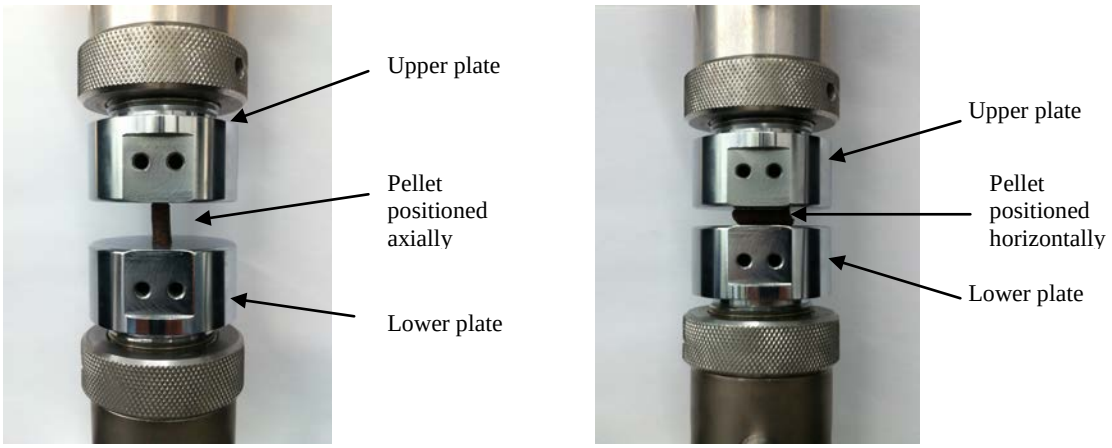
On a daily basis fifteen pellets were removed from each of the trials and axial compression, diametrical compression and shear/flexural tests were carried out. Five pellets were used for each of the tests to allow assessment of

variability and repeatability as biomass is inhomogeneous, although pellets exhibit more homogeneity than unprocessed biomass.

3.2 Compression test

In determining the strength of biomass pellet samples, an INSTRON dual column table top universal testing system (model 5969) was used to compress the pellets both axially and diametrically. The strength was determined as the minimum force at which the pellet cracks, similar to the approach used in [7] – [9]. The INSTRON mechanical tester was operated at a load cell capacity of 5kN at a ramp rate of 1mm per minute.

For the daily axial compression testing (Figure 3a), five pellets were ground at the end surfaces to 20 mm (±2 mm) in length. The grinding ensured that pellets could stand cylindrically with maximum stability on the 50mm metal base of the compression equipment. The opposing surface for compression tests was provided by a 50 mm diameter probe attached to the load cell. In the diametrical compression testing (Figure 3b), the pellets were positioned horizontally.



Figures 3a and b: Axial and diametrical compressions

In the axial and diametrical compression tests, the load was applied at a constant ramp rate and aborted after pellet failure (mostly by barrelling), with a plot of the compressive extension against compressive load being generated automatically. The pellets mean average compressive strength and maximum load at failure, including standard deviation of measured values, were calculated using five pellets per test per biomass type, in order to accommodate the wide range of variations in the pellet samples.

3.3 Inter laminar shear/flexural test

A shear test was conducted on the pellet samples to determine and compare the shear modulus. The shear modulus is a measure of the pellets resistance to crack deformation or stiffness. This inter-laminar shear test was performed based on a 3-point flexural test setup similar to ASTM D143-09, which are standard test methods for small clear specimens of timber [9]. For this test,

pellets were picked with a length of 18 mm (±1 mm) to achieve a geometry specification of L/D<2.5 in order to prevent possible errors during shearing and to maintain a level of uniformity in the shear pattern. By placing the pellets on the metal contact probes after measuring the diameter, the shear tests were executed on the same INSTRON mechanical tester used for the compression tests with the contact probes changed as shown in figure 4 below. The lower contact probe on which the pellets are placed has two circular contact points (5mm diameter) with a span of 10.2 mm between the centres of the two contact base. The force is applied from another probe attached to the load cell of 5kN, and with an extension ramp rate of 1mm/min. For each pellet type, five tests were carried out and standard deviations calculated. Flexural load-extension profile plots were generated for each repeat and the shear modulus calculated automatically.

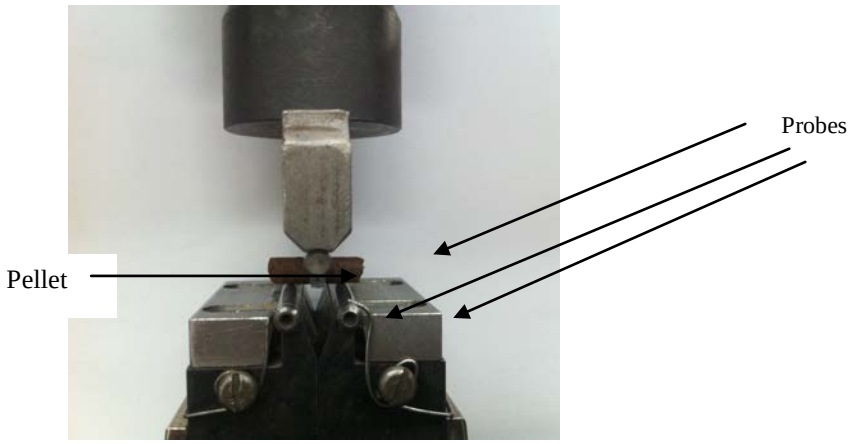


Figure 4: Shear test set up

3.4. Durability test

Mechanical durability test was conducted on fresh and degraded pellets, i.e. before the storage experiments and at the end of the storage period. This test was conducted to quantify the tendency of pellets to break during handling. The durability of biomass pellets is a common property used to compare the handleability of different pellets. The test simulates either mechanical or pneumatic handling and the tumbling can, Holmen tester and Lingo tester have all been used for measuring the durability of pellets [10]. Tumbling can method [11] is used to estimate the pellet quality in terms of pellet durability index (PDI), or, simply percent durability. This test simulates the mechanical handling of pellets and predicts the possible fines produced due to mechanical handling. During tumbling, pellets abrade and produce fines due to impact, and shearing of pellets over each other and over the wall of the tumbling can. After tumbling, the pellets are sieved using a sieve size of about 0.8 times the pellet diameter. The PDI or durability is calculated as the ratio of weight after tumbling over the weight before tumbling, multiplied by 100. [12] and [13] have both used mechanical durability as a test to characterise biomass pellets.

The pellet mechanical durability was conducted at E.ON New Build and Technology Limited, Nottingham, using a Dural II durability tester. For each of the two degradation routes assessed; approximately 100g sample of pellets was placed, and tumbled at a speed of 1600 rpm for 30 seconds, in the durability tester. The tumbled sample was then placed in a stack of sieves of varying sizes 4750, 3350, 2360, 1180, 710, 500, 250 and 75 µm arranged in descending order. The weight of biomass sample retained on each of the sieves was measured. The durability of the pellets was calculated as the weight percentage in the oversize fraction.

$$Durability = \frac{\left(M_{sample}\right) \times 100}{M_{total}}$$

Where M_{sample} = Mass of sample larger than 4750 µm, M_{total} = Total mass of sample

4 RESULTS AND DISCUSSION

The results from the artificial degradation enclosed bucket experiments are firstly described, including the shear, compression, durability and moisture trends. The results from the environmental chamber tests are then explained.

4.1 Enclosed bucket tests

The three types of pellets behaved differently when exposed to humidity, at ambient and elevated temperatures as summarised in table 2 below. For the high humidity (ambient) conditions, the period of testing was three weeks. For the high humidity (elevated temperature) conditions, the test lasted one week.

Table 2 – Physical appearance of biomass pellets at the end of testing.

	Steam exploded	**Torrefied**	**White wood**
High humidity (ambient)	- Pellets completely wet, - Sticky brownish condensate on container lid	- Crack formation on pellet surface, - Pellets mouldy after degradation	- No longer shiny surface, lighter colour - Pellet crack propagation to the core of structure imminent.
High humidity (elevated temperature)	- Pellets completely wet, - Brownish sticky condensate - Pellet crack, surface degradation	- Pellets crack and swell, - Integrity completely gone after second day of degradation	- Shiny coloration gone, - Pellets swelling and crack are drastic after first day; and disintegration starts after second day with pellets breaking down.

From visual inspection, the steam exploded pellets appeared to have been less affected by these degradation tests than the other two types of pellets. Figures 5 to 7 below show the steam exploded, torrefied and white wood pellets respectively before and after the humidity test at ambient temperature and elevated temperature.

Fig 5a: Fresh steam exploded

Fig 5b: Degraded (humidity ambient temp)

Figure 5c: Degraded (humidity elevated temperature)

Figure 6a: Fresh torrefied

Figure 6b: Degraded (humidity ambient temp)

Figure 6c. Degraded (humidity elevated temperature)

Figure 7a: Fresh white wood pellet

Figure 7b: Degraded (humidity ambient temp)

Figure 7c: Degraded (humidity elevated temperature)

The extent of degradation is reflected in the shear, compression and durability tests results detailed below.

4.1.1. Shear tests results

Figures 8 and 9 below show the average shear modulus against time for the three types of pellets in the humidity without heat (figure 8) and humidity with heat experiments (figure 9). The sample variation is illustrated by the error bars in each of the graphs.

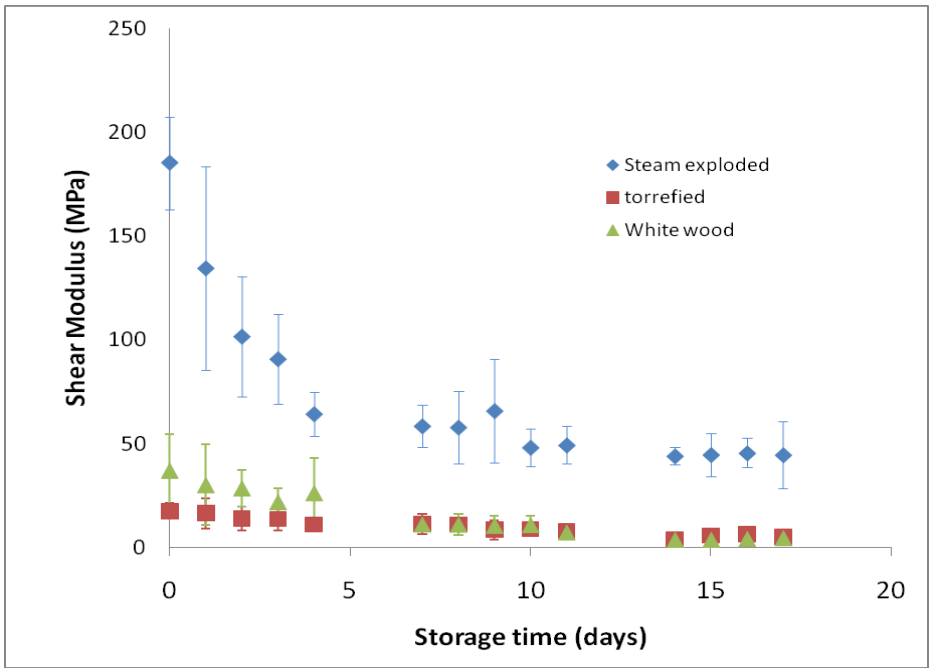


Figure 8: Shear test results for humidity experiments at ambient temperature

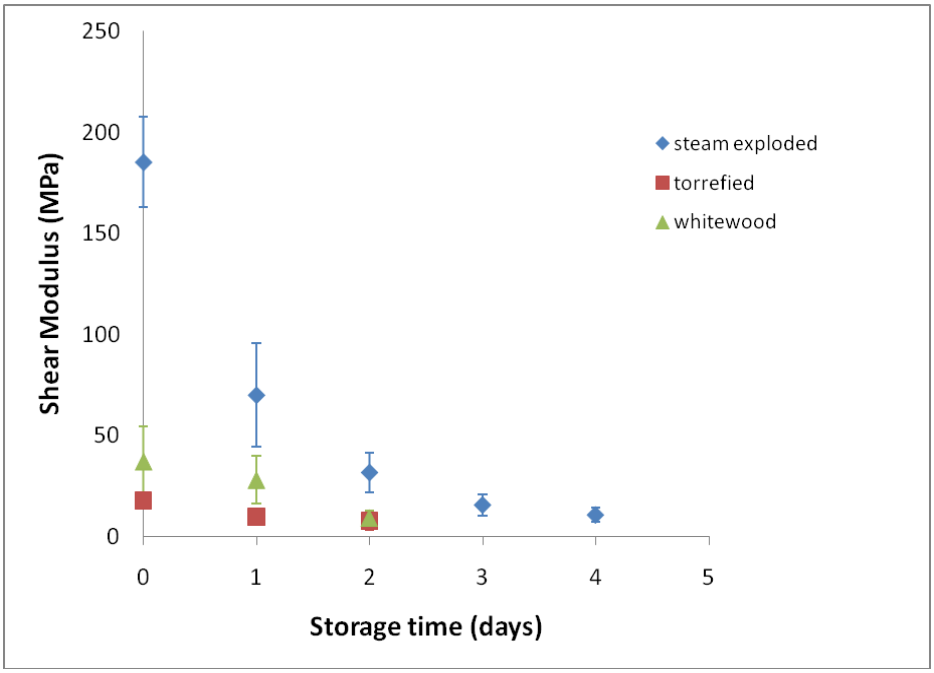


Figure 9: Shear test results for humidity experiments at high temperature

The introduction of heat to the humid environment (figure 9) results in more severe mechanical degradation, as evidenced by the drop in values for all pellets at day 5 of testing when comparing figures 8 and 9.

4.1.2. Compression tests results

Similar trends were observed when the axial and diametrical compression strengths of the pellets were plotted against time (figures 10-13). For both the white wood and torrefied pellets, a significant decrease in the compression strength is seen for both test cases. However when exposed to humidity and heat the torrefied and white wood pellets showed severe and rapid disintegration, meaning it was not possible to test axial compressive strength after day 1 or diametrical compression testing once exposure occurred. For the steam exploded pellets the drop in compressive strengths was more significant in the humidity coupled with heat experiments but it was still possible to test the pellet for both axial and diametrical compression. This shows that a warm and humid environment is not favourable for the storage of pellets.

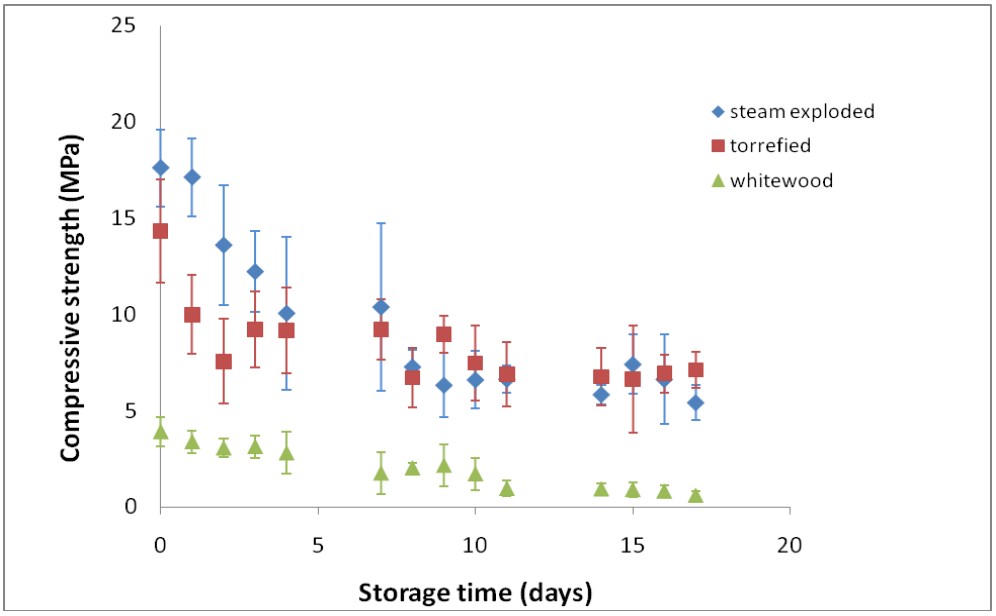


Figure 10: Axial compressive strengths (high humidity at ambient temperature)

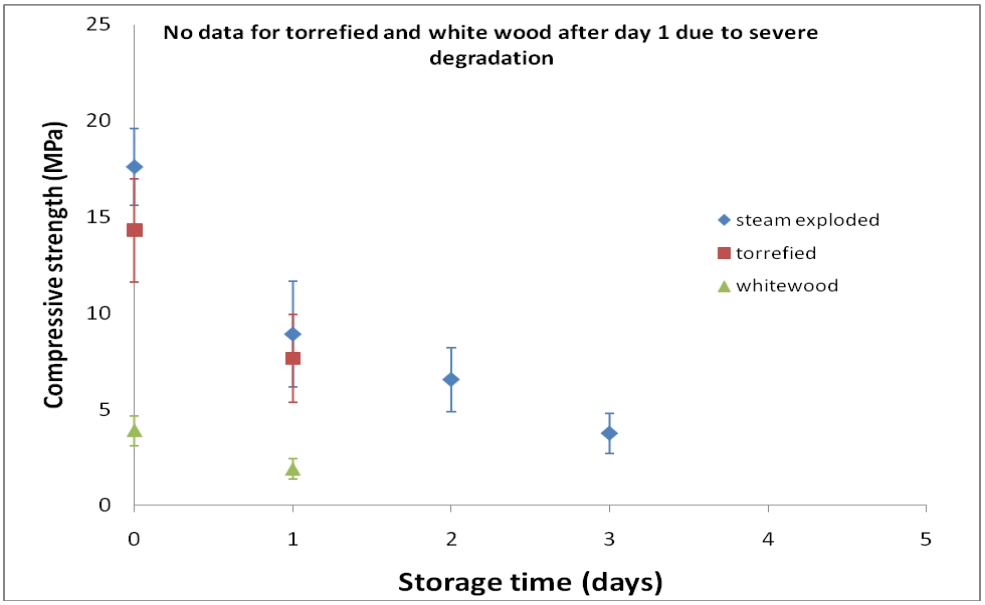


Figure 11: Axial compressive strengths (high humidity at elevated temperature)

An interesting observation is that the whitewood pellets have a much lower axial compressive strength than the torrefied and steam exploded pellets. This could be due to its larger and less uniform particle size distribution, causing the particles to slip with respect to one another while the compressive force is applied. The coarser and less uniform particles on the white wood pellet could be observed visually.

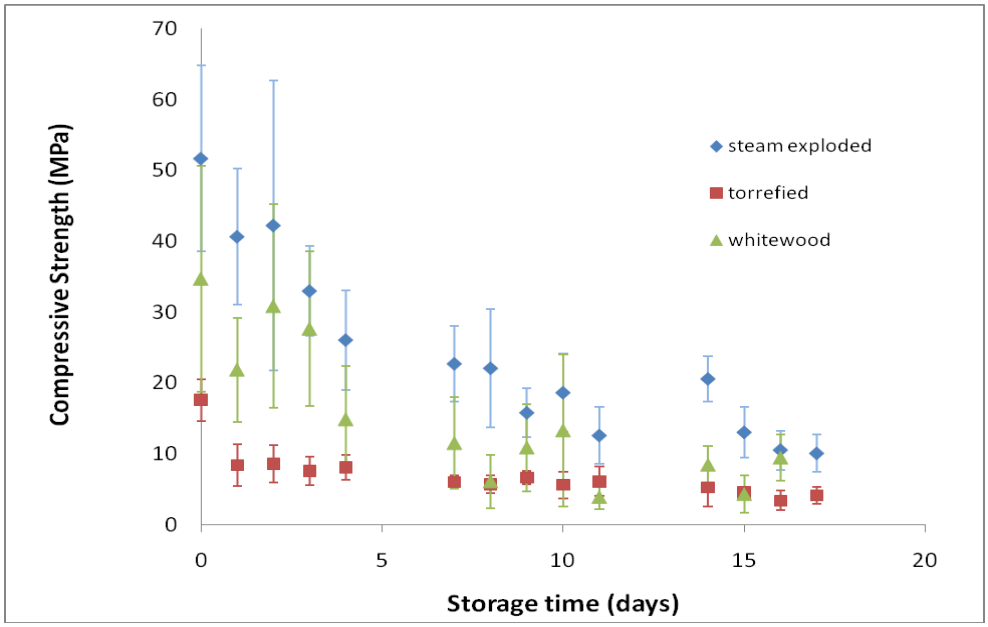


Figure 12: Diametrical compressive strengths (high humidity at ambient temperature)

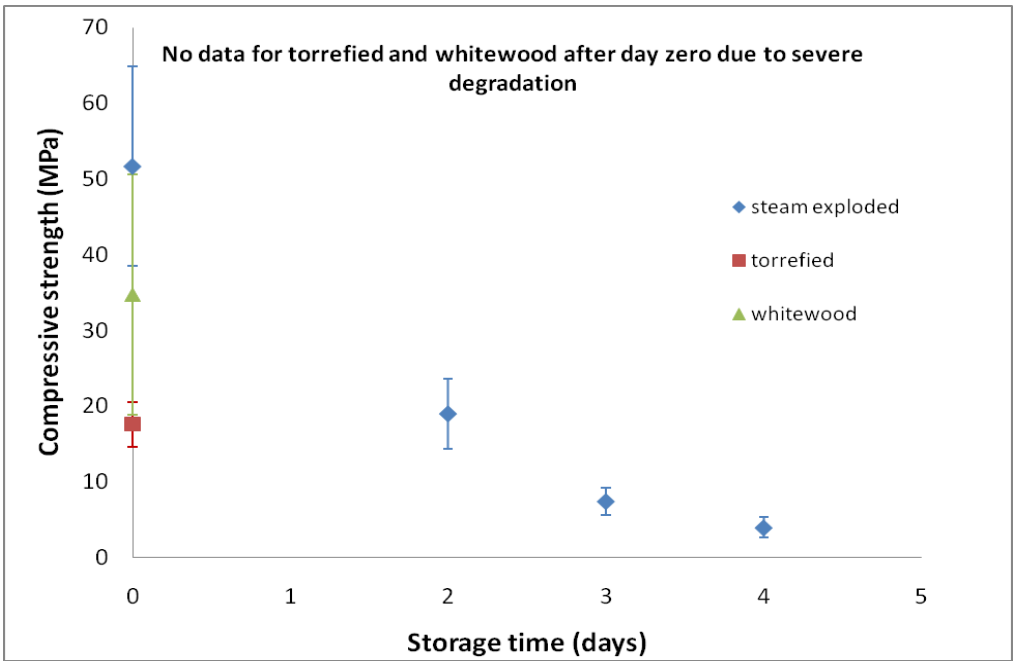


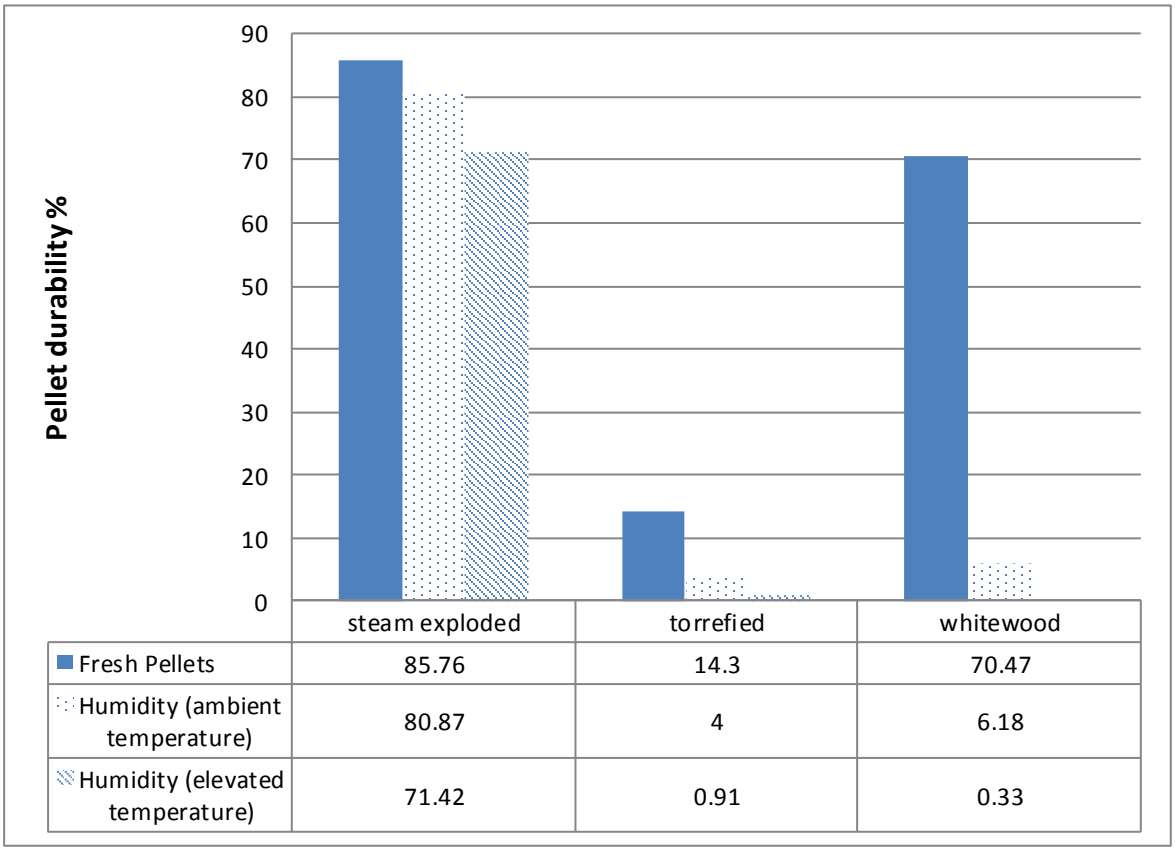
Figure 13: Diametrical compressive strength (high humidity at elevated temperature)

The diametrical compression strength of the white wood pellets at the beginning of the experiment is higher than that of the torrefied pellets, but the degree of sample variation is also much larger.

4.1.3. Durability test results

The durability test was carried out on fresh pellets and on degraded pellets at the end of the testing period. The results, summarized in figure 14 below,

confirm the degradation trends shown by the shear and compression tests.



	steam exploded	torrefied	whitewood
Fresh Pellets	85.76	14.3	70.47
Humidity (ambient temperature)	80.87	4	6.18
Humidity (elevated temperature)	71.42	0.91	0.33

Figure 14: Durability of biomass pellets before and after storage

4.2 Environmental chamber experiments

Figure 15 below shows the changes in the shear modulus of the steam exploded pellets at different combinations of humidity and heat, with figures 16 and 17 showing the same data for the torrefied and white wood pellets respectively. The data from the axial and diametrical compression tests was less conclusive than for shear tests due to large sample variability and possibly because the environmental chamber tests were run over a short time period. Durability tests were not performed on the pellets after environmental chamber testing.

As shown in table 1 in section 2.2 below, the different relative humidity-temperature combinations were run over different time periods. Due to the limited availability of the chamber, not every combination could be run for 3 days or more. The high humidity-high temperature (90% rH/20°C and 90% rH/30°C) experiments were run for 3 days while the 90% rH/10°C test was run for 24 hours. For the 90% rH/30°C combination, daily sampling and testing took place. For the 90% rH/20°C combination, there were two additional samples on the first day of testing, namely after 1.5 and 4.5 hours. This was done to better understand at what point the biggest drop in strength/stiffness was encountered.

The two combinations at a low relative humidity of 10% were tested less rigorously as the bucket experiments clearly showed the high impact of relative humidity on pellet degradation. While the 10% rH/20°C test was run for 4 days, the 10% rH/30°C test lasted only 1 day.

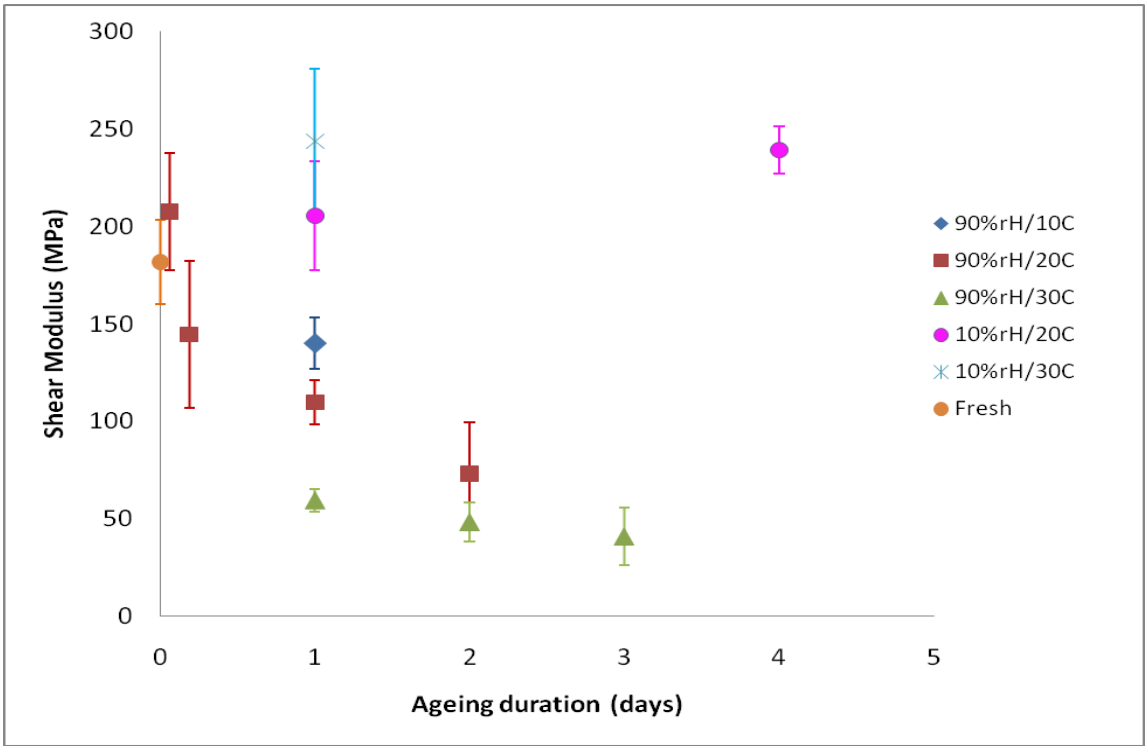


Figure 15: Shear moduli of steam exploded pellets at different humidity-temperature combinations

From figure 15, the exposure of these pellets to the highest temperature and relative humidity combination 90% rH/30^{0}C caused the largest decrease in shear modulus after 24 hours, and cumulatively after the 72 hours ageing duration, when compared to the other relative humidity/temperature pairs. At a high relative humidity of 90%, the rate of degradation increased with temperature from 10^{0}C to 30^{0}C. When the humidity is dropped to 10%, which is lower than ambient, the shear modulus increases, which further confirms the impact of humidity on the pellets' stiffness. At the low relative humidity of 10%, an increase in temperature from 20^{0}C to 30^{0}C did not result in an appreciable difference in the rate of pellet degradation. This shows that humidity is the main factor affecting the decrease in pellet integrity during storage and handling.

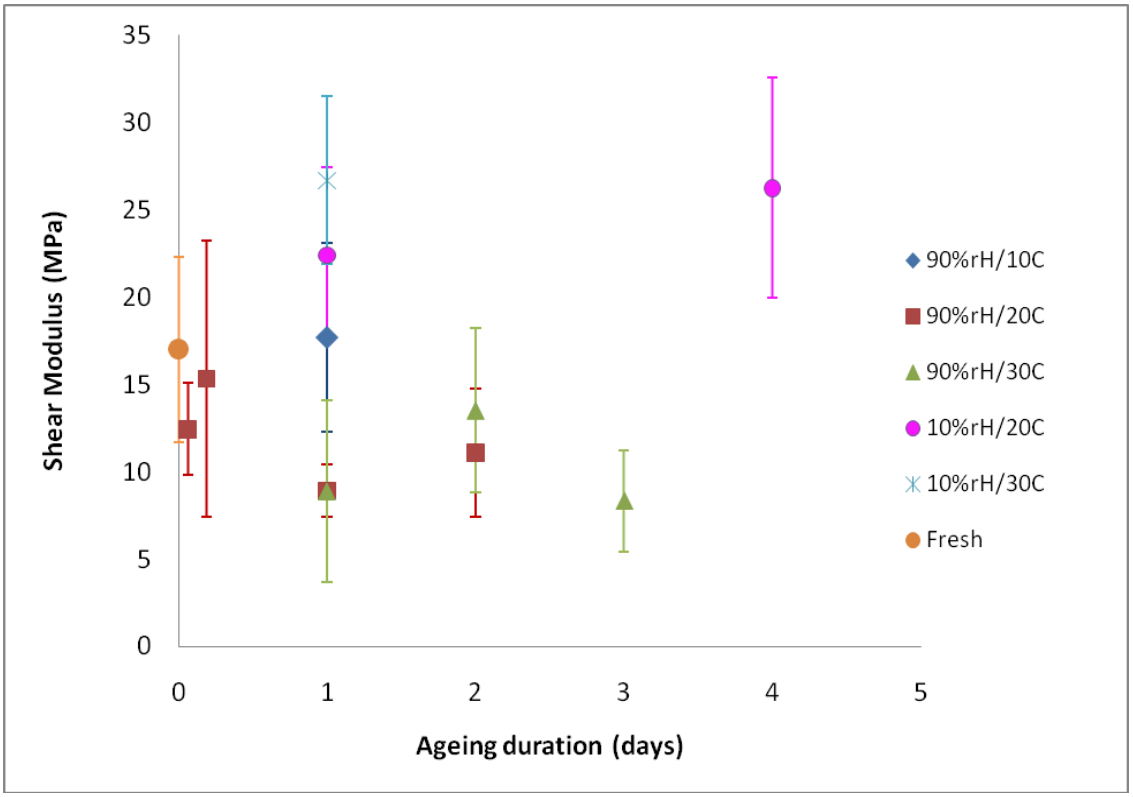


Figure 16: Shear moduli of torrefied pellets at different humidity-temperature combinations

At a humidity of 90% and a temperature of 10°C, there was no significant change in the shear modulus of the torrefied pellets. However, at the higher temperatures of 20°C and 30°C, the pellets showed lower mechanical stiffness. However, there was no appreciable difference in the shear modulus drop when the temperature was increased from 20^0C to 30^0C. Like for the steam exploded pellets at a low humidity of 10%, the shear modulus increases.

Figure 17 below shows the changes in the shear modulus of the white wood pellets at different combinations of humidity and heat.

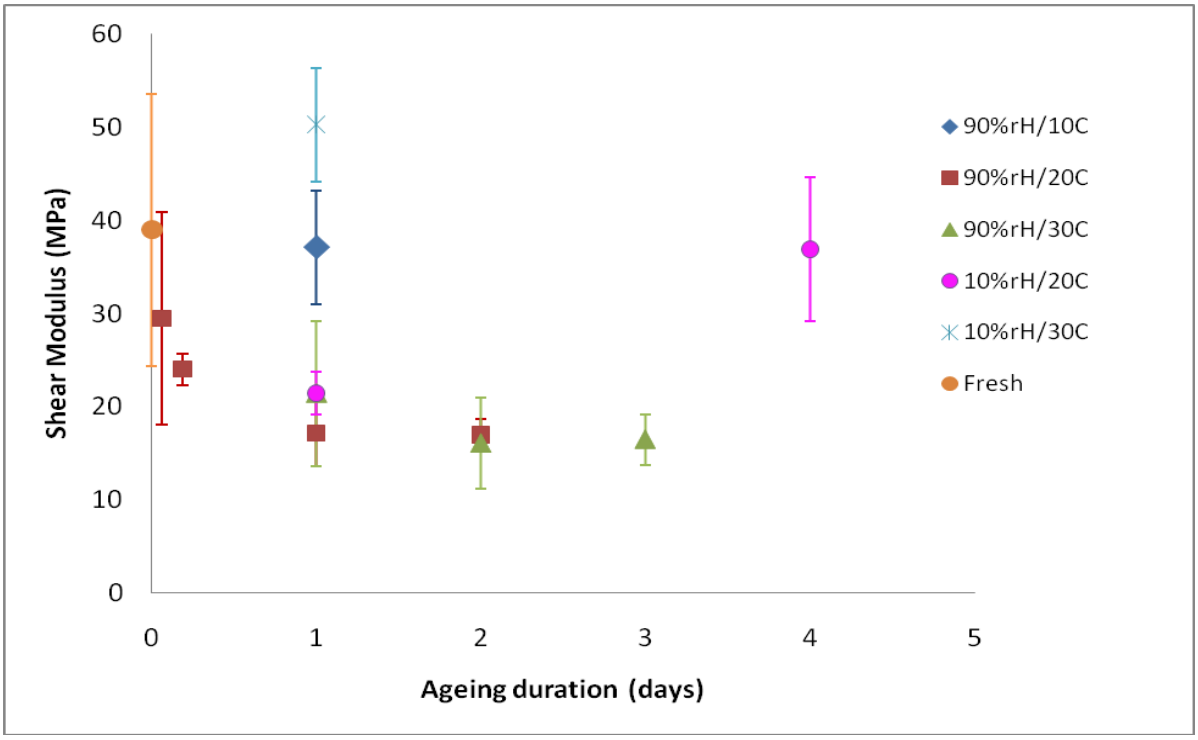


Figure 17: Shear moduli of white wood pellets at different humidity-temperature combinations

Like the torrefied and steam exploded pellets, high humidity had an impact on the whitewood pellets with heat inclusion increasing the rate of degradation further. Unlike the steam exploded and torrefied pellets, the white wood pellet exhibited high sensitivity even to the low humidity of 10%, as shown by the decrease in stiffness with time.

5 CONCLUSIONS

1. Steam exploded biomass pellets have the highest mechanical strength. The lower strength of the torrefied pellets is probably due to low content of natural binders (lignin) which could in turn be due to the high temperature at which the raw biomass materials were torrefied prior to pelletisation.

2. Exposure of all three types of biomass pellets to high humidity increases their moisture content level and reduces pellets strength. When humidity is coupled with heat, the degradation rate is more severe and faster.

3. The environmental chamber experiments confirm the results from the laboratory bucket experiments. For the three biomasses, the degradation was most significant at a combination of high temperature and high humidity, at 30^0C and 90%rH respectively. Storage at low humidity at

10%rH (20^0C and 30^0C) results in an increase in the shear modulus of the steam exploded and torrefied pellets.

6 FURTHER WORK

This project could be expanded to include a wider range of wood pellets and could be further developed and refined into an established methodology which could be used to measure and compare the mechanical degradation of pellets and the variety of pellets tested could be expanded to include non-wood pellets such as energy crop pellets and agricultural residue pellets amongst others. Moreover the set of results can be used to explain the trends observed in the long term project by [6] on the large scale indoor and outdoor storage of biomass fuels.

7 ACKNOWLEDGEMENTS

- The lead author is grateful to E.ON New Build and Technology Ltd. UK and E.ON Climate and Renewables for providing the steam exploded and torrefied wood pellets and to Coppice Resources Ltd. for providing the white wood pellets for testing.

8 REFERENCES

[1] Department of Energy and Climate Change UK. Available at www.decc.gov.uk

[2] Obernberger I, Thek G. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. Biomass and Bioenergy 2004; 27: 653-669.

[3] Lehtikangas P. Storage effects on pelletized sawdust, logging residues and bark. Biomass and Bioenergy 2000; 19: 287-293.

[4] Tumuluru JS, Kuang X, Sokhansanj S, Lim J, Bi Tony, Melin SA. Effect of storage temperature on off-gassing and physical properties of wood pellets. American Society of Agricultural and Biological Engineers Annual International Meeting 2008 – Agricultural and Biological Engineers 2008.

[5] Tumuluru JS, Kuang X, Sokhansanj S, Lim J, Bi Tony, Mani S. Studies on off-gassing during storage of wood pellets. American Society of Agricultural and Biological Engineers Annual International Meeting 2008 – Agricultural and Biological Engineers 2008.

[6] Graham S, Eastwick C. Snape C, Quick W. Degradation of biomass fuels during artificial
storage in a laboratory Environment. International Journal of Low Carbon Technologies
2012; 7(2): 113-9.
[7] Stelte W, Holm JK, Sanadi AR, Barnsberg S, Ahrenfeldt J, Henriksen UB. A study of bonding and failure mechanisms in biomass pellets from different biomass resource. Biomass and Bioenergy 2011; 35: 910-918.
[8] Rose E, Graham S, Eastwick CN. Investigating the effects of temperature, humidity and precipitation on the mechanical and chemical properties of thermally treated hardwood pellets. MEng Mechanical Engineering individual research paper 2012. The University of Nottingham UK.
[9] ASTM Standard D143-09, "Standard test methods for small clear specimens of timber", ASTM International, West Conshohocken, PA, 2009, DOI: 10.1520/D0143-09, www.astm.org.
[10] Kaliyan N, Vance Morey R. Factors affecting strength and durability of densified biomass products. Biomass and Bioenergy 2009; 33: 337-359.
[11] ASABE Standards. S269.4: Cubes, pellets, and crumbles – definitions and methods for
determining density, durability, and moisture content. St. Joseph, MI: ASABE; 2003.
[12] Gil MV, Oulego P, Casal MD, Pevida C, Pis JJ, Rubiera F. Mechanical durability and
combustion characteristics of pellets. Bioresource Technology 2010; 101: 8859-8867.
[13] Theerarattananoon K, Xu F, Wilson J, Ballard R, Mckinney L, Staggenborg S, Vadlani P, Pei ZJ, Wang, D. Physical properties of pellets made from sorghum stalk, corn stover, wheat straw and big bluestem. Industrial Crops and Products 2011; 33: 325-332.