An Industry-Led Investigation for Safe Storage at Full Scale of Compressed Wood Pellets including Self-Heating and Spontaneous Combustion

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The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Large scale self-heating of wood pellets in storage is a major concern worldwide during long term storage due to the potential for fire with safety concerns for both personnel and plant. Additionally, any adverse publicity resulting from an incident involving biomass is likely to result in negative effects to the biomass industry as a whole.

Self-heating could lead to serious accidental fires, causing enormous damage and danger to workers. The aim of the research in this thesis was to provide underpinning data and understanding in order to implement safe storage of wood pellets at Drax Power Ltd. Thus, the self-heating rates at different temperatures, and under different levels of inerting, were experimentally determined, and the thermal properties were measured for wood pellets produced for Drax Power Ltd. In addition, the thesis covers measurements at three scales; laboratory, temporary storage of approximately 40,000 tonnes through to largescale storage at approximately 280,000 tonnes spread equally over 4 domes… the largest storage of pellets ever investigated.

The factors such as moisture content, pellet age and environment temperature were investigated and their impacts on the self-heating process were analysed. Moisture content has a significant effect on effective on self-heating but ventilation of the store was found to be more critical. Pellets age and environment temperature are two major factors impacting the self-heating and off-gassing process. The self-heating rate is significantly increased at higher a temperature and eventually will lead to a thermal runaway when the ambient temperature is high enough.

Based on all measured properties, a self-heating model was developed to predict the self-heating process and thermal runaway in large wood pellet dome of ~120,000m^3. This work contributed to the inerting of nitrogen gas to maintain an atmospheric (and therefore assumed within biomass) oxygen content less than 10% and monitoring protocols with the focus on carbon

monoxide along with the understanding of temperature tracking for the large-scale dome storage of wood pellets, which is now used by Drax Power Ltd.

Safety of all personnel working with biomass is paramount concern for Drax Power Ltd., which this thesis contributed to personal exposure monitoring and standard setting for gas exposure, mainly carbon monoxide and dioxide along with dust exposure. The handling of pellets through the supply chain and on site can cause the pellets to degrade and fine wood particles and dust is present within bulk pellets. Any release of wood dust into the atmosphere can pose a risk to health. Wood dust can cause serious health problems. Wood dust is a recognised respiratory irritant, sensitizer, asthmagen and for a limited number of species, a potential carcinogen (hard woods). Contact with wood dust can also lead to skin sensitisation and dermatitis.

Drax Power Ltd, recognises it’s duties under Health and Safety and is committed to minimising the risk to health from wood dust in its premises. Both hardwood and softwoods dusts have a Workplace Exposure Limit (WEL) of 5mg/m^3, which must not be exceeded. These are limits placed on the amount of dust in the air over an eight–hour shift. However the Control of Substance Hazardous to Health Regulations 2002 (as amended) requires exposure to wood dust to be “As low as reasonably practicable” (ALARP).

Drax Power Ltd will manage exposure to wood dust to as low as reasonably practicable. The primary means of preventing exposure, is by containment of wood dust within the materials handling and processing plant. Dust control equipment such as Local Exhaust Equipment (LEV), will be used in conjunction with handling and processing plant to ensure that dust levels are kept to as low as is reasonably practicable. For certain operational and maintenance tasks it is necessary to use additional procedural controls to ensure that the risk of exposure to wood dust are managed effectively.

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Preface

The rapid increase in the production and use of various types of biomass as energy carrier also leads to an increase in handling and storage activities throughout the supply chain. Biomass is a broad description of many plant materials with different chemical composition, moisture content and physical characteristics, each requiring special attention in order to comply with safety and health regulations. Some types of biomass used today such as wood (pellets) are commercialised as biofuel commodities traded around the globe, while others are under-going intense research to explore the potential for commercial use.

The properties of a biomass material and the intended use determine how the material should be safely transported and stored. Self-heating, off-gassing and dust explosions are significant challenges for the industry that have already resulted in significant losses of capital investments and even tragic loss of life. Likewise, exposure to biologically active material, such as moulds and spores may form a serious hazard for the health of workers involved. With the growth of the bioenergy sector, it is important not only are that opportunities for bioenergy implemented in an efficient and economic manner, but also safely.

Although this publication does provide the reader with significant understanding of the relevant safety issue as well as several guidelines for handling, storage and transportation, it is important to realise that differences in material also lead to differences in risks and needs for safety measures. Every individual situation needs to be carefully assessed. The topic also remains important as new solid biofuels enter the market.

CHAPTER 1. INTRODUCTION AND CONTEXT

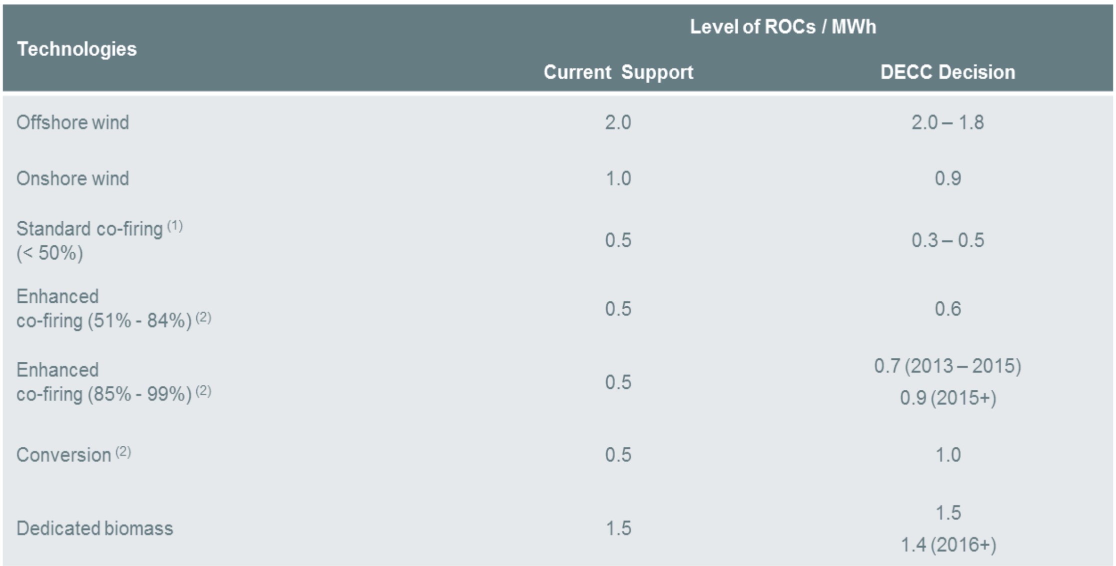
1.1. Drax Power Ltd. Power Station General Background

Drax Power Ltd. is the operating subsidiary of Drax Power Ltd. Group plc and the owner and operator of Drax Power Ltd. Power Station, the largest, cleanest and most efficient coal-fired power station in the UK. (Drax Power Ltd., 2016). Originally built, owned and operated by the Central Electricity Generating Board (CEGB), Drax Power Ltd. Power Station was constructed and commissioned in two stages. Stage one (units 1, 2 and 3) was completed in 1974 and some 12 years later in 1986 stage two (units 4, 5 and 6) was completed. It is the newest and therefore most efficient coal-fired power station in the UK. (Drax Power Ltd., 2016). Each of the units has a capacity of 660MWe, giving a total capacity of just under 4,000MWe, making Drax Power Ltd. the largest coal-fired power station in the UK. (Drax Power Ltd., 2016). Drax Power Ltd. sell the large majority of power through the wholesale market, with the remainder sold through recently acquired supply company, Haven Power Limited. (Haven, 2016) Drax Power Ltd. currently provide enough power to meet 7% of the UK's electricity needs. (Drax Power Ltd., 2016). As well as being an important strategic asset nationally, Drax Power Ltd. is also vital to the local economy. Drax Power Ltd. Power employs some 760 people and supports many other local jobs indirectly. (Drax Power Ltd., 2016)

In 1988, Drax Power Ltd. became the first power station to invest in the retrofit of flue gas desulphurisation (FGD) equipment, making Drax Power Ltd. the cleanest coal-fired power station in the UK by removing at least 90% of the sulphur dioxide (SO_2) from emissions. Through retrofitting boosted over-fire air (BOFA) technology on all their boilers Drax Power Ltd. are reducing still further emissions of oxides of nitrogen (NO_X). At the same time, by-products of the coal combustion and FGD processes are recycled through their further use in the construction industry. (Drax Power Ltd., 2016). Drax Power Ltd. is committed to reducing their emissions of carbon dioxide (CO_2) and have announced two major initiatives that together will have the capability to save over three and a half million tonnes of CO_2 each year. The largest steam turbine modernisation project in UK history will see the high pressure and low pressure turbines upgraded and on completion will save one million tonnes of CO_2 a year. (Drax Power Ltd., 2016)

By mid-2010, Drax Power Ltd. had the capability to deliver a target of producing 12.5% of their output from renewable fuels, this saved over two and a half million tonnes of CO_2 a year. Previously, this capability was not utilised to the full due to today's low level of regulatory support available for biomass co-firing. However, in July 2012 the Government announced its decisions on the future support levels for all renewable technologies, including biomass electricity. The support levels for biomass electricity demonstrate a clear preference for fully converting individual generating units to run on biomass. The level of support for different renewables via Renewable Obligation Credits (ROC's) is given in Table 1.1 Level of Renewable obligate credits.

Table 1.1. Level of Renewable obligate credits



Technologies	Level of ROCs / MWh	
	Current Support	DECC Decision
Offshore wind	2.0	2.0 – 1.8
Onshore wind	1.0	0.9
Standard co-firing (1) (< 50%)	0.5	0.3 – 0.5
Enhanced co-firing (51% - 84%) (2)	0.5	0.6
Enhanced co-firing (85% - 99%) (2)	0.5	0.7 (2013 – 2015) 0.9 (2015+)
Conversion (2)	0.5	1.0
Dedicated biomass	1.5	1.5 1.4 (2016+)

The mechanism underpinning any future investment is the Renewables Obligation. This involves Renewable Obligation Certificates ('ROCs') being awarded for electricity that is generated using a range of specified technologies, which includes biomass co-firing and biomass conversion. The preliminary announcement of ROC bandings in October 2011 detailed that enhanced co-firing (i.e. more than 85% by heat) of biomass would receive support of 1

ROC/MWe of generation and dedicated biomass would receive 1.5 ROC/MWe (falling to 1.4 ROC/MWe in 2016). No mention was made to support for conversion at that time. At this level of support, Drax Power Ltd. further expanded its co-firing operations and between 2011 and 2012 undertook significant further research and development to ascertain whether it was possible to co-fire increasing quantities of biomass (including 100% biomass) at the Drax Power Ltd. site.

The final ROC bandings were confirmed in July 2012 and revealed that support for co-firing (at levels less than 85%) had reduced from 1 ROC/MWe to 0.5 ROC/MWe of electricity generated. The final ROC support for full conversions was also confirmed at 1 ROC/MWe. Due to the lower level of support being made, co-firing biomass was considered to be uneconomic. Following the announcement of the final ROC bandings, and based upon preliminary research and development findings, Drax Power Ltd. confirmed plans to fully convert three of the six generating units to run entirely on sustainable biomass.

1.2. Drax Power Ltd. Power Station Conversion History

1.2.1. Co-Firing Of Coal And Biomass

The station tested co-firing biomass in the summer of 2003, and in doing so was the first power station in the UK to be fueled by wood. The initial trial of 14,100 tonnes of willow was locally sourced from nearby Eggborough. (Gow, David 2004). Since the trial, the station's use of biomass has continued. It invested in direct injection for firing the biomass, whereby it bypasses the pulverising mills and is either injected directly into the boiler or the fuel line, for greater throughput. (Drax Power Ltd., 2009).

In 2009 a target was set for 12.5% of the station's energy to be sourced from biomass, and the shift to biomass was intended to contribute to the aim of cutting CO_2 emissions by 15%. (Drax Power Ltd., 2009). At that time the station burnt a large range of biomass, mostly wood pellets, sunflower pellets, olive, peanut shell and rape meal. The majority came from overseas (Drax Power Ltd., 2007) which is still the case today. To support this, a 100,000 tonne per annum capacity Straw pelletisation facility was constructed at Capitol Park, Goole in 2008 and opened 2009 (Drax Power Ltd. 2010, Hull Daily Mail 2007). Construction of specialised biomass handling facilities began in 2009 at the Port of Tyne and at Drax Power Ltd. (Port of Tyne 2009).

1.2.2. Proposed New Build Biomass Plant

In the 2000's Drax Power Ltd. Group applied for planning permission to build a new 300 MW power station, fueled entirely by biomass, to the north of the station; the Ouse Renewable Energy Plant was expected to burn 1, 4 million tonnes of biomass each year, saving 1,85 million tonnes of CO_2 emissions, and expected to create 850 construction jobs and 150 permanent jobs created once opened, through direct and contract employment (Drax Power Ltd., 2009). Plans were submitted to the Department of Energy and Climate Change in July 2009 for review; if permission was granted, construction was scheduled to begin in late 2010 and to take up to three and a half years (The Pres, 2013). Two other 300 MW biomass plants were planned by Drax Power Ltd. at the ports of Hull and Immingham (CoalTrans, 2008). In 2012 Drax Power Ltd. group abandoned plans for the discrete biomass plant development, due to changes in government subsidies for biomass energy production favoring plant conversion over new build plant. It switched to a project to convert half of the units at its existing plant to biomass firing. (Macalister, 2012).

1.2.3. Full Firing With Biomass

In September 2012 Drax Power Ltd. Group announced the conversion to full firing with biomass of three of its six units. The first unit was online by June 2013, the second unit by 2014; and the third will be completed by 2017; initially a biomass supply had been secured for the first unit. The cost was estimated at £700 million ($1.13 billion), including modifications to fuel mills and boilers and the construction of storage structures and conveyors for the wood pellet fuel. Each unit consumes about 2.3 million tonnes of biomass yearly, requiring an estimated annual total of 7.5 million tonnes by 2017. This is equivalent to two-thirds of Europe's entire energy biomass consumption in 2010, and requires 1,2 million ha (4,600 sq mi; 12,000 km^2) of forest to supply on a continuous basis

(Lundgren and Morales, 2012). North America was expected to be the source of the vast majority of the biomass, although some would be domestically sourced willow and elephant grass (Selby Times, 2009)

Drax Power Ltd. Group's decision was enabled by a new UK government policy, effective in April 2013, to award 1.0 tradable ROCs (renewable obligation certificates) per megawatt of power generation from coal power plants that are fully converted to burn biomass; CEO of Drax Power Ltd., Dorothy Thompson stated the company intended to become a predominately biomass-fueled energy producer (Haven, 2012). By April 2013 financing for the scheme included £190 million through sale of shares, £100 million from Prudential/ MandG UK Companies Financing Fund, £50 million from the UK Green Investment Bank, and £75 million Friends Life (underwritten by HM Treasury), as well as a £400 million credit facility (www.pennenergy.com, 2013).

2013 also saw construction of 1-million-tonne-per-year wood pelletizing plants at Morehouse Parish, Louisiana, and Gloster, Mississippi. Fuel would be shipped by road and rail to the port of Baton Rouge, Louisiana then shipped in 50,000-tonne cargo ships to UK (Lovell, 2013). In the financial report for 2013, Drax Power Ltd. announced that an additional 2 million tonnes pelletisation capacity was being considered, likely to be built in the US (Fordaq, 2014). The final outcome of this construction was 2 plants at Drax Power Ltd. Biomass with the capacity to produce approximately 900,000 tonnes of wood pellets annually at two plants: Morehouse BioEnergy and Amite BioEnergy

These facilities are designed to minimize waste by fully utilizing all sourced wood material – including bark and other residue – in the manufacturing process. Both facilities are outfitted with industry leading process automation to improve safety and efficiency. Drax Power Ltd. Biomass operates the Baton Rouge Transit facility at the Port of Greater Baton Rouge, the closest deep-water port to the two plants. Drax Power Ltd. custom-built the facility to process and ship up to two million tonnes of pellets annually. Drax Power Ltd. pellets arrive at the facility by rail from the Morehouse plant, and by truck from the Amite plant. The Baton Rouge Transit Facility also receives pellets from third party manufacturers in the region. The pellets are safely off-loaded and stored in specialized domes outfitted with dust collection and fire detection/suppression technology. The Transit Facility is operated in conjunction with a local partner, Host Terminals, and it serves as the final domestic stop for all Drax Power Ltd. Biomass pellets destined for export. Figure 1.1 shows the locations of the Drax Power Ltd. Biomass USA sites

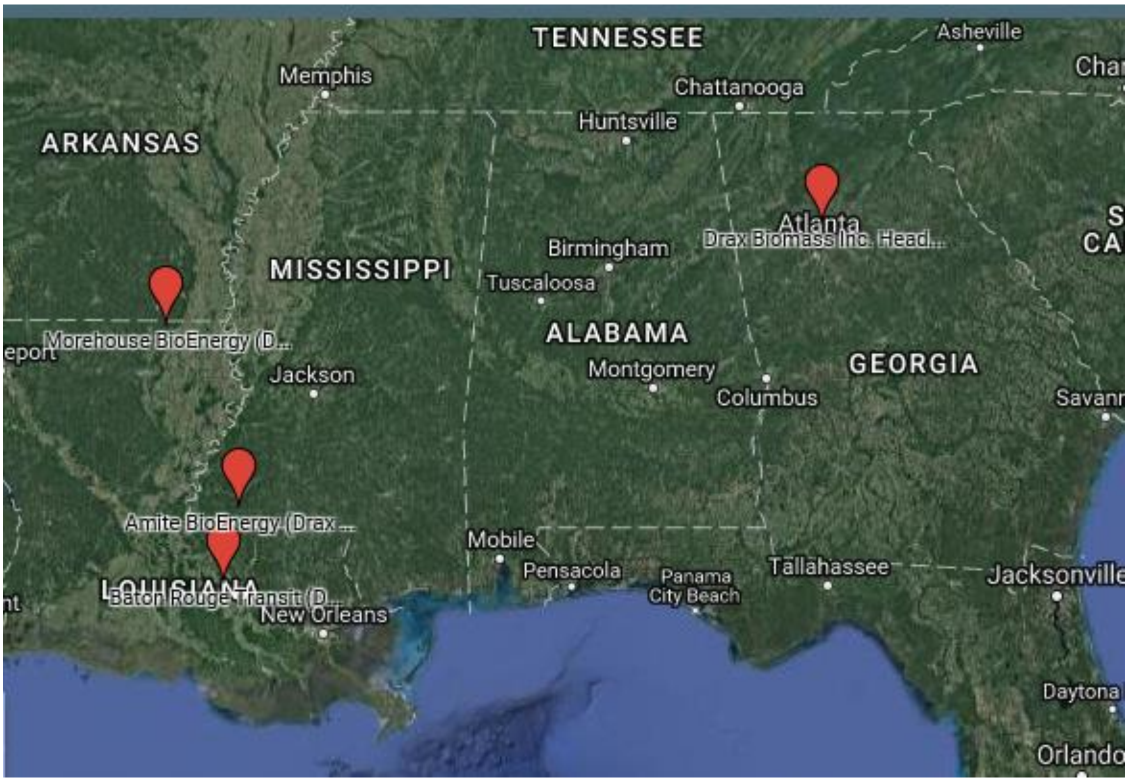


Figure 1.1. Locations of Drax Power Ltd. Biomass USA sites shown by the red markers

In 2013 the company signed an agreement with ABP to develop handling facilities at the Port of Hull, Immingham and Grimsby (ClimateWire, BBC 2013). Construction of automated facilities began in 2013, creating capacities of 3 and 1 million tonnes per year at the ports of Immingham and Hull respectively, adding to the 1.4 million tonne per year Port of Tyne biomass facility built in 2009 (biomassmagazine.com, 2013). In the same year a new design of a covered rail wagon with high volumetric capacity for transporting the low density biomass pellets was unveiled for use by Drax Power Ltd. in the UK; 200 wagons of the type were ordered (Railway Gazette, 2013). At Drax Power Ltd., pellets would be stored in domes, and transferred by a pneumatic conveyor system before grinding to dust for use (ClimateWire, BBC 2013).

The Shepherd Building Group was contracted to construct the biomass handling and storage facilities at Drax Power Ltd., with RPS Group as the civil engineer. The design included automated rail to storage handling, screening and storage facilities consisting of four 50 by 63 m (164 by 207 ft) high by wide storage domes with a capacity of 110,000 m^3 (3,900,000 cu ft) (www.rpsgroup.com. 2013). The concrete dome technology was supplied by E and D Company, PLLC (trading as Engineering System Solutions, ES2) and Dome Technology LLC (www.dometechnology.com 2013).

By July 2013 one firing unit had been converted, and was functioning correctly. The second unit was converted by May 2014, initially co-firing an 85% biomass/coal mix due to limited biomass supply (McKenna, 2014).

In April 2014 Drax Power Ltd. was awarded a renewable Contract for Difference (CFD) subsidy for biomass based power generation on another converted coal firing unit, but a third unit, which had been previously marked as eligible for CFD funding was excluded; Drax Power Ltd. Group then legally challenged the decision, initially obtaining a ruling in its favor, which was overturned in the Court of Appeal (Chazan, 2013. In July 2014 the High Court ruled in Drax Power Ltd.'s favor. (The Telegraph, 2014)

Biomass conversion at Drax Power Ltd. led to it requiring 82% of UK biomass imports from the USA in 2014 (60% overall of all US wood pellet export), a large factor in a 40% yearly increase in biomass export from that country; USA sourced imports represented 58% of Drax Power Ltd.'s biomass use in 2014, with 22% from Canada (U.S. Energy Information Administration, 2015). The Baton Rouge port facility was completed by April 2015 (Drax Power Ltd., 2015). In mid-2015 Drax Power Ltd. reached an agreement with Peel Ports to construct a 3 million ton per year biomass importation facility at the Port of Liverpool, estimated at a cost of £100 million. The rail connected facility was to include 100,000 tonnes storage, and be constructed by Graham Construction (www.bioenergy-news.com, 2015), this was successfully completed and operational by 2015. In

September 2015 Drax Power Ltd. Group and Infinis began a legal action against the UK government due to claimed insufficient notice being given about the withdrawal of a climate related tax exemption (see Climate Change Levy) - Drax Power Ltd. claimed the change would reduce its earnings by £30 million (Reuters, 2015). The claim was rejected by the High Court in February 2016 (utilityweek.co.uk. 2016).

Work in this thesis supported the progression to biomass and in particular, the development of storage protocols and monitoring approaches.

1.3. Benefits Of Biomass Utilisation

Biomass can provide a clean, renewable energy source that could dramatically improve the environment, economy and energy security (Ayhan, 2001, Demirbas and Demirbas, 2010). Biomass is considered to be CO_2-neutral (Ayhan, 2003, Sami et al., 2001, Ayhan, 2001, Müller-Hagedorn et al., 2003, Gupta and Demirbas, 2010, Abbasi and Abbasi, 2010) as it does not contribute to a net release of CO_2 into the atmosphere during combustion and/or other conversion. The same amount of CO_2 used for its previous plant growth and photosynthesis is released during this conversion process (Abbasi and Abbasi, 2010, Gupta and Demirbas, 2010, Ayhan, 2003, Ayhan, 2001). When a new batch of biomass is reproduced using CO_2 via photosynthesis, the whole cycle repeats (Gupta and Demirbas, 2010) and this helps with the recycling of atmospheric CO_2 which consequently does not contribute to the greenhouse effect (Ayhan, 2003). Also, other harmful emissions like SO_2 and NO_x are greatly reduced, particularly when displacing coal with biomass, due to the inherent low amount of sulphur (Molcan et al., 2009, Sami et al., 2001, Ayhan, 2001) and nitrogen (Molcan et al., 2009, Sami et al., 2001) in certain biomass.

In addition the use of otherwise disposed/landfilled biomass for power generation potentially reduces the problem of shortage in landfill area. More importantly, it reduces the release of methane gas, CH_4 (Ayhan, 2003, Sami et al., 2001), which is produced through the natural decomposition of biomass (Ayhan, 2001). CH_4 is 21 times more potent than CO_2 in terms of greenhouse effects (Ayhan, 2001, Demirbas, 2000).

1.4. Sustainability Of Biomass

Biomass is a clean, renewable source of energy (Ayhan, 2001, Demirbas and Demirbas, 2010). And if well managed can provide a long term consistent supply of energy. It is fundamental to Drax Power Ltd. that the biomass they consume is sustainable and legal. They have a dedicated sustainability team whose role is to ensure the biomass meets the requirements they have set in the Sustainability Policy and the criteria for sustainable biomass as established by the UK government.

Many factors affect the sustainability of the biomass supply chain and these are detailed in the following sections. As the sustainability of the biomass is a fundamental part of Drax Power Ltd.'s business, they make every effort to ensure that all their supplies comply with the following principles:

- Significantly reduce greenhouse gas emissions compared to coal-fired generation. (>65% reduction compared to some standard coal power stations).
- Not endanger food supply or communities where the use of biomass is essential for subsistence (for example heat, medicines and building materials)
- Not adversely affect protected or vulnerable biodiversity and, where possible, give preference to biomass production that strengthens biodiversity
- Deploy good practices to protect and/or improve soil, water (both ground and surface) and air quality
- Contribute to local prosperity in the area of supply chain management and biomass production
- Contribute to the social wellbeing of employees and the local population in the biomass producing areas
- No net release of carbon from the vegetation and soil of either forests or agricultural land

These biomass sourcing principles are based on the developing regulatory and policy initiatives of the UK, European Union and other markets (Drax Power Ltd., 2016). Over time Drax Power Ltd. is seeking to amend or improve these principles by working with accredited bodies to develop the use of internationally recognised standards and principles which will apply to all of their biomass procurement activities. Accordingly, Drax Power Ltd. will:

1. Use their purchase contracts to ensure their suppliers comply with these principles and provide Drax Power Ltd. with the required information to demonstrate that these sustainability principles are being met.
2. Participate with applicable regulatory and policy initiatives to share experience, learn, and help shape policy that will ensure sustainable biomass fuels throughout the UK and abroad.
3. Systematically review these principles and their application to anticipate, meet and lead sustainability policy in the UK and all of the countries in which we operate.
4. Engage a qualified third party to implement a rigorous programme of audit and verification of biomass supply chains to ensure compliance against these principles and our policy.

As a result of this policy Drax Power Ltd. aims to procure biomass only from supply chains that comply with these principles and Drax Power Ltd. strives to reduce greenhouse gas emissions by at least 70% in comparison to coal-fired generation. Furthermore, Drax Power Ltd. engages with qualified third parties (E.g. Forestry Commission, or consultants) to develop and implement a rigorous programme of audit and verification of biomass supply chains to ensure compliance against these principles and policy.

1.4.1. Other Benefits Of Biomass

There is no region within the UK that cannot produce biomass (Biomass Energy Centre, 2008). This reduces the heavy reliance on fossil fuels, which in general, are imported from a limited number of countries. More rural areas will be developed under different grants and schemes offered by the government to promote green energy, particularly through energy crops, such as the Energy

Crops Scheme (DEFRA, 2011). This helps to revitalise the rural communities (Ayhan, 2001). In addition the development and utilisation of biomass creates up to 20 times more jobs than coal and oil do (Macedo, 2005). This ranges from transportation, pelletisation to downstream maintenance. The National Non-Food Crops Centre, (NNFCC) estimates 30,0000 new jobs in the bioenergy sector by 2020 – with more than half of those jobs being permanent. Electricity from biomass could similarly offer up to 18,000 jobs by 2020 and anaerobic digestion a further 2,500.

In total this could generate between 35,000-50,000 jobs in bioenergy by 2020. The majority of jobs are likely to be technical roles, primarily in the engineering and construction sectors, required during both the construction and operation phase of new bioenergy plant. In addition to this there are clear employment opportunities for the UK biomass supply sector; including roles in feedstock production, harvesting, processing and haulage. However the number of people employed in the sector will be highly dependent upon the level of uptake of the technologies, origin of the feedstock's and the supply chain structures used.

In certain countries like the US and Western Europe, the agricultural sector is producing food surpluses, which has led to a policy to set aside land to prevent excessive food production (Peter, 2002). The introduction of energy crops to these lands is desirable as compared to being kept fallow. Also, the food surpluses contribute to biomass production in the form of waste.

In addition to the benefits brought about by biomass mentioned previously, there are other factors which play a role in encouraging the establishment and development of biomass utilisation. The potential threat posed by climate change, due to the high emission of greenhouse gases, has become a major stimulus for renewable energy sources in general (Peter, 2002). Biomass, which is considered as CO_2-neutral (Ayhan, 2003, Sami et al., 2001, Ayhan, 2001, Gupta and Demirbas, 2010, Abbasi and Abbasi, 2010), is desirable in mitigating the global warming issue as it does not contribute to greenhouse effect (Ayhan, 2003). Other emissions like SO_2, NO_x and CH_4 are also greatly reduced.

Advancement in technology and research relating to more efficient conversion methods and crop improvement promises the application of biomass at lower cost and better stability. This allows the cost of electricity produced from low cost biomass Residues to compete with fossil fuel-based power generation (Peter, 2002).

1.5. Government Policies On Biomass

The UK Government has, for many years, been actively involved in establishing and developing the application of biomass in energy supply. This is done via different schemes, obligations and grants to promote the use of biomass in replacement of the more environmentally detrimental fossil fuels. The UK Biomass Strategy (DECC, 2012) states the Government's intention to bring about a major expansion in both the supply and use of biomass in the UK, indicating that biomass will have a central role to play in meeting the EU target of producing 20% renewable energy by 2020 (Sherrington et al., 2008).

Between 1990 and 2002, the Non-Fossil Fuel Obligation (NFFO) was the main government support measure for renewable energy in the UK, which consisted of a Fossil Fuel Levy used to fund the feed-in tariffs which supported renewable electricity (Perry and Rosillo-Calle, 2008). In 2005, the on-going biomass projects then accounted for 81MWe, which is about 7% of the NFFO capacity. The final contract awarded is due to expire in 2018.

In the year 2002, the NFFO was succeeded by Renewables Obligation (RO), which is a system of tradable permits known as Renewables Obligation Certificates (ROC) (Perry and Rosillo-Calle, 2008). The Renewables Obligation is the UK Government's key policy mechanism for increasing the proportion of electricity derived from renewable sources (Sherrington et al., 2008). Every licensed electricity supplier is obliged to supply a fixed percentage of electricity from eligible renewable sources with the initial level of RO at 3% and due to rise to 15.4% by 2015 (Perry and Rosillo-Calle, 2008). The evidence of compliance is submitted to the Office of Gas and Electricity Markets (OFGEM) in the form of ROCs (Sherrington et al., 2008). One ROC is awarded to the supplier for every MWe of electricity generated from eligible renewable sources. 10 million ROCs having been sold on the platform since the first auction back in October 2002 (ePower, 2016). Alternatively, suppliers can fulfil the obligation by buying ROCs from other generators (currently auctioned at about £41.65 per ROC (ePower, 2016) or paying a buyout price of £41.35 per ROC (ePower, 2016). In order to provide further incentive to produce ROCs, the buyout fund collected from buyouts sold every year is redistributed to the ROC holders at a current rate of £14.32 per ROC (ePower, 2016). The RO is guaranteed to remain in place until at least 2027, in order to assure investors that a long-term market exists for renewable electricity (Perry and Rosillo-Calle, 2008). Co-firing biomass and coal is also entitled to receive ROCs, although there was debate when it was first introduced in 2002. It is said that from the year 2006, at least 75% of biomass co-fired should be energy crops, and that eligibility of co-firing is due to cease in 2011 (Perry and Rosillo-Calle, 2008, Sherrington et al., 2008). There are other policies and obligations that favour the use of biomass relative to fossil equivalents, including the Climate Change Levy (CCL). This surcharge is levied on the use of fossil fuels at a rate of 0.15 pence per kWh of electricity for natural gas and 1.17 pence per kilogram of solid fuels (Perry and Rosillo-Calle, 2008). Biomass is not subjected to the levy.

1.6. Drawbacks Of Biomass Utilisation

1.6.1. Combustion Issues Of Biomass

Generally, biomass has very high moisture content, both intrinsically and extrinsically (Ayhan, 2003, Sami et al., 2001, Grammelis, 2011, Puigjaner, 2011, Chen and Kuo, 2010). This may not be too much of a hindrance for conversion methods like enzymatic fermentation (Peter, 2002), but this property is particularly disadvanategous in combustion processes. The high moisture content can cause ignition and combustion problems (Ayhan, 2003, Sami et al., 2001). The inherent high oxygen content of biomass (Ayhan, 2003) coupled with the high moisture content results in the reduction of the heating value of biomass, and thus can cause flame instability and the flame temperature decreases (Ayhan, 2003, Sami et al., 2001). But, if the low heating value is due to the high oxygen content, the flame temperature increases (Ayhan, 2003). The flame stability problem will persist if the temperature drops below 1600K, due to the reduced rates of chemical reactions (Sami et al., 2001) unless high levels of flame recirculation are used.

1.6.2. Size Reduction Issues Of Biomass

The grindability and milling performance of biomass is poor compared with coal (Puigjaner, 2011, Arias et al., 2008) and this is especially true while using existing mills suited for the pulverisation of more brittle fuels like coal. This is attributed to the fibrous and non-friable nature of biomass (Schmidt, 2007, Grammelis, 2011), coupled with its high moisture content (Baxter, 2005, Surmen and Demirbas, 2003). The particles tend to agglomerate or flatten, rather than break. The high moisture content of biomass also disturbs the heat balance of the mill (Schmidt, 2007, Loo and Koppejan, 2008). Attempting to reduce the size of biomass to that similar to coal is uneconomical (Baxter, 2005), unnecessary (Schmidt, 2007), unfeasible (Schmidt, 2007, Grammelis, 2011), and difficult (Ayhan, 2003, Arias et al., 2008a, Chen and Kuo, 2010). It is stated that a larger size fraction of biomass (up to 0.25 inches) is acceptable (Grammelis, 2011, Ayhan, 2003, Spliethoff and Hein, 1998), as it is compensated by the high volatile content of biomass which increases overall reactivity.

1.6.3. Quality And Quantity Issues Of Biomass

Larger sized biomass generally has a higher aspect ratio, relative to coal (Ayhan, 2003, Brown, 2011), resulting in low packing density and high bulk volume (Puigjaner, 2011, Arias et al., 2008). This makes storage and transport difficult and costly (Ayhan, 2001), and also poses challenges in biomass handling by blocking fuel flow passages during milling and feeding (Baxter, 2005). Biomass with average aspect ratio ranging from 3 to 7 tends to create problems while being transported, either pneumatically or by other means (Schmidt, 2007).

The low density coupled with low heating value results in low energy density, which is one of the main drawbacks of biomass (Obernberger and Thek, 2010). In order for biomass to produce an equivalent amount of energy as coal, a higher load (Arias et al., 2008) and more volume flow into the boiler is needed (Schmidt, 2007). This means that not only is the cost of storage and transport higher, the operational and maintenance cost also increases as the fuel conveying and feeding system needs to handle and deliver more fuel. The high bulk volume, high moisture content and relatively low calorific value make raw biomass an expensive fuel to transport (Arias et al., 2008).

1.6.4. Storage Issues Of Biomass

Apart from the large storage space needed for biomass, the storing conditions are equally important. The hydrophilic and hygroscopic nature of biomass creates additional problems for safe (Phanphanich and Mani, 2011) and long term (Chen and Kuo, 2010) storage. Biomass is an organic compound which will eventually undergo various biological and biochemical degradations, which may lead to self-heating and self-ignition, especially when involving large amounts of wet biomass for a long period of time (Schmidt, 2007). High moisture content may lead to composting, and thus loss of biomass, whilst not forgetting the growth of moulds and fungi which poses a threat to human health. If a pile of biomass gets rained on, it tends to absorb the water and starts to decompose soon after, but the same conditions will have minimal effects on coal. Therefore existing storage space needs to be retrofitted before storing biomass. It is of prime importance that the storage facility has good ventilation and drainage system to keep the humidity and moisture content at an acceptable level.

1.7. Differences Between Biomass And Coal

Since most of the combustion and/or co-firing of biomass is being carried out in an existing or a retrofitted coal fired power plant, this amplifies the adverse effects brought about by biomass because of its significant differences with coal. Biomass differs from coal in many important ways (Ayhan, 2003), both physically and chemically. Coal, a complex polymer containing combustibles, moisture, intrinsic mineral matter and extrinsic ash, is the aged form of biomass (Sami et al., 2001). It is formed following the coalifaction sequence:

Vegetation → Peat → Lignite (low rank coal) → Sub-bituminous Coal → Bituminus coal →Anthracite (high rank coal)

Over time, dead plants were exposed to high pressure and temperature in dense swampy conditions. Anaerobic micro-organisms converted plant debris into peat-like deposits, which were eventually covered in sediment. As the pressure and temperature increase further, chemical decomposition occurred and decreases the oxygen and hydrogen content. The C/O and C/H ratio increases during the coalifaction process whereby anthracite becomes almost all carbon (Sami et al., 2001), thus Biomass is 200-300 million years 'younger' than coal.

The major organic compounds that constitute coals are called macerals (Nip et al., 1992), which can be sub-divided into three main groups of vitrinite, liptinite and inertinite (Killops and Killops, 2005). As for biomass, the major organic components are cellulose, hemicellulose and lignin (Centi and Santen, 2007). As shown in Table 1.2, traded biomass (e.g wood pellets) In general, biomass has lower moisture content (Ayhan, 2003, Sahu et al., 2010) and higher volatile matter (Molcan et al., 2009, Arias et al., 2008b) relative to coal, which has higher fixed carbon and ash content. On a dry, ash free basis, biomass has about 70-80% of volatile matters as compared to coal with 10-50% (Sami et al., 2001, Van Krevelen, 1993, Easterly and Burnham, 1996). This means that biomass will more likely undertake homogeneous ignition rather than heterogeneous ignition (Sami et al., 2001).

On an elemental scale, biomass has greater amount of H and O (Ayhan, 2003, Molcan et al., 2009, Sahu et al., 2010) but a lower amount of C (Ayhan, 2003) and S (Sami et al., 2001, Ayhan, 2003). This is shown in the Van Krevelen diragram in Figure 1.2. The lower amount of S reduces the level of SO_2 emissions; it may also be lower that that for coal on thermal basis. The high O and moisture content of biomass result in lower heating value compared to coal (Molcan et al., 2009, Arias et al., 2008b).

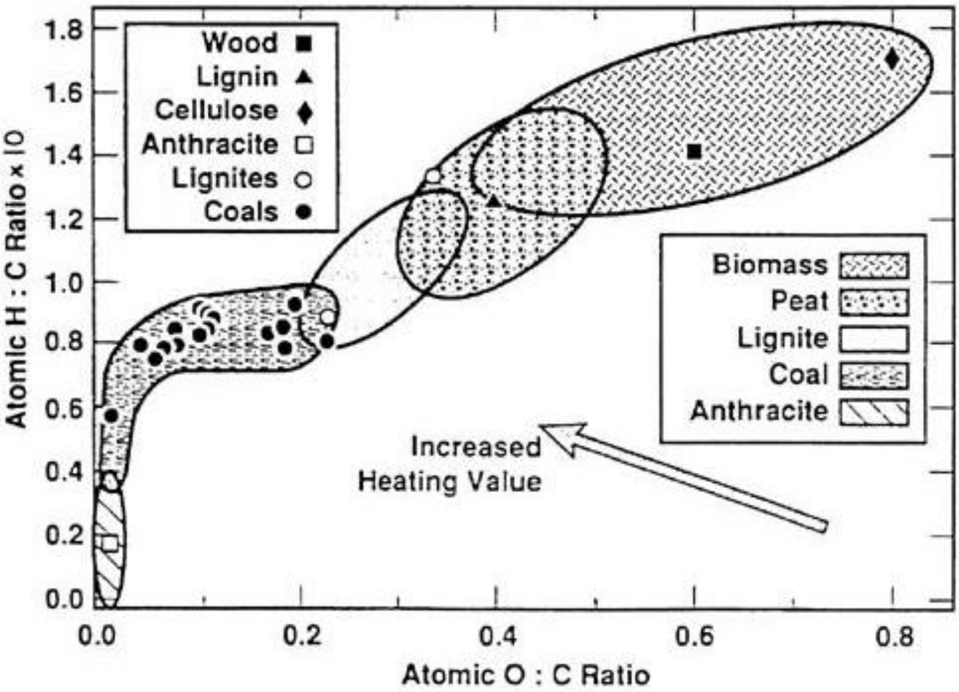


Figure 1.2. H/C and O/C ratio for several solid fuels (Van Krevelen diagram)

The bulk density of biomass is about 1/5 that of coal due to the high aspect ratio and irregular shapes of biomass, while the particle density is around 1/2 that of coal due to the high porosity and internal cellular structure of biomass (Grammelis, 2011). This makes the fuel density of biomass about 1/10 that of coal. Typically, the density of biomass ranges from 100 kg/m^3 for Straw to 500 kg/m^3 for forest wood pellets (Tillman et al., 1981, Sami et al., 2001), while for the denser coal, it ranges from 1100 kg/m^3 for low rank coals to 2330 kg/m^3 for high density pyrolytic graphite (Essenhigh, 1979, Sami et al., 2001). The lower bulk density of biomass does not only pose challenges during milling and handling, but it also increases the transport and storage cost (Mani et al., 2006, Sokhansanj et al, 2009, Phanphanich and Mani, 2011).

The composition of biomass ash is very different compared to coal ash (Wigley et al., 2007). (Bridgeman, Jones, Williams 2010). Although the ash content of biomass is lower than that of coal, it still poses a threat in terms of heavy slagging and fouling during combustion. Biomass ash usually has greater concentration of potassium and silicone, but a lower amount of alumnium and iron (Ayhan, 2003). Compared to coal, trace metals are generally lower as shown in Table 1.2.

Table 1.2. Drax Power Ltd. analysis of typical biomass and coal (all results as received)

	Coal	Wood
Total Moisture %	15.6	5.4
Ash %	5.4	0.85
Volatile Matter %	32.9	80
CV Net kj/kg	24.08	17.98
Sulphur %	0.62	0.01
Nitrogen %	1.25	0.07
Aluminium mg/kg	6489.53	170
Cadmium mg/kg	0.31	0.04
Calcium mg/kg	1581.43	1028
Chromium mg/kg	10.12	6.9
Copper mg/kg	11.36	205
Iron mg/kg	3061.80	0.07
Magnesium mg/kg	680.40	223
Mercury mg/kg	0.10	0.05
Phosphorus mg/kg	1068.06	54
Potassium mg/kg	716.94	555
Silicon mg/kg	131.04	169
Sodium mg/kg	1482.39	47
Tin mg/kg	243.00	0.22
Zinc mg/kg	19.32	9

1.8. Background To Use Of Biomass Pellets

Making pellets from wood is now a well-established industry in Europe and in North America. Wood pellets production has been increasing rapidly over the past decade and total wood pellet demand was c.17Mt in 2010. The largest demand and growth is in Europe, rising from current day 17Mt to 25Mt by 2020. World demand by 2020 is projected to be 48Mt. There has been significant growth in wood pellet imports into Europe rising from 3Mte Import to 9Mte by 2020. World production is expected to increase from 29Mte to 48Mte by 2020. US production is projected to exceed demand by 5Mte in 2020 and the industrial market is projected to represent c.50% of total pellet market by 2020 (Poyry, 2011)

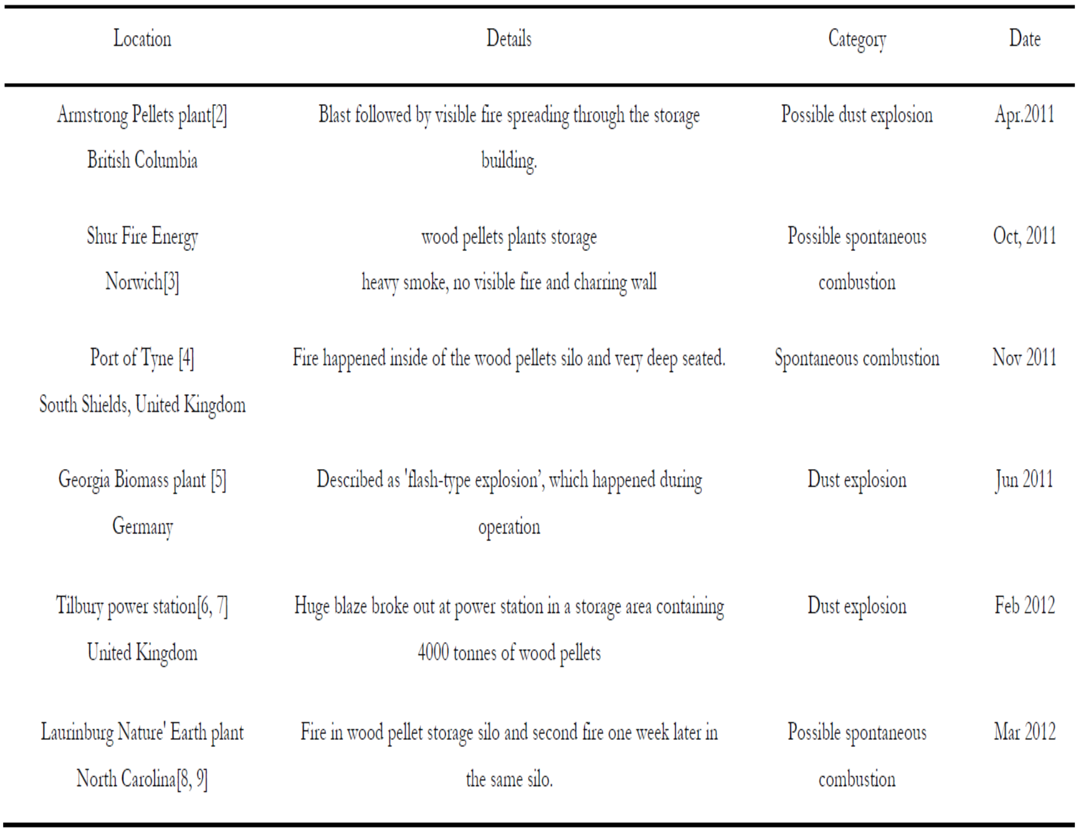
At a bulk density of 650 to 750 kg/m^3, the energy content of pellets by volume is roughly twice as much as that of round wood loaded on a truck. Pellets have a typical moisture content of 4-6% and an energy density of 18 GJ/tonne compared to 8 GJ/tonne for hog fuel at 50% moisture (British Columbia Biomass Conference, 2008).

Wood pellets are used as a direct substitute for coal and natural gas or co-fired in small and large facilities for the production of heat and electricity. However, wood pellets are hydrophilic and have to be protected from moisture during storage and handling. The pellets are sold in bulk, one-tonne jumbo bags or in small 40 lbs (18.2 kg) bags. Most of the pellets have so far been exported to Europe and are transported in large ocean vessels in volumes of 7,000 to 20,000 tonne lots. Pellets may also be transported in bulk containers, railcars or tank trucks and are the most transportable bio-fuel available today. Wood pellets are today shipped in large bulk volumes across the oceans. Before shipping wood pellets are stored in large silos typically 15 m in diameter and 20 m in height holding 2500 -3500 tonnes for a period of one to ten weeks.

Accidental fires have become the biggest concern during the storage and handling of pellets, which could cause real danger to the workers, enormous economy loss, damage to the storage structure and huge air pollution. Table 1.3 lists known wood pellet fires which happened last during this thesis research period. Among those accidents, there are mainly two categories, dust explosion and spontaneous combustion. Dust explosions are caused by fast combustion of dust powders, which would happen to any powdered combustible material in an enclosed location. Dust explosions normally occur during activities such as transporting or operating, starting with an explosion and followed by visible fires and smokes. Spontaneous combustion often happens from the inside of a piled combustible material during storage, starting with invisible combustion and followed by heavy smoke, visible charring of the pellets as well as on the wall, which may or may not be followed by an explosion.

Both categories are extremely dangerous and need to be studied and prevented. However, this study, only focuses on the self-heating and spontaneous combustion of wood pellets during the storage. Self-heating may occur in piled biomass depending upon storage conditions (temperature, moisture content and ventilation) and storage period. The heat starts to accumulate and causes temperature rise when the heat does not get dissipated quickly from the piled wood pellets.

Table 1.3. List of wood pellets fires accidents over time of thesis writing



Location	Details	Category	Date
Armstrong Pellets plant[2] British Columbia	Blast followed by visible fire spreading through the storage building.	Possible dust explosion	Apr.2011
Shur Fire Energy Norwich[3]	wood pellets plants storage heavy smoke, no visible fire and charring wall	Possible spontaneous combustion	Oct, 2011
Port of Tyne [4] South Shields, United Kingdom	Fire happened inside of the wood pellets silo and very deep seated.	Spontaneous combustion	Nov 2011
Georgia Biomass plant [5] Germany	Described as 'flash-type explosion', which happened during operation	Dust explosion	Jun 2011
Tilbury power station[6, 7] United Kingdom	Huge blaze broke out at power station in a storage area containing 4000 tonnes of wood pellets	Dust explosion	Feb 2012
Laurinburg Nature' Earth plant North Carolina[8, 9]	Fire in wood pellet storage silo and second fire one week later in the same silo.	Possible spontaneous combustion	Mar 2012

Although self-heating is an important factor to consider, it must be put into perspective of other potential sources of ignition. Table 1.4 would suggest that other sources of ignition i.e rubbing conveyour belts, sparks or electical fires are more likley to start biomass fires.

Table 1.4. Other potential sources of ignition (Chemical Safety and Hazards Investigation Board, 2006)

Reason for accident or incident	% of Total
Mechanical spark	30.0
Unknown	11.5
Static electricity	9.0
Smoulder spots	9.0
Friction	9.0
Fire	8.0
Hot surface	6.5
Self-ignition	6.0
Welding	5.0
Electrical equipment	3.5
Other	2.5
Total	100.00

Thus, in addition to spontaneous ignition, there are a number of possible causes that could result in a potential fire. Some common causes are sparks generated by metal pieces, stones, etc. that are present in the bulk material by accident.

Other causes could be overheating of electric motors, (Chin, Darvell,. Lea-Langton, Jones, and Alan Williams, 2016) bearings in conveyer and elevator systems, friction between e.g. a conveyer belt and accumulated material, fines and/or dust or careless hot work. The ignition could also be a secondary effect of a spontaneous ignition if material containing small pieces of smouldering material ("hot spots"), is transported to a new storage location by mistake, e.g. via conveyors. In heat generation plants, ignition might also be a result of back-fire or sparks near the boilers. A risk that should not be neglected is the possibility for a fire in wheel loaders, which are frequently used for unloading material from heaps. In some situations there is also a risk of intentional fires (arson). The most important measures to avoid these risks are to

1. Include control measures for impurities when receiving the material, e.g. magnetic separators, sieves, etc.
2. Spark detectors connected to an extinguishing system by fast acting valves at strategic locations in the transport system.
3. Install a full sprinkler protection system in large conveyor systems, as these are often located at elevated positions and/or in underground spaces making a manual firefighting operation very difficult.
4. Control schemes to check the condition of bearings (temperature measurement)
5. Control schemes for cleaning to avoid accumulation of material in conveyers, elevators
6. Control schemes for hot work within the facility
7. Routines for observations and controls

This thesis is focused on studying the self-heating mechanism at both low and high temperatures and investigating conditions that may lead to the spontaneous combustion. Full aims and objectives given in Chapter 3.

CHAPTER 2. LITERATURE REVIEW

2.1. Biomass

The term ‘biomass’ refers to any and every organic substance which stores solar energy in the form of chemical energy. These energies are stored as chemical bonds between the adjacent carbon, hydrogen and oxygen atoms/molecules. Energy is released when these bonds are broken by conversion, either through digestion, combustion or decomposition (Peter, 2002). Therefore, biomass could be a product directly or indirectly derived from photosynthesis or plant growth (Ayhan, 2001). By definition, this includes a wide range of materials which, generally, could be sub-divided into four different classes, namely the energy crops (Peter, 2002, Ayhan, 2001), agricultural (Sami et al., 2001, Peter, 2002, Ayhan, 2001), municipal/domestic waste (Sami et al., 2001, Peter, 2002, Ayhan, 2001) and industrial waste (Sami et al., 2001, Peter, 2002a, Ayhan, 2001). Biomass is sometimes referred to as the organic petroleum substitute which is renewable (Ayhan, 2003, Ayhan, 2001).

2.2. Biomass Types

Despite the vast variety of different biomass types available, not all are suitable for solid fuel combustion purposes. Some biomass, especially those with very high moisture content, are more suited for other conversion technologies such as biological enzymatic fermentation. It has been reported that in actual practice, combustion is feasible only for biomass with moisture content less than 50% (Peter, 2002); good examples would be Straw (Agricultural Residues), Miscanthus (energy crop) and wood chips (industrial waste). Therefore, the term ‘biomass’ hereafter refers to those which are suitable for solid fuel combustion, unless otherwise stated.

The two common types of biomass used to generate electricity at Drax Power Ltd. are Agricultural Residues and forestry products including Residues and energy crops. The focus of this thesis is compressed wood pellets on a practical industrial scale.

2.2.1. Energy Crops

Energy crops are dedicated plants which are grown specifically for energy generation (Ayhan, 2001). These crops have higher biomass output per hectare of land used as compared to conventional forestry, although the latter is more attractive in terms of lower cost per unit mass of biomass produced. Thus, in a country like the UK where there is a limited green land area of 11.6% (Biomass Energy Centre, 2008), dedicated energy crops are more advisable. There are four classes of energy crops including short rotation, herbaceous/non woody, Agricultural Residues and aquatic energy crops, but the last is not utilized at Drax Power Ltd. and therefore will not be discussed.

Short Rotation Energy Crops: The harvest cycle of this group of plants operates on a relatively short timescale (2-4 years) compared to conventional forestry (more than 20 years), thus harvesting occurs more frequently. This is important in the effort to balance rate of consumption and the rate of biomass production. The key idea behind the success of short rotation cropping is that the rate of plants growth is greater at a younger age rather than later years. Examples of this class include willow and poplar (Ayhan, 2001). The Energy Crops Scheme (DEFRA, 2011) which operated from 2007 to 2013 has been set up by the Department of Environment, Food and Rural Affairs (DEFRA) to help establish the development of short rotation energy crops in the UK.

Herbaceous/Non-woody Energy Crops: This class includes grasses and other herbaceous plants with low lignin content. The harvest cycle commonly operates on an annual basis instead of longer periods as seen with other plant species. The perennial grass of Miscanthus is the primary crop of this class, while others include hemp, switchgrass and Reed canary grass. The Miscanthus plant was also included in the Energy Crops Scheme (DEFRA, 2011) to encourage its development.

Agricultural Residues Energy Crops: This class includes a rather wide range of plants such as sugar crops (cane and beet), starch crops (corn and wheat), forage crops (grasses and clover) and oilseed crops (rapeseed and sunflower). The plant oils are important as they have high energy density while the crops are hardy (Ayhan, 2001). They include the first generation transport fuel crops and have the disadvantage of requiring good agricultural land and thus compete with food production.

2.2.2. Agricultural Residues

This class includes waste from plants whose primary purpose is not to produce energy. These are by-products originating from agricultural activities. Rice husk, which makes up 25% of rice by mass, is a common Agricultural Residue (Ayhan, 2001). Others include Straw, bagasse and coconut shell. Some Residues are more moist compared to the ones mentioned (dry Residues), and hence termed ‘wet Residues’. With only just 6 to 10% of dry matter when collected (Biomass Energy Centre, 2008), they are clearly not economically suited for combustion. Animal slurry and grass silage are examples of this type, and the favoured technology for their use is anaerobic digestion.

2.3. Chemical And Physical Properties Of Wood Pellets

The majority of wood pellets are produced by milling dried wood chips, bark, planer shavings or sawdust into a fine powder. The ground material is compressed and extruded through a die system, which produces a dense cylindrical shaped pellet (6 to 8 mm in diameter). Depending on the compression technology used, the woody material is exposed to temperatures around 100°C during the compression. The stepwise thermal compression process causes the lignin to plasticize and act like glue that provides for cohesion of the pellets. Wood pellets are essentially composed of cellulose, hemicelluloses, lignin and extractives. Table 2.1 lists typical ranges of example of the chemical composition of wood pellets feedstock in British Columbia.

Table 2.1. Chemical composition of wood pellets feedstock (Wood pellet association of Canada, 2010)

Oxygenated Compounds	in % weight
Cellulose	30-40
Hemicelluloses	25-30
Lignin	30-45
Extractives	3-5

Cellulose is the major chemical component of cell wall that consists of linear chains of glucose units with an average degree of polymerization (DP) at least 9,000-10,000 in wood cellulose (Rowell, 1983). X-ray diffraction experiments indicate that in native cellulose, the glucose units are linked together to form a crystalline structure (Klemm et al, 2005). The presence of the crystalline structure restricts the cellulose to access water and chemicals and is less reactive than other non-crystalline components. Hemicelluloses are another group of carbohydrate components, with major compositions of (galacto) glucomanan and arabinoglucuronoxylan (referred to asxylan for short) in softwood (Laine, 2005); they have a degree of polymerization (DP) of 50-300 (Klemm et al, 2005), much lower than cellulose. The hemicelluloses together with cellulose provide the structural components of the cell wall. Compared to cellulose, hemicelluloses are more reactive due to the lower DP value. Lignin is a polymer consisting phenylpropane units and linked by ether or carbon-carbon bonds. Lignin is an important component in wood materials. It is bound to the sugar unit in hemicelluloses by covalent linkages and generates the lignin carbohydrate complexes (Eriksson, 1980). Lignin provides the stiffness to the cell wall and a physical barrier to enzymatic decomposition of cellulose and hemicelluloses.

Table 2.2 lists the chemical composition and properties of pine wood chips and pellets (Teixeira, 2012). This demonstrates that wood pellets have similar chemical composition as wood chips. Pellets are generally lower in ash content and moisture than wood chips, hence have higher net CV. The big advantage of pellets over wood chip is their much higher energy density. Manufactured from ground wood, even though wood pellets still maintain a similar chemical composition with wood, the physical structure of wood particles and wood pellets are significantly different.

Figure 2.1 shows the scanning electron microscope (SEM) pictures of wood particle surface ground by a hammer mill and the cross section of a wood pellet (Lam, 2011).

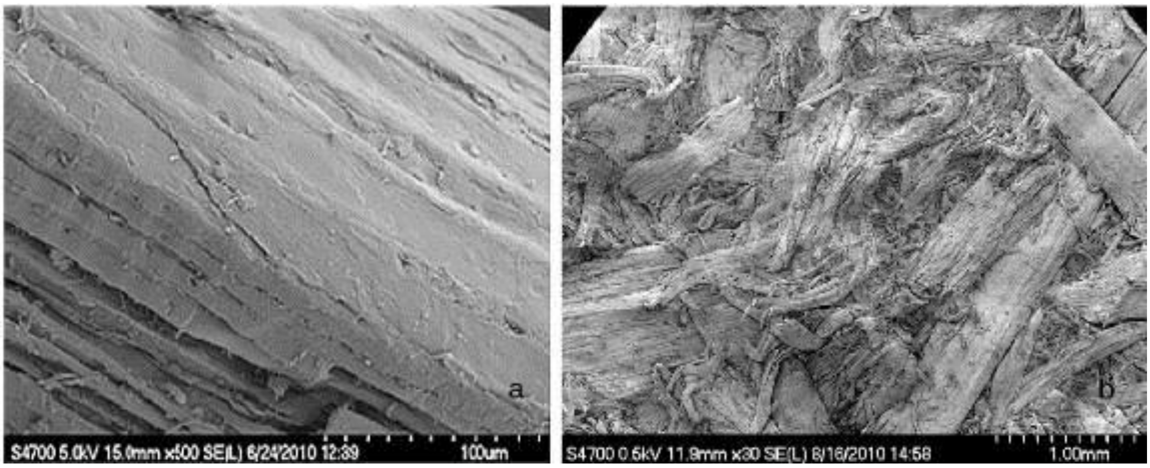
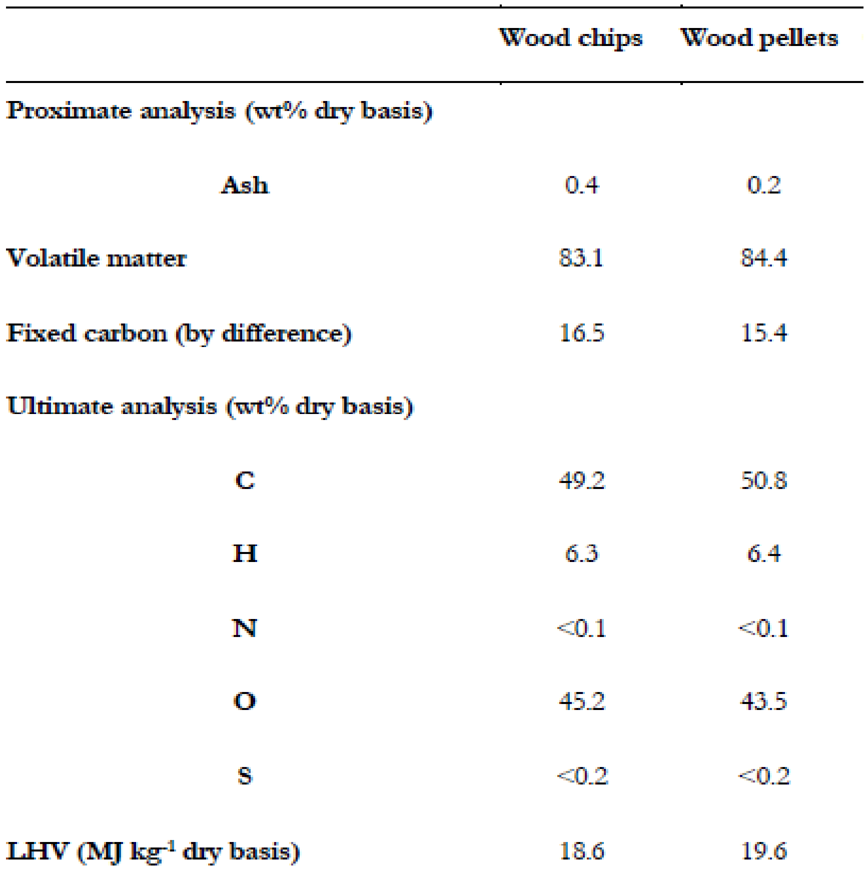


Figure 2.1. SEM Pictures. Left ground wood particle by hammer mill with 1.7 mm screen opening with x500SEM Pictures Right. Cross section of pellets with x30 magnification (Lam, 2011)

In raw wood, long fibres are distributed in a parallel order, Figure 2.1 shows that in wood pellets fibres are composed of short broken fibres compressed together and distributed in a random order. Due to structural differences, thermal properties that are related to physical properties are expected to be different from the solids wood.

Table 2.2. Composition and properties of pine wood (chips and pellets) and prepared chars. (Teixeira, 2010).



	Wood chips	Wood pellets
Proximate analysis (wt% dry basis)		
Ash	0.4	0.2
Volatile matter	83.1	84.4
Fixed carbon (by difference)	16.5	15.4
Ultimate analysis (wt% dry basis)		
C	49.2	50.8
H	6.3	6.4
N	<0.1	<0.1
O	45.2	43.5
S	<0.2	<0.2
LHV (MJ kg^{-1} dry basis)	18.6	19.6

2.4. Introduction Biomass Self-Heating

When a stored material increases in temperature by generating heat without drawing heat from its surroundings the process is called self-heating. (Millls 1989). The self-heating of a stored commodity to its ignition temperature is called self-ignition. The terms spontaneous ignition and spontaneous combustion are also used but the term self-ignition is preferred. Self-ignition may be affected by a variety of chemical and physical factors (American Insurance Association 1983; Bowen 1982):

1. The rate at which heat is generated by the fuel material.
2. The oxygen supply available.
3. The rate of heat loss to surroundings.

Self-heating of carbonaceous materials is a common phenomenon, occurring in particular when large quantities of reactive materials are stored for extended periods of time. In large-scale silo storage of wood fuel pellets, self-heating has become a serious problem, sometimes causing self-ignition (Blomqvist, Persson 2008). Self-heating is initiated by exothermal chemical, physical, or biological activity inside a stored quantity of material. Figure 2.2 shows graphically shows the three types of processes that are believed to occur to raise the temperature of a fuel heap; physical adsorption of moisture, microbiological, and oxidation. Of these three processes oxidation is by far the most exothermic, thus if a biomass heap self-heats beyond a critical temperature, thermal runaway will occur if it is not attended to.

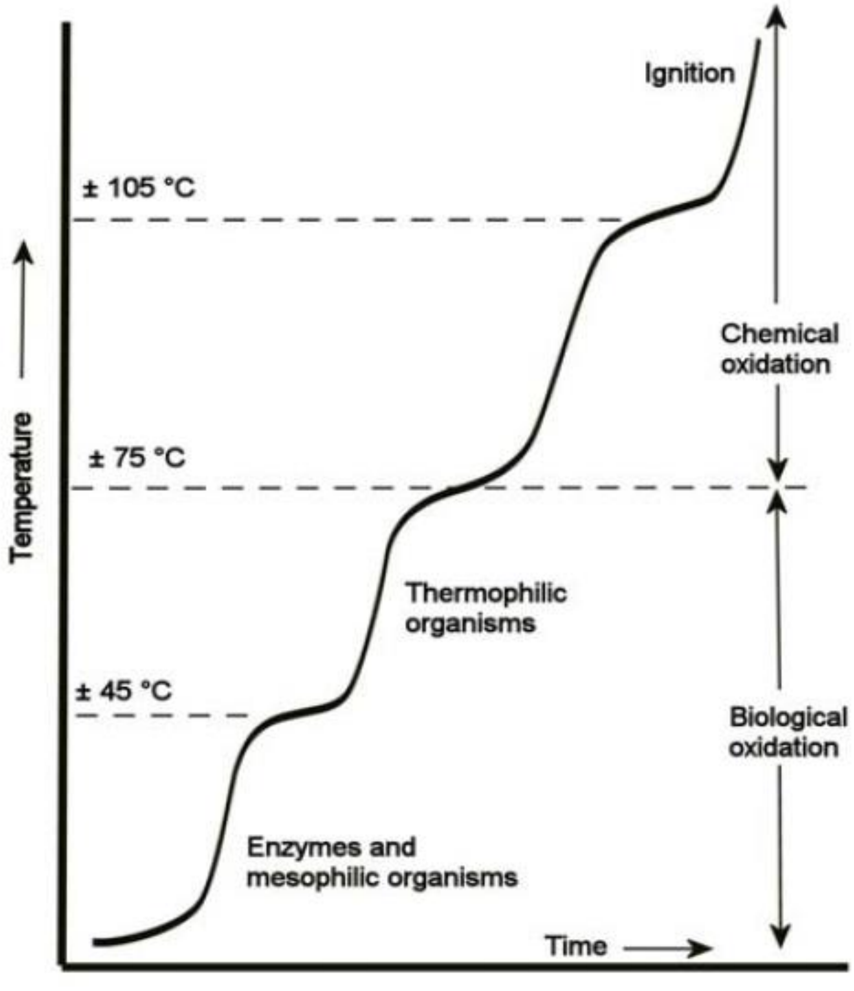


Figure 2.2. Proposed reactions in biomass (Meijer, Gast, 2007)

Compared to stored pellets, freshly produced pellets are considered to be more prone to self-heating (Guo et al 2012). Arshadi et al (2009) showed an initial temperature increase to approximately 55°C in large piles of freshly produced pine wood pellets. Arshadi et al (2009) recorded that the temperature slowly declined over a four week storage period simultaneously with a decrease in fatty/resin acid contents. Emissions of oxidation products such as aldehydes and ketones were initially high, but declined over the same time period. Thus, the content of oxidative fats and resins was found to be a measure of the reactivity of the pellets. To avoid pellet storage problems, it was suggested to control the content of fatty/resin acids in pellets by monitoring the storage of raw material outdoors prior to pelletizing (Arshadi et al 2009). The reaction rate in an oxidation process increases with increasing temperature. Temperature was positively correlated to emissions of CO, CO_2, and CH_4, and with oxygen depletion when wood pellets were kept in sealed containers for 30 days (Kung et al 2009). Hence, self-heating of wood pellets accelerates with increasing temperatures.

There is historical evidence for self-heating and combustion of wood and other biomass materials at temperatures of less than 100°C. Even 100 years ago, it was evident that ignition of grain and hay stacks were, in some sense, different from those with external heating ignition and that a different explanation had to be provided. The original explanation that was proposed for these cases was put by the German scientist Ernst von Schwartz in 1902 (Schwart, 1904). Based upon a theory suggested earlier by the German scientist H. von Ranke as an explanation for haystack fires, the theory claims that low temperature, long-term heating of wood converts the wood to “pyrophoric carbon,” and that this pyrophoric carbon is much more readily ignitable than is virgin wood. The question of how hay stacks heated to these elevated temperatures was the unknown at that time.

It was not until 1907 that most of the early information regarding thermophilic fungi was published primarily in part by Miehe (Cooney and Emerson, 1964). Miehe showed that damp, packed hay or leaves self-heated to 60^{o}C within one to several days (Miehe, 1907). He also showed that steamed hay did not heat and that steamed hay inoculated with soil suspensions did (Miehe, 1907). Firth and Stuckley, (1947) developed the concept of biological activity to the chemical by products of the process which also allowed the concept to the self-heating to progress beyond the biological constrained temperatures of approximately 75^{o}C.

Today, due to modern farming methods, natural drying of grains are not practical, and silo storage is the preferred way. The major causes of grain quality loss during storage result from self-heating, insects, moulds, grain respiration and moisture migration. All of these storage risks depend on moisture content and temperature and control of these two factors ensures safe storage. Moisture is most critical as grain stored at moisture levels above 13.5% for any length of time is at risk. (Darby, 1997) Mould grows rapidly on warm, moist grain. Incomplete drying, moisture migration, condensation leading to self-heating. In modern farming and storage facilities, as shown in Figure 2.3. Pre-treatment of the stored commodity is routinely performed to reduce the likelihood of self-heating. This is further enhanced through the use of well ventilated (mechanical and natural) stores.

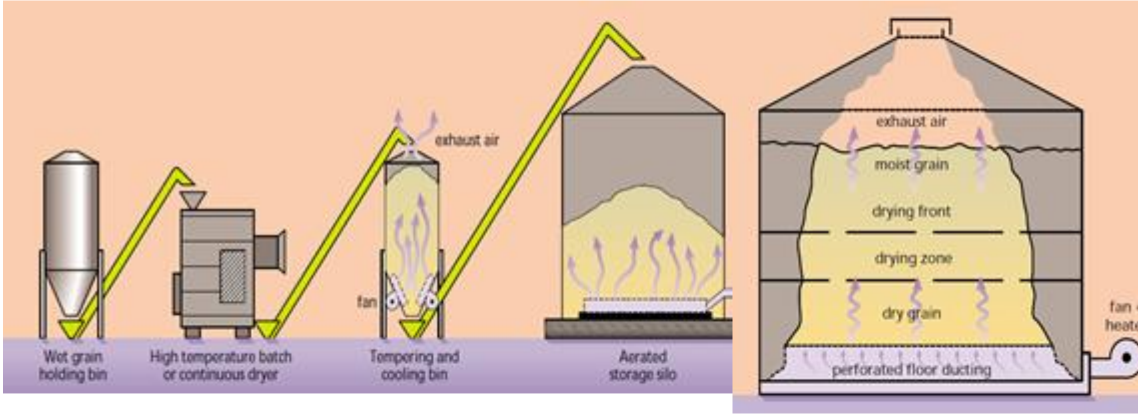


Figure 2.3. Current farming method for grain pre-storage treatment (Darby, 1997)

2.4.1. The Role Of Moisture

Adsorption of moisture in an exothermic process and migration of moisture through the material will create both exothermic and endothermic reaction zones (Pixton and Griffith, 1971). Heat and moisture is carried by air flows in large scale wood pellet silo storage. The particle sizes of wood pellets create bulk conditions where heat and moisture transfer is most likely dominated by natural convection (Smith, 1990). In cases of forced ventilation, air flows will have substantial impact on temperature and moisture patterns (Larson, et al, 2011). Three additional interacting factors affect the chain of events leading to thermal runaway and self-heating: dimensions of the stored material, ambient temperature, and heat conduction through the material (Pauner and Bygbjerg, 2007). Chemical heat production rates and risk for spontaneous ignition have been evaluated in laboratory experiments (Pauner and Bygbjerg 2007) (Wadsö, 2007) and these methods are discussed in Section 2.

The specific heat of water is approximately 4.186 MJ/kgK (CRC 1994). Water takes three times more energy to heat up the same number of degrees, compared to wood. Moisture in pellets acts as a heat sink delaying the temperature rise by up to three times compared to dry pellets. High moisture pellets do not cool down as quickly, and tend to hold their heat High moisture pellets also lead to a warm humid atmosphere promoting bacterial activity (Mills, 1989).

The specific heat of dry softwood is approx. 1.420 MJ/kgK (Szokolay, 2008) and that of dry hard wood is approx. 1200 kJ/kgK (Szokolay, 2008). Thus mixtures of hard wood pellets and softwood pellets will heat up quicker than softwood alone. Mixtures of pellets with different moisture contents can lead to accelerated heating, as moisture is transferred from high to low moisture pellets, releasing sensible heat in the process. Areas of low moisture are found at the seat of hot spots and fires (Firth and Stuckley, 1947) as the pellets heat there is loss of moisture, the low moisture pellets have a lower heat capacity, hence heat up more quickly. The specific heat capacity of softwood falls with lower moisture contents (Szokolay, 2008). The reduction in heat capacity accelerates below 4% moisture. Pellets at approximately 0.75% moisture have half the heat capacity of pellets with >4% moisture and will therefore heat up at twice the rate (Szokolay, 2008).

2.4.1.1. Heat of Wetting

There is evidence that the more hygroscopic woods are characterized by a higher value of heat of wetting, W_o. This would seem reasonable if woods with larger numbers of sorption sites per unit of dry mass are also more hygroscopic. Such seems to be the case if the hygroscopicity is measured by the magnitude of the fibre-saturation point, M_f, for example. Raczkowski (1963) reported that W_o was linearly related to the fibre-saturation point such that the ratio W_o/M_f was essentially constant and equal to 0.8. Furthermore, he noted that W_o for sapwood was up to 30% higher than for heartwood and that alcohol-benzene extraction increased W_0 by as much as 38%. This is probably due to the increase in hygroscopicity resulting from removal of extractives (Higgins 1957)

Kajita and Mukudai (1971) reported that the total heats of wetting, W_o, for heartwood ranged from 12.6 to 18.6 cal/g for 16 Japanese woods and 14 woods imported into Japan. In general, those woods with higher extractive content showed lower values of W_o. He noted also that the values for sapwood were generally greater than those for heartwood, probably because of the greater hygroscopicity associated with the lower extractive content of sapwood.

Delgado (1970) found, for 34 different Venezuelan woods segregated into six groups based on their equilibrium moisture contents (EMC) at 67% humidity and room temperature, that W_o was higher for those groups with higher EMC. Morton and Hearle (1970) showed that the integral heat of sorption, W_o—W, for a number of textile materials conditioned to 65% relative humidity, is a linear function of the regain (EMC) at this humidity.

Kajita (1976) also reported a positive relationship between W_o and EMC calculated at 100% humidity for ten Japanese woods (Figure 2-1). A linear relationship was observed, described by the regression

$$W_o = 0.5+0\text{-}67\ M_f\ \text{(cal/g wood)} \qquad \text{Equation 2-1}$$

with an R^2 of 0.902. The zero intercept in Equation (2.4) is close to zero, indicating that the ratio W_o/M_f is essentially constant. Kajita (1976) reported that the mean ratio was 0.704 for the ten woods he tested.

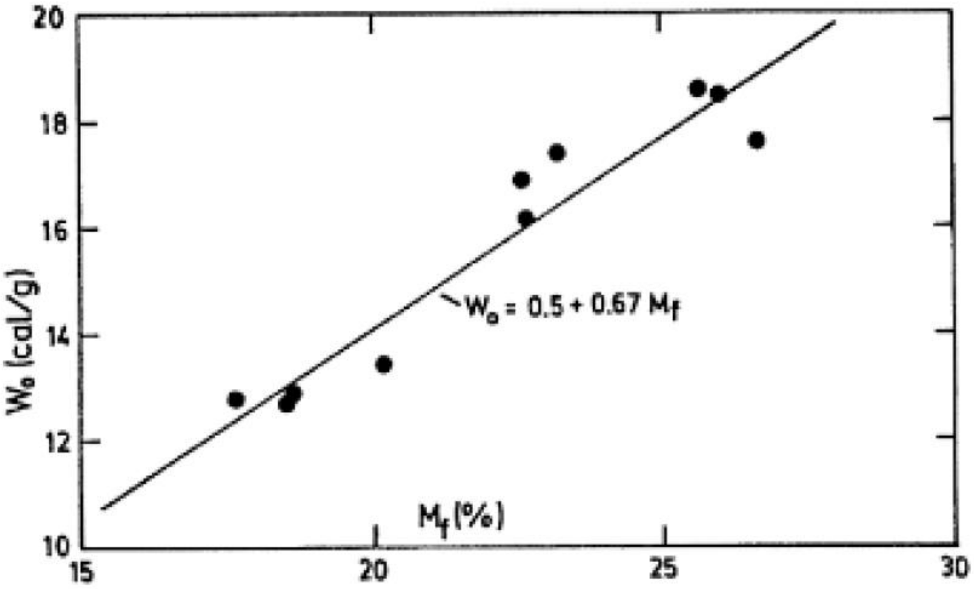


Figure. 2.4. Plotted points and calculated regression curve of total of wetting W_o, against estimated fibre saturation moisture content M_f (Kajita 1976)

Kajita (1977), also measured the total heats of wetting W_o for 22 US hardwoods grown on southern pine sites in the United States. Choong and Manwiller (1976) measured the fibre-saturation points by the shrinkage intersection method for the same woods, A linear regression of W_o against M_1 resulted in

$$W_o = 4.64+0.480\ M_f \qquad \text{Equation 2-2}$$

with all R^2 of 0.55, This was not as good a fit as was the case for the Japanese woods cited above, possibly because the heats of wetting and fibre-saturation point measurements were carried out on different samples.

The various components of wood have been shown to vary with respect to their hygroscopicities the hernicelluloses being most and lignin the least hygroscopic, Kijita. (1977) reported mean values for hemicelluloses, cellulose, and milled wood lignin of Pinus densiflora and fagus crenata of about 28, 19 and 14 cal/g dry material, respectively. This is in general agreement with the correlation between the hygroscopicity and total heat of wetting of wood, noted above. Kajita (1976) also used the method of mixtures to determine the contribution of each component to the total heat of wetting of wood.

Kajita (1977) measured the total heats of wetting W_0 for woods, comparing untreated wood with wood treated to remove extractives and to decrease lignin and hemicellulose contents. He reported that W_0, generally increased after extraction with alcohol-benzerte, increased with removal of lignin, particularly for short treatment times, and decreased with removal of hemicelluloses from the holocellulose constituent. Raczkowski (1963) also reported a substantial increase in W_0 after alcohol-benzene extraction.

Kajita (1976) found that the total heats of wetting of the inner barks of 22 hardwood species from the United States ranged from 14.16 to 20.45 cal/g, essentially similar to those for wood. However he noted that values for outer bark were generally considerably lower, indicating the lower hygroscopicity of outer compared with inner bark.

Other factors also influence the total heat of wetting. For example, the measured value of W_0 increases as particle size decreases, according to Kelsey and Clarke (1956). Kajita (1976) reported that W_0 increased from 17.15 to 20.04 cal/g when the fineness of the wood particles was reduced from that passing through 20 to 40 mesh screen to wood flour passing through a 250 mesh screen.

It has been shown that the heat of wetting W_0 for a hygroscopic material decreases with increasing moisture content. However, a hysteresis effect has been observed, in that wood conditioned to a given moisture content by desorption yields a higher value for W than when conditioned to the same moisture content by resorption. Figure 2.5 shows curves obtained by Kijita (1976) with Japanese Hinoki (Chamaecyparis obtuse) and also with cotton cellulose.

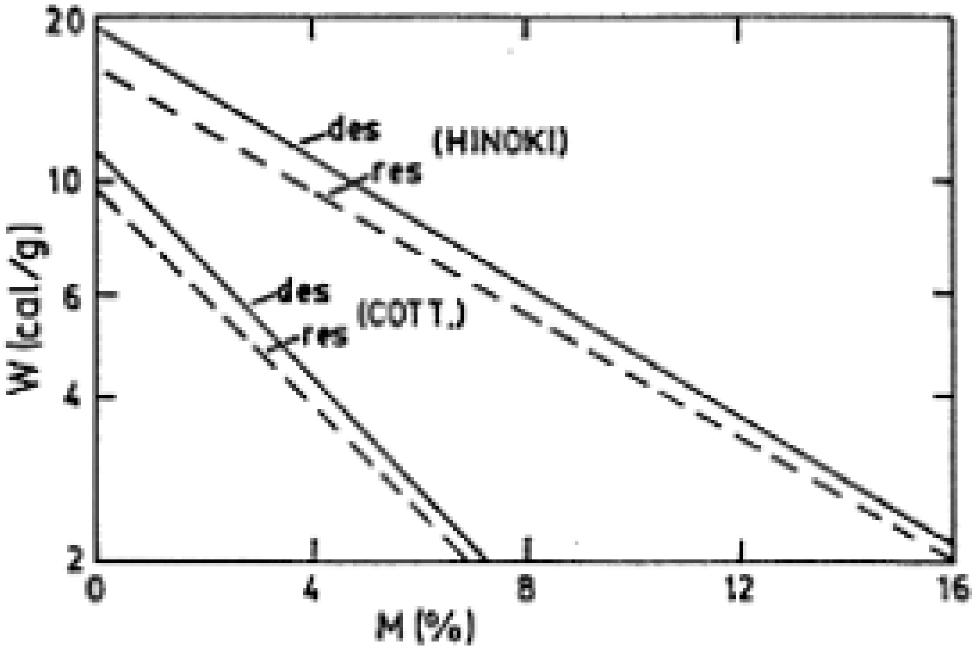


Figure 2.5. Curves of heat of wetting W_o (Log scale) plotted against initial wood moisture for both Hinoki cypress and cotton, for both resorption and desportion (Kajita 1976)

It has been shown that the differential heat of sorption, Q_s, and the heat of wetting W_o are interrelated. Furthermore Q_s is obtained by calculation from sorption isotherms using the isosteric method, while W is measured directly by calorirnetry, However, Rees (1960) has noted several sources of inaccuracies in calculating Q_s, from the sorption isotherms, These are

1. Plots of sorption isosteres (in (a) vs.1/T)m are not always accurate or linear.
2. The assumption in the Clausius Clapeyron that Qs is constant with temperature is not necessarily correct.
3. The Clausius-Clapeyron equation assumes reversibility in the sorption isotherm, which is not true because of sorption hysteresis.

Based on the inherent inaccuracies in the isosteric method of calculating Qs (and W_o), it is concluded that values obtained by classical calorimetric techniques are generally more reliable and reproducible than those based on isosteric calculations from the sorption isotherms.

2.4.2. Self-Heating In Large Scale

As discussed earlier in this chapter, the critical temperature of ignition decreases as the biomass heap size increases. Thus, when storing large amounts of biomass, there is a high tendency of decomposition with release of heat and emissions of toxic gases, depending on the storage condition (Lavery, 2001; Meijer, 2007; Arshadi, 2005; Wihersaari 2005). A significant pattern of temperature increase was reported recently in a 21.9m diameter wood pellets storage silo (Larson, 2012). A maximum rate of temperature increase of 1.7 $^oC/h$ was observed and a maximum temperature of 60 ^oC at the centre of the pile was recorded during storage (at which point the silo was discharged). Significant temperature increases were also normally found in other biomass storage, and temperature can easily rise to 60-70 ^oC for fresh wood (Meijer, 2004) at which thermophilic fungi can still survive (Maheshwari, 2005).

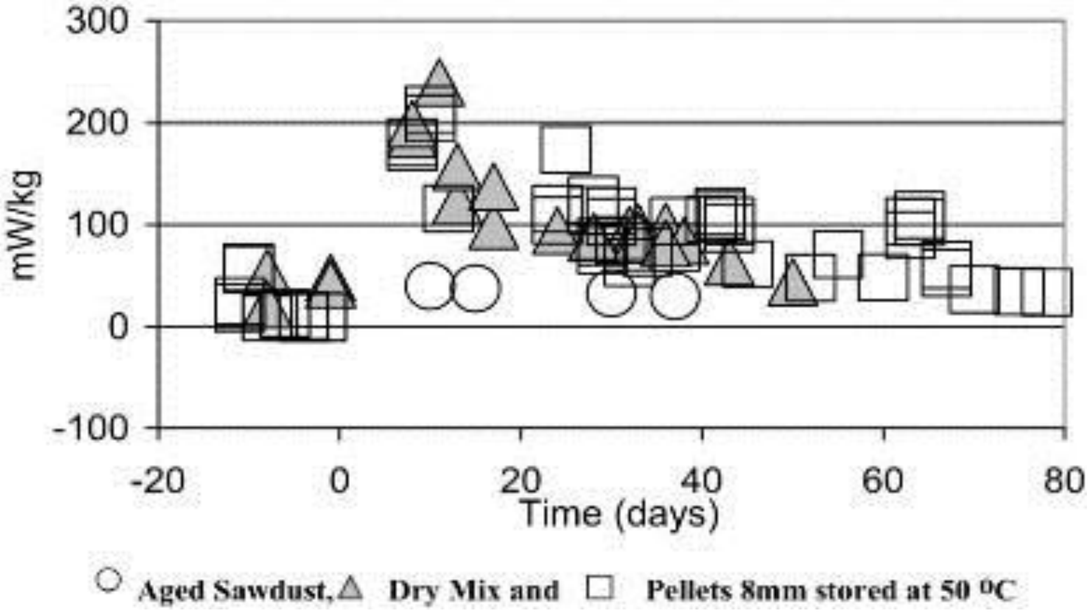


Figure 2.6. Heat generation three forms of biofuels at 50°C. (Rupar-Gadd, 2006)

The self-heating phenomenon was investigated on various biofuels (mainly sawdust and pellets) in the range of 20 to 60 °C using micro-calorimetry (Rupar-Gadd, 2006). The results showed that there was a peak in heat production after about 10 days for the sample stored at 50 °C during the storage period Figure 2.6. Beyond 10 days, the heat release level decreased and then remained at a lower and constant value for up to 74 days. Constant heat production rate was also found at 50 to 90 °C for wood pellets in Sweden (Wadso, 2007). After several spontaneous fires, more research has been focused on the storage problems and hazard control (Chico-Santamarta, 2011: Letikangas, 2000). For instance, blowing air through storage to cool down the bulk material can effectively eliminate self-heating (Yazdanpanah, 2010). However available data on heat production rate for predicting self-heating, and designing air flow are quite limited in the literature and urgently needed to be investigated.

2.4.3. Off-Gassing

In addition to self-heating problem, off-gassing is another serious hazard caused by decomposition of pellets during storage, which is especially dangerous for ocean transportation. Study on off-gassing of wood pellets was initiated after a fatal accident occurred on-board a vessel in the Port of Helsingborg, Sweden, in November 2006, when one seaman was killed, and a Stevedore was seriously injured (Pa, 2010). Ocean transportation of wood pellets in confined spaces may rapidly produce lethal levels of CO and an oxygen-deficient atmosphere that may affect adjacent access space and make those spaces dangerous for people to enter (Svedberg, 2008).

The Biomass and Bioenergy Research Group (BBRG) have been carrying out investigations on off-gassing of BC wood pellets during storage. Five 45-Liter metal containers and ten 2- Litre aluminium canisters were used to study the off-gassing of different types of biomass at different temperatures (Kuang, 2009). CO, CO_2 and CH_4 were the major gases emitted from the stored wood pellets at the test range, with CO_2 concentration being the highest and CH_4 being the lowest. The concentrations of the toxic gases in the sealed space of the reactors increased over time, fast at the beginning but levelling off after a few days (Svedberg, 2008). It is thus reasonable to assume that the decomposition process is a combination of an oxygen dependent reaction group and an oxygen independent reaction group. Kuang et al. (Kuang, 2009) developed a first order kinetic model and predicted the off-gas emissions and concentrations in storage containers at temperatures ranging from 10 to 55 ^{o}C. As the temperature increases, both the oxygen dependent and oxygen independent reaction rates increase with the increase of both CO_2 and CH_4

concentrations (Kuang, 2008). Comparing to wood pellets, more VOC emissions were found in stored sawdust and wood chips, such as hexanal and Pentanal compounds (Risholm-Sundman, 1998: Wihersaari, 2005). This is probably because during drying and pelletisation process, sawdust material is exposed to relatively high temperatures, resulting in decomposition, modification or destruction of extractives in the sawdust (Manninen, 2002: Banerjee, 2001).

2.5. Mechanism Of The Decomposition During Self-Heating

2.5.1. Metabolism And Microbial Activities

The vast majority of fungi grow best between 20 and 37°C, this temperature range is universally accepted as moderate. (Cooney and Emerson, 1964). The vegetative mycelium of these fungi, called the mesophilic fungi, cannot survive prolonged exposure above 40°C.Figure 2.7 shows ranges of growth.

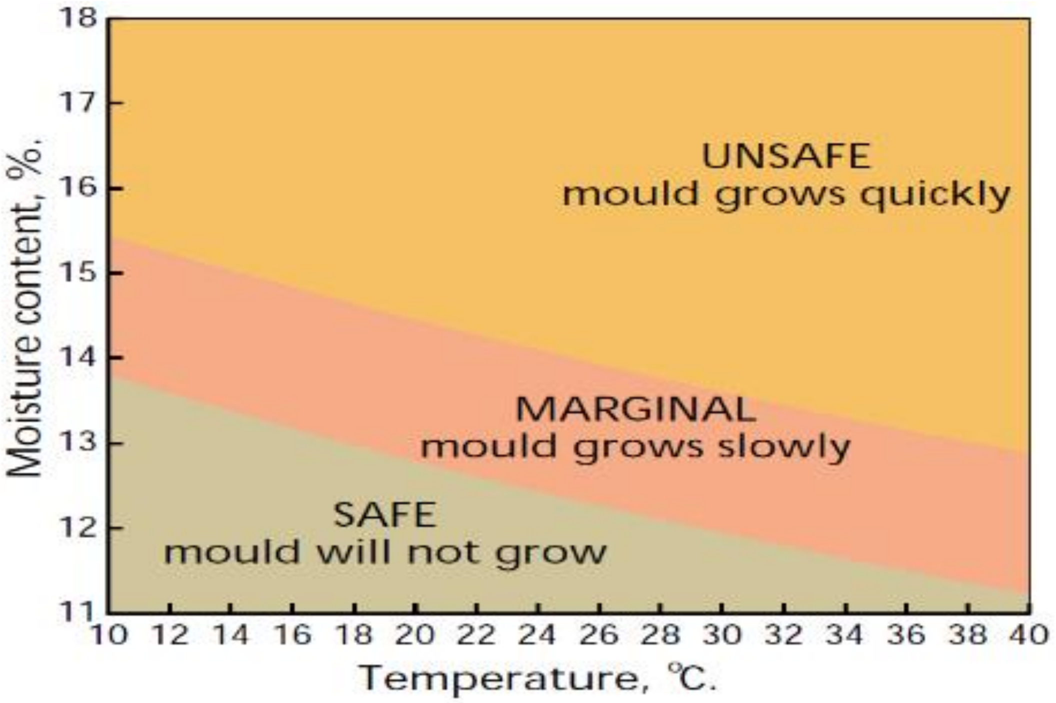


Figure 2.7. Safe moisture and temperature conditions (Darby, 1997)

However, currently some 30 species of fungi (Brock 1978; Blöchl et al., 1997) are known which show optimum growth between 40 and 50°C, with a few species capable of growth up to 62°C. These species are grouped as thermophilic fungi with their minimum temperature of growth around 20 to 25°C.

Thermophilic fungi were discovered as chance contaminants of bread or potato that had been inoculated with garden soil (Cooney and Emerson, 1964; Maheshwari et al., 2000). The inhabitants and growth conditions were discovered when Hugo Miehe (1907) of Germany investigated the cause of self-heating and the spontaneous combustion of damp stacks of hay. He studied the role of microbial flora in thermogenesis. From the self-heating haystacks, Miehe isolated several microorganisms, including four species of thermophilic fungi: Mucorpusillus (renamed Rhizomucor Pusillus), Thermomyces Lanuginosus (syn. Humicola Lanuginosa), Thermoidium Sulfureum (renamed Malbranchea Cinnamomea) and Thermoascus Aurantiacus.

To assess their role in the self-heating of Agricultural Residues, Miehe inoculated moist hay and other plant materials kept inside thermal flasks with pure cultures of individual fungi. Whereas sterilized hay did not generate heat that inoculated with the fungus did and the final temperature attained by the material showed a correlation with the maximum temperature of growth of the fungus used. Further, by controlled experiments, Miehe demonstrated that the naturally occurring microorganisms in moist haystacks or other plant materials caused its heating.

Cooney and Emerson (1964) explained spontaneous combustion as follows: Initially, the heat produced from the exothermic metabolic reactions in the mesophilic fungi raises the temperature of the compacted mass of vegetable matter to approximately 40°C, with this warm environment favoring the development of thermophilic fungi and actinomycetes present therein. The latter raise the temperature to about 60°C or higher, which corresponds with their upper temperature limit of growth. Above 60°C, the mycelial growth of thermophilic fungi declines and they survive as heat-resistant spores, whereas the actinomycetes raise the temperature of the mass up to their maximum around 75°C. Beyond this temperature, autocatalytic chemical reactions are triggered which can ignite the haystack. These reactions are discussed further in Chapter 2. The discovery of thermophilic fungi provided a link in the puzzle of spontaneous combustion of stored agricultural products.

Biomass decomposition is a complex process involving numerous biological and chemical reactions. The microbial metabolic activity is one of the important causes of self-heating and decomposition at low temperatures (Ryckeboer, 2003). For instance, the fundamental exothermic reaction, oxidation of glucose, as presented below (Petrucci, 2007), releases 282.88MJ of heat and 6 mole of CO_2 from the oxidation of one mole of glucose.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta G = -2.88 MJ/mol \qquad \text{Equation 2-3}$$

The microorganisms produce heat and water by breaking down the sugar, and enhance the environmental factors favouring further microbial activities (Meijer, 2011). This leads to deterioration in biomass quality, substance losses, health hazards due to the release of toxic VOCs (Kuang, 2008) and oxygen depletion (Svedberg, 2008), and potential for further self-heating of the material. Self-heating can in some cases lead to fire when heat from other sources in combination with self-heating in the biomass pile reaches the critical self-ignition point although the ignition delay can be several weeks.

Wood is a hygroscopic material which always contains some water. The water content has a significant influence on microbial activities. The study on biomass showed that the temperature in a pile depended on the initial moisture content (Meijer, 2004). Drying biomass will lower the microbial activity, but rewetting can revive dormant spores (Richardson, 2002). Lehtikangas, (2000) investigated the storage effect of nine assortments of wood pellets, and found that even though the pellets are relatively dry, temperature development, moisture content increase and microbial growth were still observed at some lots during five months storage. The increased activity in stored lots caused deterioration of the pellets quality especially durability. Some researchers also showed that humidity could significantly accelerate the decomposition of biomass by releasing heat and gas, and thus the speed to self- ignition. (Meijer, 2004; Wihersaari, 2005: Yang, 2007:

Fasina, 1995) however, the knowledge of microbial activities during pellets storage is very limited in the open literature

2.5.2. Chemical Degradation

Chemical degradation of woody materials involves a series of oxidation reactions such as hydrolysis and pyrolysis. Hydrolysis is a chemical reaction leading to the breakdown of the long chain molecules, hemicelluloses, cellulose (and lignin, to a lesser extent), accompanied by the uptake of water. The hydrolysis process is very complex and has been studied mainly for the purpose of producing bioethanol (Lynd, 1996). The hydrolysis of cellulosic biomass is generally a rate limited reaction with a very slow conversion and is normally accelerated by acid or enzymes during bioethanol production (Lynd, 1996). The suggested mechanisms of hemicelluloses and cellulose hydrolysis are illustrated in Figure 2.8. Two types of hemicelluloses were identified based on the reaction rate, fast-hydrolysing and slow-hydrolysing (Kobayashi, 1956).

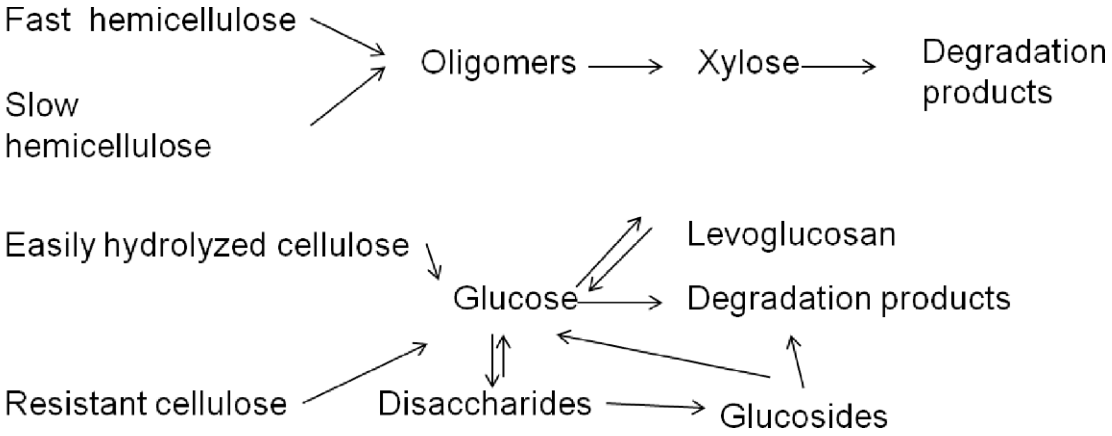


Figure 2.8. Hydrolysis mechanism, hemicelluloses and cellulose. (Jacobsen et. al. 2000)

Having a lower degree of polymerization and consisting of branched sugar chains, hemicelluloses are broken down more easily than cellulose. Long chains of hemicelluloses are broken down to shorter oligomers and then further to xylose, which breaks down to other degradation products (Saeman, 1945). Due to the crystalline structure of cellulose and the physical protection provided by hemicelluloses and lignin, the hydrolytic reactivity of cellulose is limited (Burns, 1986). The amorphous portion of cellulose, i.e. the non-crystalline portion, breaks down more easily to generate glucoses (Young et al, 1945: Mohan et al, 2006), which further break down to other degradation products, including the release of CO_2.

Pyrolysis becomes significant in the high temperature environment with a low oxygen concentration. Oxygen attacks the biomass surface, leads to degradation of biomass, and this can produce heat, solid char and volatiles, mainly CO_2, CO, CH_4 (Mohan et al, 2006: Yang, 2007)]. Many authors have studied pyrolysis in the absence of air. For example, Yang et al. found different pyrolysis behaviour for hemicellulose, cellulose and lignin. Figure 2.9 shows the pyrolysis behaviours of these components using the thermogravimetric analyser (TGA). The plot shows the loss for the three components and differential, the rate mass loss. Hemicelluloses are the easiest and fastest to be pyrolyzed among the three components, with a significant reaction rate beyond 220 ^oC. Cellulose is the most difficult to be pyrolyzed due to the crystalline structure (Rowell, 1983). And starts to decompose at approximately 315 ^oC. The lignin pyrolysis is different from hemicelluloses and cellulose due to the aromatic rings within the lignin, which lead to an extremely wide reaction temperature range of 200- 900 ^oC (Yang, 2007). Fast pyrolysis is studied as an important approach of producing biofuel and charcoal (Mohan et al, 2006) and slow pyrolysis is the significant cause for smouldering combustion and spontaneous ignition in woody biomass (Yang, 2007; Bilbao, 2002: Bilbao, 2001). Overall, pyrolysis is a very complex thermochemical process during which biomass goes through a huge series of reactions (Manya, 2003; Varhegyi, 1997).

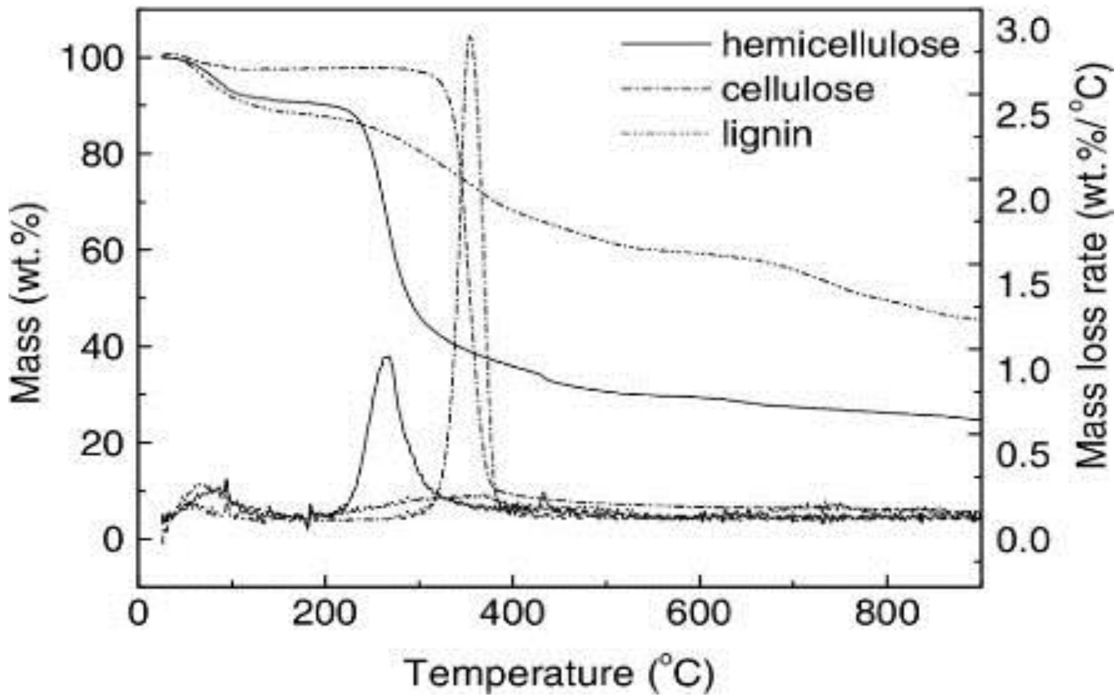


Figure 2.9. Pyrolysis behaviour of hemicellulose, cellulose and lignin in TGA. (Yang et. al. 2007)

2.6. Combustion

2.6.1. Smouldering And Flaming Combustion

Instead of burning directly, cellulose materials, such as woody materials, decompose and produce a mixture of volatiles, highly reactive char and tarry components under strong heat flux (Shafizadeh, 1984). Combustion of wood material involves a series of oxidation reactions depending on the air flow rate and the oxidation rate. Under an high oxidation rate, the combustion of flammable volatiles and tarry components creates flaming combustion. See figure 2.10 gives a presentation of the flaming and smouldering combustion showing the respective roles of combustible volatiles and active char produced by pyrolysis under heat flux at different conditions. (Adapted from Rowell, 1983) At low air flow rates, the production of gas phase can be limited or diluted, which cannot maintain the gas phase combustion (Ohlemiller, 1991). Under certain conditions, the oxidation of the solid phase creates glowing and smouldering combustion (Bilbao, 2001). During this stage, the solid phase temperature increases while heat and toxic gases are released from the combustion even though a flame does not occur (Ohlemiller, 1985). The smouldering reaction can be invisible developing into a rapid flame spreading combustion once the air flow increases, or other condition changes which might increase the oxidation rate (Ohlemiller, 1985). Both flaming combustion and smouldering combustion are affected by the air flow rate. Smouldering propagation rate increases under higher air flow rate and the development to flaming combustion takes place much faster (Ohlemiller, 1991).

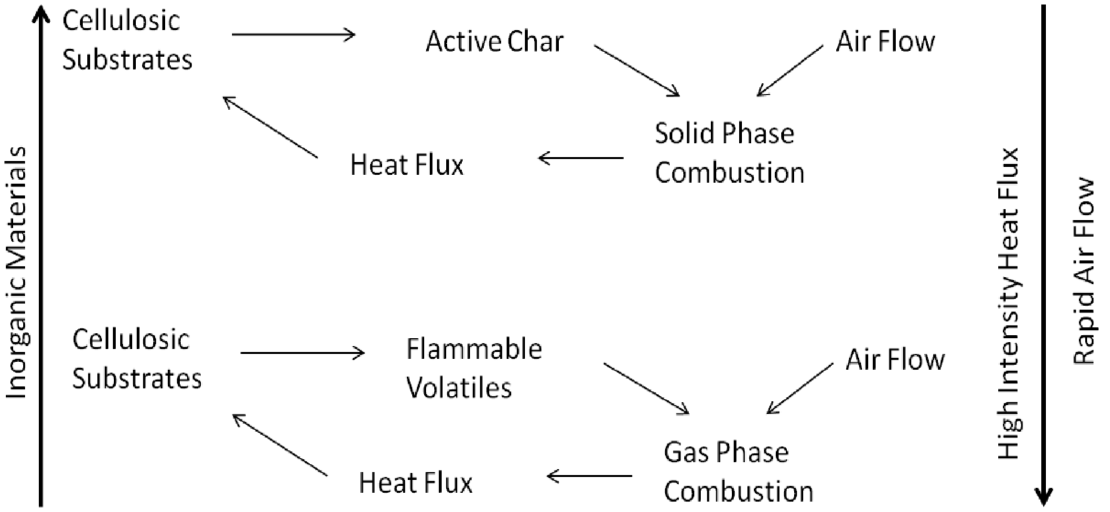


Figure 2.10. Presentation of the flaming and smouldering combustion showing the respective roles of combustible volatiles and active char produced by pyrolysis under heat flux at different conditions. (Adapted from Rowell,1983)

Due to the low permeability of solid wood, the oxidation zone remains close to surface of the solid wood (Ohlemiller, 1985). Wood pellets have a greater permeability and faster oxygen diffusion (Yazdanpanah, 2010) than solid wood, which suggests that wood pellets might have a greater chance to smoulder with a faster smouldering spread rate than solid wood.

2.6.2. Spontaneous Combustion

Smouldering is one of the most important phenomenon that may follow spontaneous combustion. Large amounts of heat and flammable gases are generated while the solid phase is slowly charring when the pyrolysis reaction rate is high enough. Spontaneous ignition occurs when the smouldering develops into flaming combustion.

There have been a number of investigations on the self-combustion of biomass and wood Residues (Yang, 2007; Bilbao, 2002; Miao, 1994; Liodakis, 2002). For the piles studied, the results showed that at temperatures above 100 °C, wood started to pyrolyze and become charred; the black residue of pyrolyzed organic material is called charcoal. If a pile of stored material is exposed to oxygen during the ongoing pyrolysis, the smouldering will turn into an overt fire.

Smoulding combustion produces heat, but no light and can move to glowing combustion which produces more heat and some light, and finally flaming combustion which produces both heat and light. Ignition temperature is defined as the temperature at which light is emitted (Yang, 2010). McCarter, (1978) showed that hay reached its ignition temperature point at or near 200 °C, and the speed of combustion depended on the air temperature and relative humidity.

Yang (2007) found that the ignition temperature of wood was around 300 °C, and the time to reach ignition increased with the increase in the density of wood. Dust from wood pellets suspended in air has been found to ignite at 450 °C in ambient conditions with limited oxygen supply, tested according to the ASTM E 1491 standard for determination of minimum autoignition temperature. For a stationary sample of the same dust and with ample air supply, the ignition temperature was 225 °C as tested in accordance with the Bureau of Mines RI 5624 Standard (Melin, 2008).Liodakis 2002 showed that retardant, such as $(NH_4)_2HPO_4$ (DAP) and $(NH_4)_2SO_4$ (AS) reduced considerably the ignition properties of the forest species, affecting their ignition delay (combustion time) and fire point values, defined as the minimum surface temperature at which flaming combustion (ignition) occurs.

2.6.3. Dry Matter Loss

Dry matter loss, which results from the degradation of lignin, cellulose, and hemicellulose, occurs when wet woody biomass, in any form, is not utilized immediately. (Richardson et al, 2002). The degree to which dry-matter loss occurs, is largely dependent on the materials moisture content. Woody biomass, having higher moisture content, is more susceptible to colonization by fungi and mould and at a faster rate (Richardson et al, 2002). 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 results in a reduction of overall energy content as well as leads to an increase in ash content (Richardson et al, 2002)

Several studies (Thornqvist and Jirjis 1990; Fredholm and Jirjis 1988) have observed dry matter loss in stored woody biomass. Green chips stored in a large pile for seven months lost approximately 12 percent of their dry matter, and bark stored in a large pile for six months lost approximately 26% of its dry matter. The dry-matter loss in the bark pile resulted in a 20 percent decrease in energy content.

Dry matter loss is particularly a problem in chipped material. This is because:-

- chipping increases the area of exposed surfaces on which microbial activity can occur
- the small particle size gained by chipping restricts air flow and prevents heat dissipation
- Chipping releases the soluble contents of plant cells providing microbes with nutrients (Richardson et al, 2002).

Increases in ash content due to dry-matter loss are also higher with chipped material; although, the reasons for this remain unclear (Richardson et al, 2002).

2.6.4. pH and Lignocellulosic Composition Effects

Allen (2000) observed that excessively long wood storage can result in wood deterioration such as fungal stains, brittleness and high acidity. When the temperature in wood piles reaches 60-70°C, (or similar temperatures during pellet production), a chemical reaction occurs in which the acetyl groups present in hemicellulose molecules are cleaved, forming acetic acid (Kubler, 1982). This reaction produces heat and raises the acidity of the wood pile. The increased heat, of course, drives this reaction even faster if it is not dissipated, releasing more acid. The acid, in large quantities, causes deterioration of wood by attacking the cellulose molecules. (Scallan, 1979). The increase in acidity and heat darkens the wood, and it eventually crumbles as if burned. In extreme cases, the pH can be as low as 3.5.

Table 2.3. Composition of lignocellulose in several sources on dry basis (Sun and Cheng, 2002)

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat Straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10
Primary wastewater solids	8–15	NA	24–29
Swine waste	6.0	28	NA
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Coastal Bermuda grass	25	35.7	6.4
Switchgrass	45		

Early work on the chemical constitution of the acidity showed that the non-volatile fraction consisted of lactic, malic and succinic acids, while the volatile acids included acetic and formic. Lactic and acetic acids predominated. (Firth and Stuckley, 1947). Table 2.3 shows the differences of lignocellulosic components between woods and agricultural materials. The Agricultural Residues are generally higher in hemicellulose, which according to Kubler (1982), would lead to more acetic acid being formed.

2.6.5. Formation Of n-Hexanal

n-Hexanal was the predominant straight chain aldehyde found in the volatile organic compound mixture emitted from wood pellets by Svedberg et al (2007). Apart from carbon monoxide, the volatile compounds identified by Svedberg are previously known as low level emittants from wood and wood products and are often identified in indoor air investigations. A polyunsaturated acid, linoleic acid is the major constituent in the mixture of free fatty acids and triglycerides found in such wood (Hoell and Piezconka, 1978; Piispanen and Saranpaa, 2002). Radical-induced oxidation by oxygen of linoleic acids or its esters yields n-hexanal as the major volatile component (Schieberle and Grosch, 1981). These reactions are summarised in Figure 2.11. Such reactions can be either enzyme catalysed or occur through a so called autoxidation process (Schieberle and Grosch, 1981; Noordermeer et al., 2001). Because of the high temperature involved in pellet production (70 – 90^{0}C), with enzyme denaturation as a probable consequence, the major path for this process in pellets most likely proceeds through autoxidation.

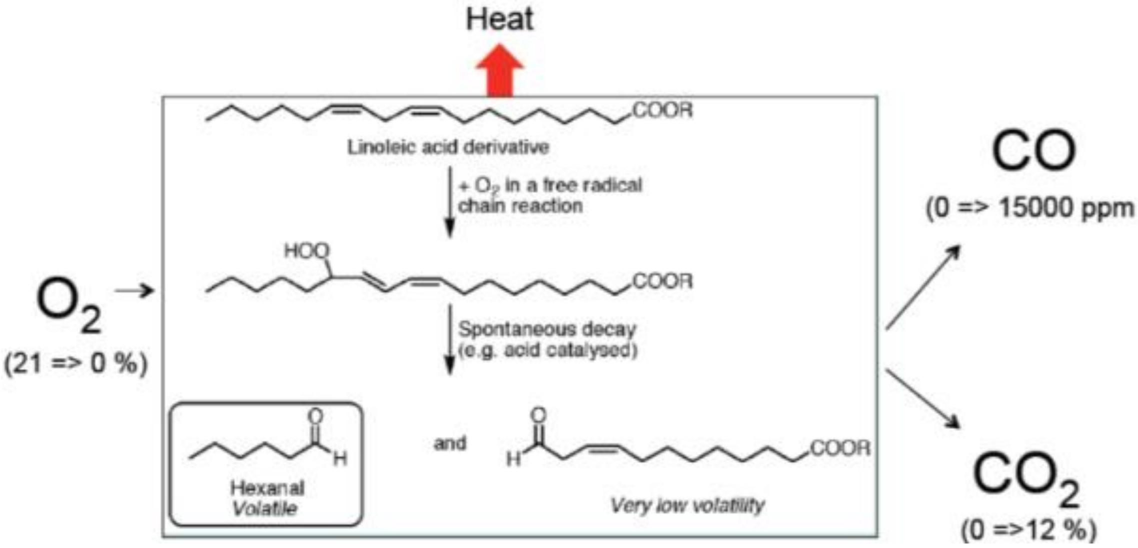


Figure 2.11. Chemical oxidation mechanism of fatty acids

2.6.6. Formation Of Carbon Monoxide

The emission of one-carbon compounds containing oxygen and hydrogen, such as methanol, formaldehyde and formic acid, from pellets is not surprising (Svedberg et al 2007). The last two compounds may be autoxidation products of methanol. Other one-carbon compounds are carbon monoxide and carbon dioxide. It is well known that during the thermal anaerobic degradation of wood (pyrolysis) carbon monoxide emission occurs. Carbon monoxide has a characteristic infrared spectrum and cannot be mistakenly identified. Microsomal lipids also produce carbon monoxide during peroxidation, initiated via different Fe (III) complexes. After initiation the reaction appears to be not enzymatic, i.e. an autoxidative process (Wolff and Bidlack, 1976). Carbon monoxide (300–400 p.p.m.) has been observed in the air above 7000 tonnes of rapeseed stored in a sealed warehouse and in this case the calculated specific emission rate has been estimated to be 200 mg/ton/day (Reuss and Pratt, 2001).

Carbon monoxide has also been found in a wheat grain warehouse with a calculated specific emission rate of 9 mg/ton/day (Whittle et al., 1994). These emission rates can be compared with the specific emission rates found in small pellet storage, ranging from 100 to 885 mg/ton/day (Svedberg 2007). The more rapid formation of carbon monoxide in materials with a high fat content (rapeseed) compared with those with a low fat content (wheat) indicates that carbon monoxide may be formed through the autoxidative degradation of fats. Svedberg suggested that carbon monoxide formation during storage of the wood pellets is caused by the autoxidation of residual lipophilic extractives present in pellets, mainly fats and fatty acids. However, carbon monoxide formation from other organic materials present in wood, like cellulose, hemicellulose and lignin, cannot be ruled out.

2.7. Dust And Explosion

Manufactured from sawdust, bulk wood pellets always contain a certain amount of sawdust (fines), which also increases during handling and transportation due to the breakage of pellets (Yazdanpanah,2010). The dust generated from wood pellets ranges from 500 to a few μm in diameter (Melin, 2008). The dust could cause some issues during handling. For instance, dust increases the resistance to airflow causing disparate temperature distribution (Yazdanpanah, 2010) and the fine dust, < 100μm, could be inhaled by people causing health issues (Melin, 2008).

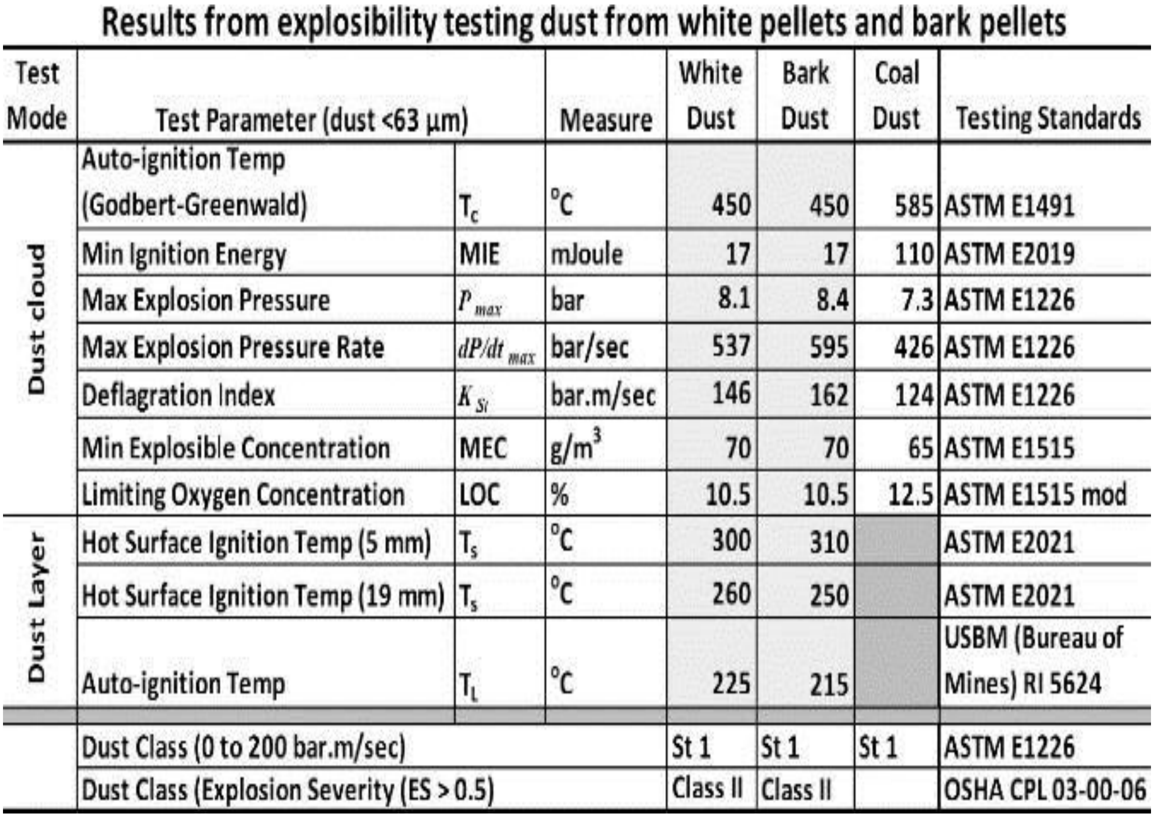
Among all the influences, dust explosion is the most dangerous hazard, which has frequently happened during the handling of combustible materials involving fine powders, such as coal, sulphur powders and wood dust (Calle, 2005). The fast combustion of fine dust causes a rapid pressure increases (Calle, 2005) and hot gases releasing in a confined space, which lead to the dust explosion. Controlling the source of dust and oxygen is very important in preventing dust explosion.

The dust limit for safe operation is provided in the Material Safety Data Sheet (MSDS) of the wood pellets (Wood Pellet association of Canada, 2011)]. The ignition source is another necessary factor that contributes to the dust explosion, which could be hot surfaces, mechanically generated sparks, lightning, electric currents or flames. The explosibility for wood pellets dust was tested under different condition using Canadian pellets (Melin, 2008), with the results listed in Table 2.4. Even though the auto-ignition temperature of dust, 450 ^{o}C, is reassuringly high, the auto-ignition temperature of dust layer is much lower, 215-225°C. This result can also be found in other Material

Safety Data Sheet (MSDS) of other dust-contained wood materials, such as, 220°C for sawdust from untreated softwood (Sawmilling, 2000) and 220°C for sawdust from untreated hardwood (Hyne, 2007)

Combustible biomass dusts are formed at various handling stages, and accumulations of these dusts can occur on hot surfaces of electrical and mechanical devices and can pose fire risks (Chin et al, 2016). Their study evaluates the ignition characteristics of dust from two types of biomass commonly used in the U.K. power stations: herbaceous Miscanthus and woody pine. The ignition risks of the individual biomass and their blends in two different weight ratios, 90 wt % pine to 10 wt % Miscanthus and 50 wt % pine to 50 wt % Miscanthus, were investigated. Biomass-biomass blends represent the power plant scenario where a number of biomass are fired under daily operation, and thus, dust sedimentation could consist of material blends. It should be noted that the result (validated for up to 5 mm thickness) is not significant enough to influence plant operations for the ignition risk from thin dust layers according to the National Fire Protection Association (NFPA) standards.

Table 2.4. Results from explosibility testing dust from white pellets and bark pellets (Melin 2008).



Results from explosibility testing dust from white pellets and bark pellets

Test Mode	Test Parameter (dust <63 µm)		Measure	White Dust	Bark Dust	Coal Dust	Testing Standards
Dust cloud	Auto-ignition Temp (Godbert-Greenwald)	T_c	°C	450	450	585	ASTM E1491
	Min Ignition Energy	MIE	mJoule	17	17	110	ASTM E2019
	Max Explosion Pressure	P_{max}	bar	8.1	8.4	7.3	ASTM E1226
	Max Explosion Pressure Rate	dP/dt_{max}	bar/sec	537	595	426	ASTM E1226
	Deflagration Index	K_{St}	bar.m/sec	146	162	124	ASTM E1226
	Min Explosible Concentration	MEC	g/m^3	70	70	65	ASTM E1515
	Limiting Oxygen Concentration	LOC	%	10.5	10.5	12.5	ASTM E1515 mod
Dust Layer	Hot Surface Ignition Temp (5 mm)	T_s	°C	300	310		ASTM E2021
	Hot Surface Ignition Temp (19 mm)	T_s	°C	260	250		ASTM E2021
	Auto-ignition Temp	T_L	°C	225	215		USBM (Bureau of Mines) RI 5624
	Dust Class (0 to 200 bar.m/sec)			St 1	St 1	St 1	ASTM E1226
	Dust Class (Explosion Severity (ES > 0.5)			Class II	Class II		OSHA CPL 03-00-06

2.8. Health Hazards

In addition to the fire and explosion hazards covered in the preceding sections, the handling, processing and storage of biomass can introduce biological health hazards. Much of the work on these hazards have been done in the agricultural and waste sectors, particularly relating to compost and the safe handling of waste materials. Potential hazards include hazards arising from bioaerosols, including dust, allergic and pathogenic responses. This issue is important for all biomass materials considered for use in combustion plant, and it is also important for anaerobic digestion.

The health and safety effects resulting from the preparation and use of biomass fuels that derive from the biological nature of the biomass and waste mainly result from the formation of dusts and “bioaerosols”. Bioaerosols are a broad term for airborne pollutants, specifically particulate matter usually associated with compounds of biological origin, this detailed in Table 2.5.

Table 2.5. Definitions of biological origin

Physical	Where the physical interaction of the particle with the respiratory tract generates heath impacts.
Irritant/ allergic	Where the biological particle generates an immunological response from the biological nature in the host such that adverse health effects are experienced
Pathogenic	Where a viable organism is inhaled and the organism propagates and infects the host causing disease

Bioaerosols can be generated in a number of ways, for example as liquid droplets or as dry materials which are suspended in the air either individually, as clusters or carried on other organic material. Bioaerosols are ubiquitous in ambient air and are generated by physical disturbance of biological material and by biological activities, such as breathing and coughing. They can be carried short or long distances by varying air currents and exposure to them is a normal part of life. As a result, human physiology has mechanisms to deal with the environmental exposure, which complicates assessing the risk factors from the use of biomass or waste fuels. However, exposure (both occupational and domestic) is greatly increased as more organic material is stored and/or reprocessed. In these circumstances, depending on the material and the type of reprocessing, it is possible to create a potentially high level source of bioaerosols within the natural environment.

The main hazard threat posed by bioaerosols to humans and animals is the increased risk of health related problems, which include respiratory diseases, acute toxic effects, allergies and cancer. These effects are due to the physical size and ability of the microorganisms and their associated products to be inhaled deep into the respiratory tract. Prolonged exposure to elevated levels significantly increases this risk.

While many of the impacts result from bioaerosols in general, there are also species specific impacts from the different forms of bioaerosols. Consequently a broad discussion of “bioaerosols” has similarities to a discussion of the impacts of “chemicals,” - the term is too generic to be useful. To gain greater resolution, subdivisions are identified through segregation of bioaerosols by bacteria, viruses and fungi as well, as the chemical compounds that induce effects such as ß-glucans and endotoxins; but even these sub-divisions are aggregate forms of analyses.

2.8.1. Physical Interaction

Physical interaction is the same for any dust of similar particle size, whether biological or inert, and there is substantive data and regulation on the risks from these sources. Regulations for dusts tend to link to the depth to which the dust particles will enter the respiratory tract, and thus inhalable, thoracic and respirable limits are set in many countries. The hazard is greater the further into the lung that the particles can travel. See Table 2.6

Table 2.6. Physical dust interactions

Inhalable Dust (PM100)	Airborne particles which can enter the nose and mouth during normal breathing. Particles of 100 µm diameter or less
Thoracic Dust (PM10)	Particles that will pass through the nose and throat, reaching the lungs. Particles of 10 µm diameter and less.
Respirable Dust (PM2.5)	Particles that will penetrate into the gas exchange region of the lungs. A hazardous particulate size less than 5 µm. Often limit values cite particle sizes of 2.5 µm (PM2.5).

Depending on size, aerosol particles easily deposit in various parts of our airways (as shown in Figure 2.12) we inhale and subsequently causes illnesses such as acute reactions, chronicle reactions or tumours (see M S D S for wood pellets ,Melin, 2008)).

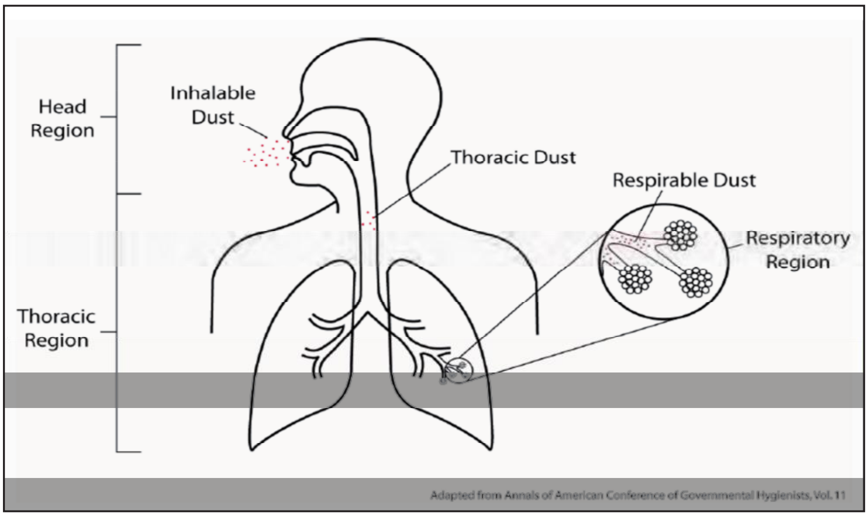


Figure 2.12. Regional particle deposition in the airways (Adapted from Annals of American Conference of Government Hygienist, Vo11)

Bioaerosols are typically derived from cells or cell fragments and will have a particle size of 1-20 µm. However, in some circumstances larger particles are generated from either agglomerates or material dusts generated by degradation of the biomass e.g. wood dusts in sawmills or chipping plant. The most serious damage is done by respirable dust particles which are able to enter our bloodstream through the alveoli where particulates inhaled during a lifetime, which amounts to about 3 teaspoons full of particles (Gudmundsson, 2007). The surface of the head region exposed to air is about 0.5 m^2, the bronchial-thoracic region about 2 m^2 and the respiratory alveoli region about 100 m^2.

In most biomass fuel environments dust will be the most significant risk factor and typical limit values for dust are presented in Table 2.7. General dust level limits exist in most countries based on occupational exposure levels, for industries that pose higher risk levels due to the nature of the dusts created more stringent levels are enforced to deal with the additional risks posed whether they be inert (e.g. asbestos, silica) or organic (e.g. flour, cotton, woodworking).

Table 2.7. Typical limit values for dust from the World Health Organisation (2016)

Country	Limit	Value
UK	Occupational dust $OEL_{8\ hour}$	10 mg/m^3
UK except Scotland	Ambient air quality annual mean PM_{10} daily limit PM_{10} annual mean $PM_{2.5}$ target for urban background ($PM_{2.5}$)	40 µg/m^3 50 µg/m^3 25 µg/m^3 , 15% reduction by 2020
Scotland	Ambient air quality annual mean PM_{10} annual mean $PM_{2.5}$	18 µg/m^3 12 µg/m^3
European Union (2008)	Annual limit PM_{10} Daily limit PM_{10} Target for $PM_{2.5}$	40 µg/m^3 50 µg/m^3 (not to be exceeded more than 35 times a year). 25 µg/m^3 by 2015 20 µg/m^3 by 2020
W H O (2005) guidelines	PM_{10} annual mean PM_{10} daily mean $PM_{2.5}$ annual mean $PM_{2.5}$ daily mean	20 µg/m^3 50 µg/m^3 10 µg/m^3 25 g/m^3

2.8.2. Irritant/Allergic Hazards Of Biomass To Humans

The organic nature of some dusts and particles can pose additional hazards due to the biological response that the body and immune system provide. This response is highly specific to the individual, which makes developing guidelines complex. In a general sense, the body reacts to markers in biological material that allow the body to identify the appropriate response to counteract the threat posed by the organisms or material. These mechanisms deal with normal day to day exposure and by and large do not cause health impacts. There are common exceptions to this in the form of allergic responses e.g. asthma and milder effects such as hay fever.

The nature of the response mechanism results in the response being related to the organism/material but in general there are two groups of conditions: Allergic - Allergic Alveolitis (sometimes called hypersensitive pneumonitis), and Asthma and Allergic Rhiniti; and - Organic Dust Toxic Syndrome (ODTS). The main distinction between these is that the allergic responses will be generated by immunological sensitisation towards a specific agent and will cause the production of a specific immunoglobin E response, whilst ODTS is a more generic and nonspecific response without long lasting effects.

The allergic effects are added to by the toxic effects of some of the biological materials and thus fungal (mycotoxins) and Gram-negative bacterial toxins (exo- and endotoxins) also play a role in the health impacts. Whilst at this stage these effects are not fully understood, the mechanisms are likely to be easier to develop dose response relationships as the mechanisms are less likely to be specific individual response as in immune responses to allergens. The impacts of these responses vary, but have a similar range of symptoms, including influenza like symptoms, chills, fever, dry cough, malaise, breathlessness and weight loss. The principal distinction is that allergic responses are chronic conditions that once the individual is sensitised by repeated exposure at low (non-toxic) doses causes a reaction; and O D TS is an acute condition that is a response to an exposure to a toxic level of the hazard that, in general, does not lead to long-term health effects.

2.9. Kinetic Parameters And Laboratory Analysis

An accurate prediction of self-heating process and self-ignition in a pellet silo is very important in order to prevent the spontaneous fires and dust explosion, as well as to minimize the quality degradation caused by self-heating. Large scale experiments are usually expensive and difficult to carry out, so mathematical modelling is an appropriate approach to predict the self-heating process and self-ignition of a pellet silo.

Self-heating and ignition behaviours have been studied on solid materials, such as wood and coal. Numerous theoretical studies have been carried out mostly using combustion models originally developed for wood and coal combustion in which the prediction of the ignition condition has been incorporated (Yang, 2007; Bilbao, 2002; Bilbao, 2001). Thermal properties and thermal decomposition kinetics parameters are needed in these models. Thermal properties of the materials are considered either constant (Bilbao, 1990; Bilbao, 1993) or varying as a function of solid conversion or temperature. Kinetics parameters also have variables depending on different reaction mechanisms. Simple first-order reaction kinetics is commonly used in the modelling of thermal degradation of solids fuels. Although some more advanced ignition models also take into account very complex phenomena such as the gas-phase process (Tzeng, 1990), the main objective of this study is to predict the self-heating process of the solid phase and self-ignition conditions using relatively simple models in a general way. The following parameters have to be accurately investigated in order to build up the self –heating model.

2.9.1. Thermal Properties

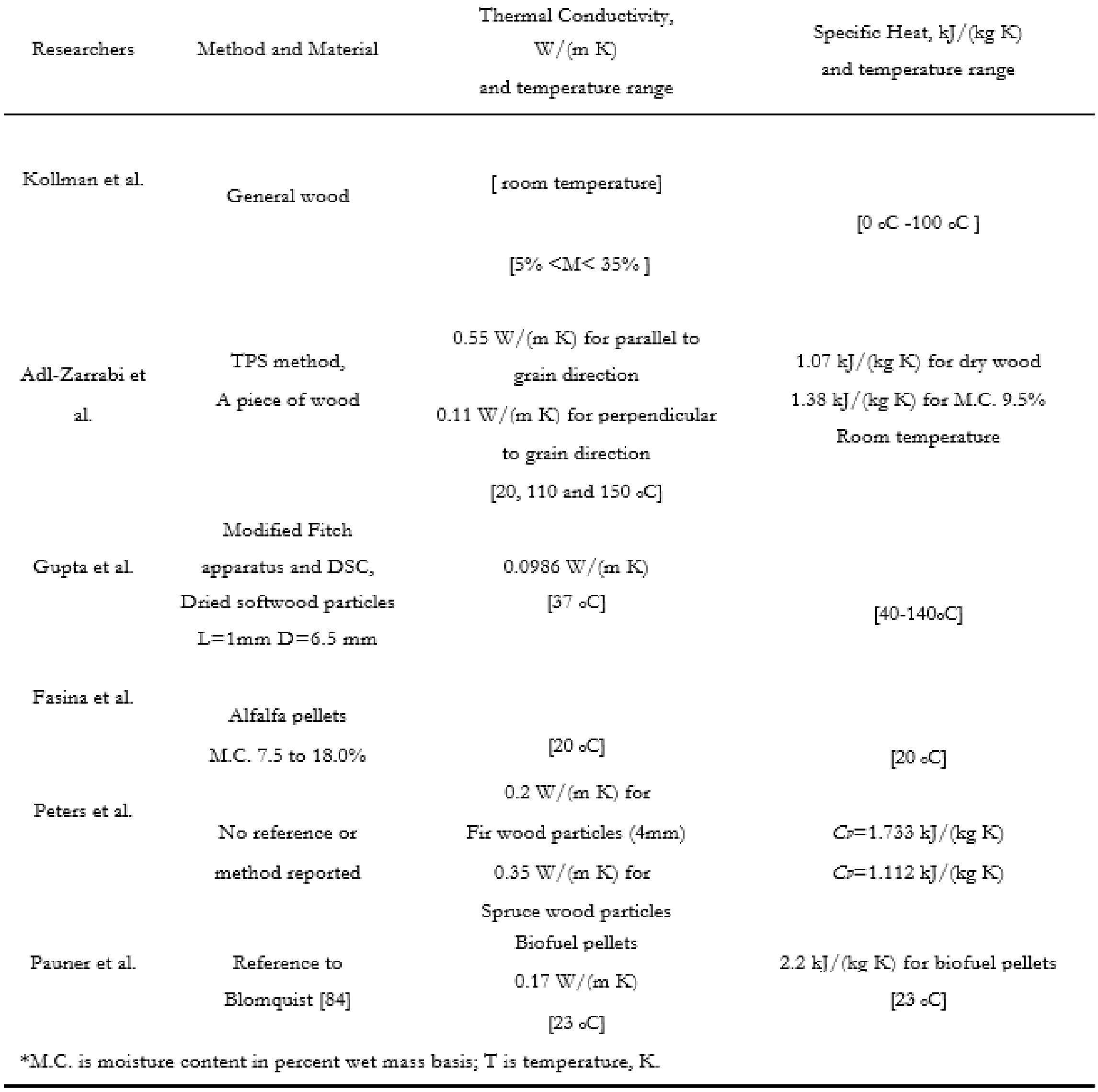
Thermal properties including thermal conductivity and specific heat capacity are very important parameters in investigating self-heating and spontaneous ignition. These parameters can be measured by several well-established methods (Mohsenin, 1990) and some new methods developed lately (Adl-Zarrabi, 2006). There are some thermal property data available in the literature (Blomquist, 2006).

Table 2.8 Published data on specific heat and thermal conductivity lists a few thermal properties data for various forms of solid wood and for agricultural materials. For solid wood, Kollman et al. 1968 proposed empirical equations for estimating thermal properties as a function of density, moisture content at room temperature for wood with moisture contents from 5% to 35%. Adl-Zarrabi et al. 2006 measured thermal properties of a dry wood piece (spruce) at 20^oC, 110^oC and 150^oC. The results showed that the thermal conductivity is highly dependent on the fibre orientation of the wood specimen, higher thermal conductivity parallel to the grain direction than perpendicular to the grain direction, and not too much on the temperature. Gupta et al. 2003 developed an empirical relation between specific heat capacity and temperature for dried softwood particles in the temperature range of 40 to 140 ^{o}C using differential scanning calorimetry (DSC). Thermal properties of typical solid wood materials were also reported in other literatures (Gupta, 2003; Peters, 2003; Vijeu, 2008).

The effect of moisture content on the thermal properties of alfalfa pellets was studied by Fasina et al. 1995 using the line heat source method for moisture content from 7.5% to 18% w.b. (wet basis). Their method was based on a lower order approximate solution of thermal diffusion equations. Pauner et al. 2007 assumed a constant thermal conductivity of 0.17 W/ m K and a specific heat of 2.2 kJ/ kg K for studying self-heating of biofuel pellets. Blanchard at Swedish National Testing and Research Institute also mentioned a value of 0.17 W/ m K for 6 mm wood pellets (bulk density of 603 kg/m^3), however, the experimental method was not given in both papers. Even though wood pellets are made of ground wood, the structure of wood particles and wood pellets are different.

Thus the thermal conductivity of wood pellets is expected to be different from the solid wood. Therefore, instead of directly applying those reported in the literature for solid wood, it is necessary to determine the thermal properties of wood pellets and their dependence on bulk density, moisture content and temperature.

Table 2.8. Published data on specific heat and thermal conductivity



Researchers	Method and Material	Thermal Conductivity, W/(m K) and temperature range	Specific Heat, kJ/(kg K) and temperature range
Kollman et al.	General wood	[room temperature] [5% <M< 35%]	[0 oC -100 oC]
Adl-Zarrabi et al.	TPS method, A piece of wood	0.55 W/(m K) for parallel to grain direction 0.11 W/(m K) for perpendicular to grain direction [20, 110 and 150 oC]	1.07 kJ/(kg K) for dry wood 1.38 kJ/(kg K) for M.C. 9.5% Room temperature
Gupta et al.	Modified Fitch apparatus and DSC, Dried softwood particles L=1mm D=6.5 mm	0.0986 W/(m K) [37 oC]	[40-140oC]
Fasina et al.	Alfalfa pellets M.C. 7.5 to 18.0%	[20 oC]	[20 oC]
Peters et al.	No reference or method reported	0.2 W/(m K) for Fir wood particles (4mm) 0.35 W/(m K) for Spruce wood particles	C_p=1.733 kJ/(kg K) C_p=1.112 kJ/(kg K)
Pauner et al.	Reference to Blomquist [84]	Biofuel pellets 0.17 W/(m K) [23 oC]	2.2 kJ/(kg K) for biofuel pellets [23 oC]

*M.C. is moisture content in percent wet mass basis; T is temperature, K.

2.9.2. Self-Heating Kinetic Parameters

As discussed in previous sections, woody materials trend to decompose and degrade due to the biological reaction and chemical reaction, causing hazards by releasing heat and gases. The decomposition is affected by various factors, including temperature, moisture content, oxygen concentration and other environment conditions. The self-heating rate is described by the kinetic parameters, activation energy (E), pre-exponential factor (A) and reaction enthalpy (ΔH_R), which have been experimentally measured for woody materials (Wadso, 2007; Pauner, 2007; Walker, 1977). The kinetic parameters vary according to different decomposition mechanisms (Mohsenin, 1990). In the measurement of self-heating rate, two approaches can be found in the literature, micro-scale experiment (calorimetric method) (Bunyan, 1977) and lab scale experiment.

2.9.3. Calorimetric Self-Heating Kinetic Parameters

Self-heating of bulk pellets at low temperatures is a slow process that mainly occurs in large vessels and easily influenced by the environment (Bowes, 1984, BBC, 2010, Fire in ship). It is difficult to study low temperature self-heating under normal laboratory conditions due to the influence of the surrounding environment. Heat conduction calorimetric methods are often used to detect small heat production and to study the thermodynamic parameters for energetic materials in the laboratory (Bunyan, 2003; Wilson, 1995; Jones, 1998; Bunyan, 2003).

In the chemical field, instruments such as differential scanning calorimeters (DSC), accelerated rates calorimeters (ARC) and thermogravimetric analyser (TGA) are precision equipment that are normally used for measuring small heat production. The DSC usually uses small (mg) samples exposed to a rapidly changing temperature to identify a critical point where the reaction accelerates. The ARC is an adiabatic (completely insulated) calorimeter in which reactions show up as a temperature increase. Although such methods have found significant practical use, e.g. for energetic materials, they require small amount of samples (Hofelich, 20020) and don’t normally work with wood pellets due to the large size of pellets. For measuring tiny heat production like wood pellets self-heating, isothermal calorimetry is the proper instrument (Rupar-Gadd, 2006; Wadso, 2007). Isothermal calorimetry is much more sensitive so that measurements can be conducted at lower temperatures. For example, a DSC used to study reactive chemicals can have a detection limit of about 45 mW for a sample size of about 1 mg. The TAM Air isothermal calorimeter has a detection limit of about 20 µW (Kung, 2008) and a sample size of about 10 g. The specific sensitivity of the isothermal calorimeter is thus about 10^4 times higher than for the DSC, which means that the TAM Air can detect a reaction at certain temperature about 100 K lower than the DSC. Instead of studying heat release at, e.g. 180°C, one can make measurements at 80°C which is much closer to the storage temperature of wood pellets in practice.

There are only a few references in the literatures on studying heat production from stored pellets. Rupar-Gadd did (2006) some tests on pellets using the isothermal calorimetry, and found that there was an increase in the heat release after 10-30 days at 50-55°C, where after the heat release decreased to a lower constant value for the remaining days of the experiment (up to 74 days). Wadso 2007 also did some test on pellets and found that at 50-90°C, close to where self-heating starts to become a problem, there was an appreciable heat production rate at the initial period. The reaction rate after 5 hours decreased because of the decrease in the oxygen pressure. The presence of metallic objects appears to have had an impact on the self-heating process where overheating and fires have started (Kubler, 1987; Wadso, 2007; Cole, 1972). However, the integral kinetic parameters have not been found in the studies reported in the literature so far.

2.9.4. Laboratory Scale Methods To Study Self-Heating Rate

The rate of the decomposition process increases with increasing temperature. Self-heating rate is higher at higher temperatures. Laboratory scale methods become more useful at higher temperatures when the self-heating rate is high. The Frank-Kamenetskii (FK) method (Bowes, 1984; Frank-Kamenetskii, 1969; Beever, 1988) and the crossing-point (CP) (Jones, 1996) method are two widely used laboratory scale methods to investigate the self-heating rate and kinetic parameters at high temperatures and the self-ignition condition. Both models are based on the one dimensional energy balance before the ignition;-

$$\rho C_P \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + Q_G$$

Equation 2-4

Where C_p is the specific heat capacity of the pellets, J/kg; λ is the thermal conductivity of the pellets, W/ (m K); t is time of the self-heating reaction, s., QG is the self-heating rate (rate of heat generation), in J/ (m^3 s). Semonov 1983 and Frank-kamenetskii 1969 introduced the earliest mathematical formulations for modelling self-ignition in bulk materials. Following these two models, it has been customary to assume that the reaction rate and, hence, heat generation rate varies with temperature following the Arrhenius equation:

$$Q_G(T) = \rho \cdot \Delta_r h \cdot A \exp(-E / RT)$$

Equation 2-5

where, Q_G (T) is the self-heating rate (rate of heat generation) at temperature T, in J/ (m^3 s); $\Delta_r h$ is the reaction enthalpy of the self-heating reaction, J/kg; ρ is density, kg/m^3; A is a pre-exponential factor; in s^{-1}; E is the activation energy of the self-heating reaction, J/mol; R is the gas constant, 8.314 J/ (mol K); T is the temperature of the pellets, K.

The Frank-kamenetskii (1938) model (FK method) was developed based on the energy balance equation for one dimensional geometry. Under steady state, the transient temperature term is eliminated ($\partial T/\partial t=0$) and the energy balance equation becomes

$$-\lambda \frac{\partial^2 T}{\partial x^2} = \rho \cdot \Delta_r h \cdot A \exp(-E / RT)$$

Equation 2-6

By introducing a dimensionless parameter δ, is converted to a dimensionless form,

$$\frac{\partial^2 \theta}{\partial \xi^2} = -\delta e^{\theta}$$

Equation 2-7

In which the dimensionless parameter δ is defined as

$$\delta = \frac{E}{RT_0^2} \frac{\rho \Delta_r h A}{\lambda} r^2 e^{-\frac{E}{RT_0}}$$

Equation 2-8

Figure 2.13 shows the relationship between δ and θ_0 for cylindrical vessel (Beever, 1988) shows the relationship between the dimensionless parameter δ and the stationary solution (θ_0) of Equation 2-7. For values of δ where Equation 2-7 has a solution, a stationary solution (θ_0) is possible and the stationary temperature distribution can be obtained. For those values of δ where Equation 2-7 has no solution, the stationary state cannot be reached and an explosion (combustion in this situation) will take place. Therefore, the maximum δ value which gives a stationary solution (δ_C) describes the critical condition for the self-ignition (thermal explosion)

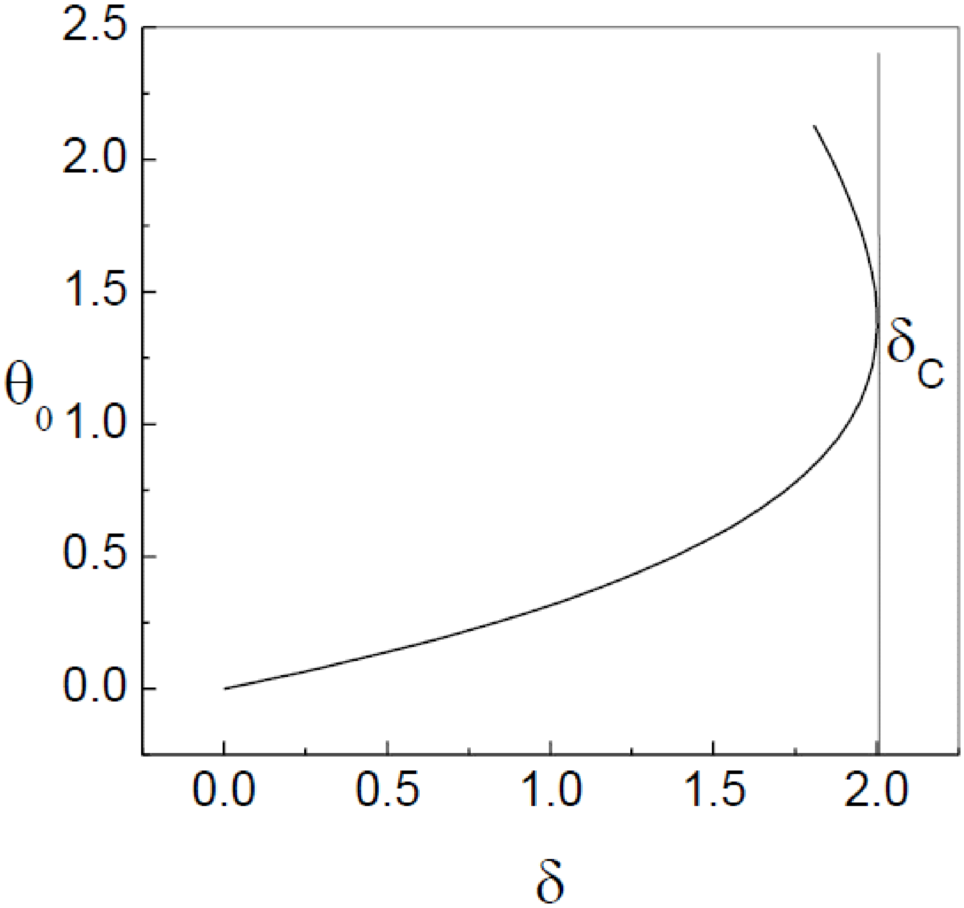


Figure 2.13. Relationship between δ and θ_0 for cylindrical vessel (Beever, 1988)

The critical δ value has been found for different geometry, including cubes, spheres and cylinders (Bowes, 1984; Frank-Kamenetskii, 1969). Experimentally the critical oven temperature T_0 (the minimum oven temperature when the ignition occurs) is determined for a particular reactor size r. Rearranging Equation 2-7 the activation energy E is obtained by plotting θ_0 as y coordinate and δ as x coordinates.

F-K method can also be used as a tool to predict the critical temperature. Once the kinetic parameters (E and $\Delta_r hA$) are found, the critical temperature can be calculated using Equation 2-8 (Bowes, 1984; Frank-Kamenetskii, 1969). Critical δ (shown in Table 2.9) values were determined for different geometry, including cubes, spheres and cylinders, some of them are listed in the table.

Table 2.9. Critical δ values

Body	δ_c
Infinite plane slab	0.857
Infinite cylinder, radius r	2.000
Infinite square rod, side 2r	1.720
Sphere, radius r	3.333
Short cylinder, radius r, height 2r	2.844
Cube, side 2r	2.569
Regular tetrahedron, radius of insphere r, Side 2a=2√6 r	2.228

The crossing-point (CP) method is another widely used method to experimentally determine E. Instead of a stationary solution, the CP method uses a transient solution of Equation 2-8 by assuming that when two temperatures inside of the container are identical, there will be no conductive heat transfer between these two points, and Equation 2-8 becomes;

$$\rho C_P \left.\frac{\partial T}{\partial t}\right|_P = \rho \cdot \Delta_r h \cdot A \exp(-E / RT_P)$$

Equation 2-9

The identical temperature between this two location points is defined as the crossing point (P). After T_P (the crossing point, and the temperature increase rate at this point) being determined experimentally, the activation energy E can be calculated from the slope by plotting

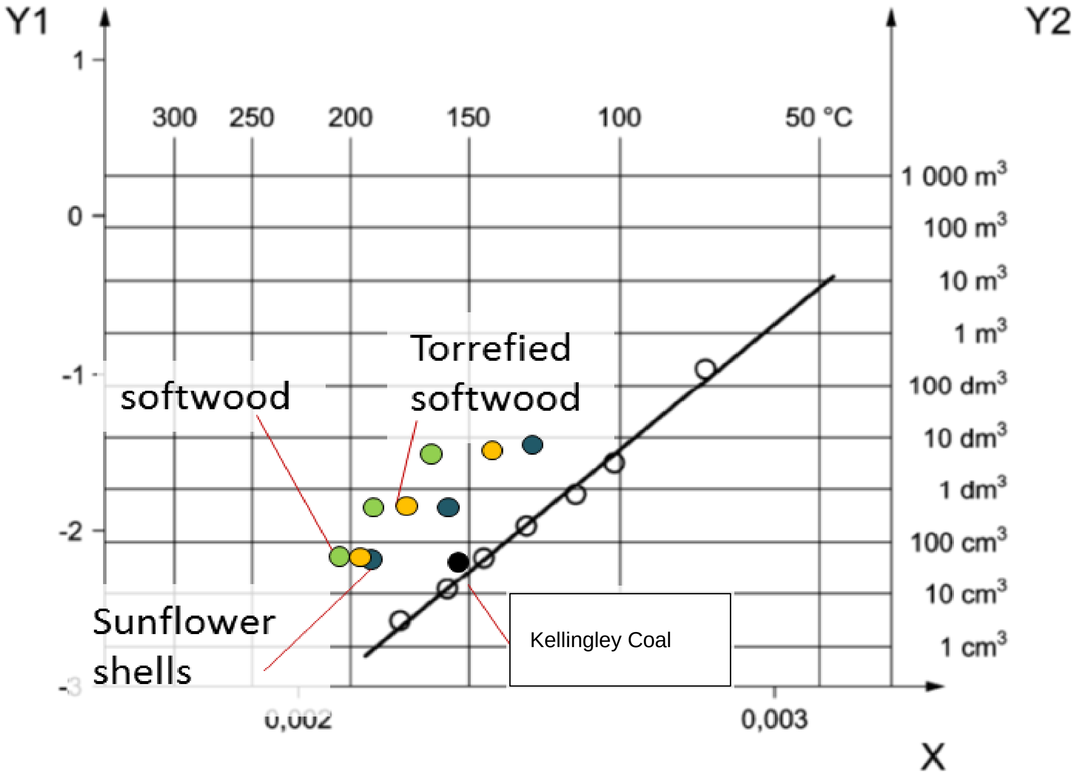
$$\ln(dT/dt)\big|_P \text{ versus } (1/T_P)$$

Equation 2-10

Theoretically, CP method doesn’t need as many experiments as the FK method, but the no-conduction assumption will cause a systematic error. Therefore the CP method by itself cannot be used as a tool to predict the critical temperature for self-ignition (Pauner, 20017).

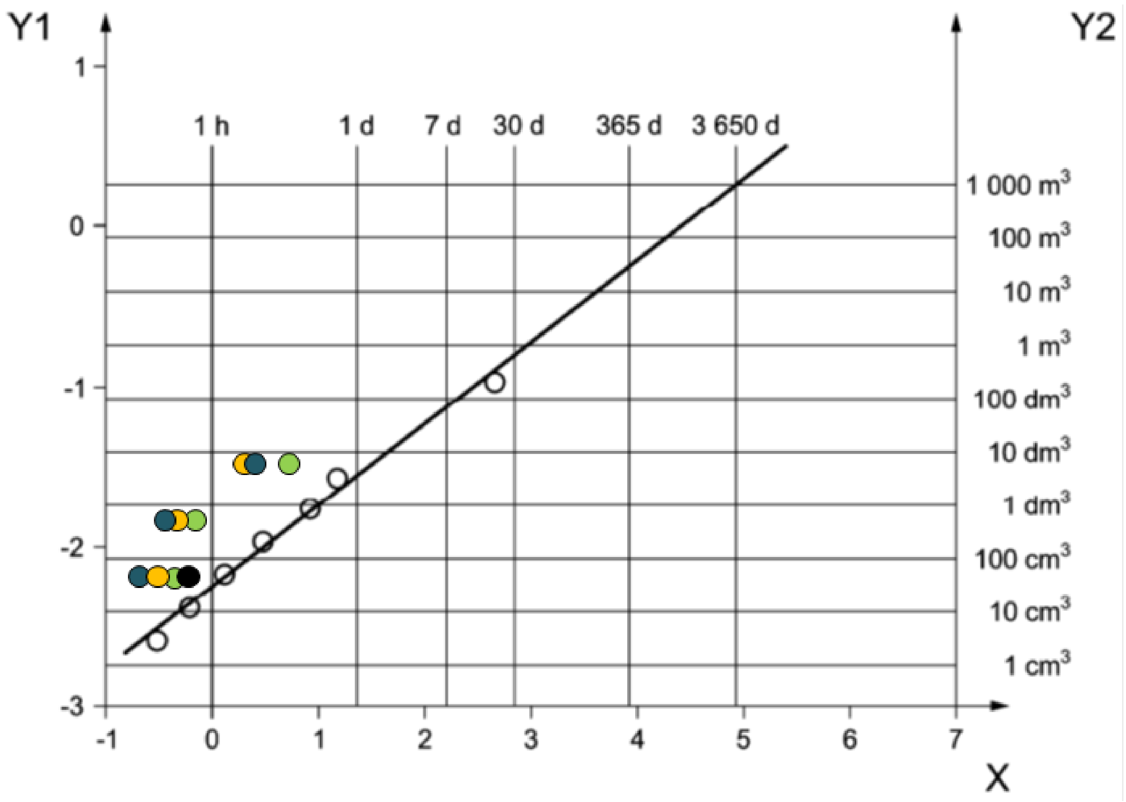
From this extrapolated data, critical ignition temperatures can approach ambient temperatures at large scales – rendering the threat of self-heating ever present. Others have also utilised basket tests for prediction of large scale self-heating (Blomqvist, et al, 2007).

A number of researchers have modelled self-heating in large quantities of biomass. Usually this involves a simple chemical decomposition model and does not show the differences between biomass. Research by Saddawi et al (2013) used the scaling method given in BS EN 15188:2007 to investigate the behaviour in large piles. Results of their work are plotted on the graphs given in BS EN 15188:2007] in Figures 2.14 and 2.15. These show the extrapolated size ranges.



(Self-ignition temperature)$^{-1}$ and log(pile characteristic dimension)

Figure 2.14. Plot of characteristic dimension against reciprocal temperature(K) superimposed on BS/EN line from BS EN 15188:2007 Determination of the spontaneous ignition behaviour of dust accumulations, BSI, 2008.



log(Combustion ignition delay) and log(pile characteristic dimension)

Figure. 2.15. Plot of log ignition delay against log characteristic dimension superimposed on BS/EN line from BS EN 15188:2007 Determination of the spontaneous ignition behaviour of dust accumulations, BSI, 2008

It is clear from Figure 2.14 that the value for Kellingley coal is very similar to the BS/EN line but the biomass materials would, for the same characteristic dimension, ignite at higher critical temperatures. In Figure 2.15 it is seen that for the same characteristic dimension, the coal sits close to the BS/EN line for ignition delay. This is not the case for the biomass where for the same characteristic dimension the ignition delay is shorter. Torrefied biomass characteristics move towards those for coal.

There are a number of factors that may result in the data not being coincident with that in BS EN 15188:2007 and these are outlined by Puttick. It is noted in BS EN 15188:2007 that the spread of slopes of the straight lines determined by different laboratories using differently constructed ovens is fairly large. '*Thus the* *scale up of these results to an industrial scale can lead to non-negligible errors. Much depends on the design of the inner chamber and the air flow*' which of course determines the efflux of the decomposition products and the simultaneous inflow of the oxidant. It is noted that Kellingley coal measurement data, is not dissimilar to the materials used in BS/EN method (lies on the line), but measurements for the biomass materials are different. Such materials were not studied in BS EN 15188:2007 or Puttick.

There are slight differences between the biomass materials although these may extrapolate to significant differences for large heaps. There are many factors that are different between the different biomass materials especially the extent and ease of volatile release and the differences of the reactivity of the volatiles with oxygen. There will also be differences in the porosity and heat transfer mechanism because pellets are widely used. It is apparent that further research is needed here.

As far as the possibility of ignition processes taking place in the real world, the important factors for nearing the critical ignition temperature are the ambient temperature (BS EN 15188:2007), the possibility of bacterial fermentation X.-R. Li, H. Koseki, 2006) and the heat of wetting of dry samples (B.F. Gray, G.C. Wake ,1990).

Extrapolation of Figure 2.14 or 2.15 to any size approaching Drax Power Ltd. Scale of biomass storage, would suggest very low self-ignition potential temperatures, which is not the case in practise.

CHAPTER 3. RESEARCH OBJECTIVES AND THESIS LAYOUT

Wood pellets are a relatively new product, and only limited information on self-heating and spontaneous combustion can be found in the literature for the scale of storage for this thesis.

Microbial activities are usually considered as one of the biological causes of the decomposition and self-heating, even though the moisture content is quite low.

The chemical reactions, including hydrolysis and pyrolysis, also contribute to the decomposition of wood pellets. When the temperature is high enough, pyrolysis dominates the degradation process and produces significant amount of heat, flammable gases, and active char.

The aim of this thesis is to provide insight for Drax Power Ltd. into the safe storage of wood pellets at unprecedented scale. The objectives of this research are as follows:-

1. Install instruments in biomass stores in order to probe self-heating of 40,000 m^3 piles in covered, ambient conditions to depths of 10m.
2. Extract samples of fuel with times during storage and analyse using laboratory methods
3. Develop and apply instrumentation for measuring off-gassing during storage.
4. Apply laboratory methods to measure microbial activity potential, acid formation and fuel reactivity during storage.
5. Examine the effect of pellet age on self-heating behavior.
6. Provide insight and advice in the design of the large (120,000 m^3) storage domes and their instrumentation
7. Provide guidance and safe working practice for personal work in and around biomass stores

8. Produce a simple in-house model to form the basis of a procedural safety document for safe storage of biomass specifically in Drax Power Ltd. domes.

3.1. Significance And Unique Contributions Of The Research

Wood pellets as a fuel in large power plants is a fairly new application, with limited investigation on wood pellet self-heating and spontaneous combustion behaviour. Wood pellets are stored as bulk in large silos 40,000 – 80,000 tonne with a long supply chain which is unique to Drax Power Ltd. Wood pellets are transported in bulk by ocean vessels that may hold up to 40,000 tonnes with transit time of up to 40 days. The storage periods in silos and in ships may last several months. Self-heating and spontaneous ignition are significant safety concerns during storage and transport of wood pellets.

This thesis contributes to the fundamental understanding of the self-heating process of wood pellets at low temperatures. The research identifies environmental conditions under which a thermal runaway may occur within a bulk of stored wood pellets. The improved understanding of the heat generation and self-heating process will must to control self-heating and avoid spontaneous ignition of wood pellets during transport and storage by adjusting the environmental conditions, such as ventilation air flow and optimum storage dimensions.

An understanding of the self-heating process can also help in understanding the mechanism of off-gassing and decomposition of wood pellets.

The developed numerical model in this thesis would predict temperature development and thermal runaway conditions specifically for the Drax Power Ltd. biomass domes. With the predicted critical conditions for thermal runaway, the model provides specific guidelines and information for designing a storage and transportation system. The model can also be used as part of a control strategy such as ventilation scheduling and overall management of the stored wood pellets in the Drax Power Ltd. biomass domes.

The following unique contributions are offered in the self-heating research field:

- The heat generation rates from wood pellets at low temperatures (30ºC-50ºC) are quantified. The unique semi-empirical correlation is acquired from extensive laboratory experiments and full scale testing to predict the overall heat generation rate during wood pellets storage

- This study also considered that the age of pellets is a significant factor affecting both the self-heating and off-gassing process during low temperature (30ºC-50ºC) storage of wood pellets. There are in effect three main process and storage times before the pellets are received at Drax Power Ltd., which are:

- initial pellet production and pre-shipment storage,

- ship hold storage during transit of up to 40 days

- UK port storage

All stages involve handling and turn-over of the pellets which is both good and bad for self-heating potential which will be discussed later.

The primary parameters used in the numerical model were experimentally determined specifically for Drax Power Ltd. stored softwood wood pellets. The results from this study apply only to softwood pellets, the behaviour of bark pellets and hardwood pellets might be differ. Further research on the applicability of current results to other wood types and species is recommended.

3.2. Thesis Overview

The thesis covers the background context of the development of wood pellet combustion by Drax Power Ltd. (Chapter 1), a comprehensive literature review of problems in the supply chain (Chapter 2), and the experimental results at three different scales (laboratory, temporary stores and domes) (Chapters 5-7).

3.2.1. Laboratory Scale Work

This work ran as both independent research at this scale but also to mirror on a pilot scale the temporary stores and domes scale work. The work covered the whole spectrum of biomass storage and self-heating potential, with many other aspects not included in this thesis due to requirements from Drax Power Ltd. The work and results were often initiated at short notice, with results and conclusions required soon afterwards by Drax Power Ltd.

3.2.2. Biomass Storage At ~ 40,000 Tonnes And Up To 10m Depth

This work was undertaken as Drax Power Ltd. began scaling-up its operations prior to converting the first unit to 100% biomass. Problems had been recorded at these stores including self-heating and product degradation, therefore it was decided to expand the laboratory scale research to these stores themselves by implementing fixed and mobile monitoring equipment to investigate why some stores heat and others not. The safe access of personal into these stores was paramount therefore monitoring not only for self-heating and product degradation but health monitoring and effects on people from off-gassing, dust and microbiological effects.

3.2.3. Dome Storage At ~ 70, 000 Tonnes And Up To 50m Depth

Following on from the temporary storage monitoring and results, (research moved towards the safety of the domes and instrumentation to develop) but this time to depths of 50m and volumes of 120,000m^3 (~75,000 tonnes).

The main difference was the atmosphere within the domes which is inerted with nitrogen to control off-gassing and ignition potential of the biomass. Personal access internal to the domes is therefore not to be considered, but external monitoring of vents and surroundings are still partially covered in this thesis but this work continued to run even on completion of this thesis. An understanding of what is going on inside the domes was needed to allow interpretation of temperatures, gases and movement within the dome, all effectively “blind” as physical internal examination of the dome is not possible when any biomass is inside due to the inert atmosphere from the nitrogen gas and explosive potential.

CHAPTER 4. MATERIALS

4.1. Background To Biomass Test Samples

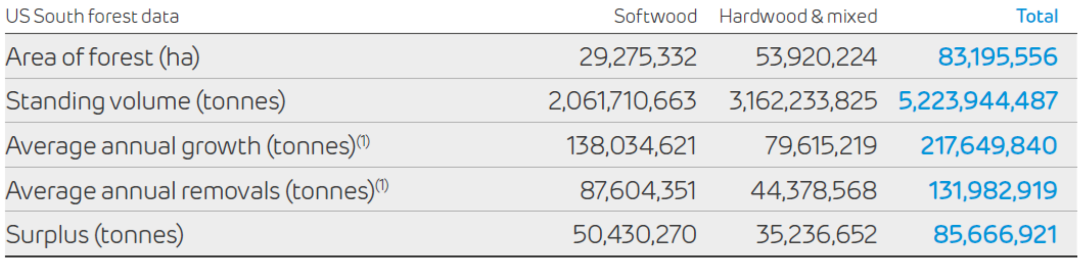
To meet Drax Power Ltd.’s demand for wood pellets they need to source from overseas regions with large working forests that produce wood in excess of the demands from other woodbased industries. However, these forestry activities need to be performed in such a way that they can be considered sustainable. Drax Power Ltd. only uses sustainable biomass and strongly supports the introduction of transparent, stable and mandatory sustainability criteria based on the best practice in the forestry sector. Drax Power Ltd. believes such criteria must apply equally to domestic and imported biomass and be audited by independent third parties. Drax Power Ltd. sources wood fibre from the US South and compressed wood pellets from suppliers around the world. Drax Power Ltd. Biomass is a major manufacturer of wood pellets.

The only wood sourced from the UK in 2015 was just over 10,000 tonnes of short rotation willow coppice (www.forestry.gov.uk, 2016). As the forest area in the UK is small compared to other countries, it is heavily reliant on imports for a range of wood products including sawn wood, wood-based panels, pulp and paper and wood pellets. Drax Power Ltd. does source a very small proportion of biomass from local suppliers, predominantly Agricultural Residues, Miscanthus and Straw.

In 2015 Drax Power Ltd. sourced more wood pellets than in previous years from the US South. This is a major region for timber production and there are large volumes of low value by-products which can be used to make compressed wood pellets, and the infrastructure is already in place to support a diverse wood based industry. This is shown in Figure 4.1

The US South is a very heavily forested region. Table 4.1 illustrates, the total area of timberland (productive forest) is over 83 million hectares (ha), representing 61% of the total area. There is a substantial quantity of standing volume (growing stock), in excess of five billion tonnes. More importantly there is also a significant annual surplus with 218 million tonnes of annual growth set alongside only 132 million tonnes harvested.

Table 4.1. Total area of timberland (productive forest) (Drax Power Ltd. 2016)



US South forest data	Softwood	Hardwood & mixed	Total
Area of forest (ha)	29,275,332	53,920,224	83,195,556
Standing volume (tonnes)	2,061,710,663	3,162,233,825	5,223,944,487
Average annual growth (tonnes)(1)	138,034,621	79,615,219	217,649,840
Average annual removals (tonnes)(1)	87,604,351	44,378,568	131,982,919
Surplus (tonnes)	50,430,270	35,236,652	85,666,921

The United Stated Department of Agriculture (USDA) has a range of sample plots randomly distributed across each State. Each year approximately one fifth are measured and used to update their forest inventory database. This data is used to calculate the average annual growth and removals from forests in the US south Figure 4.1

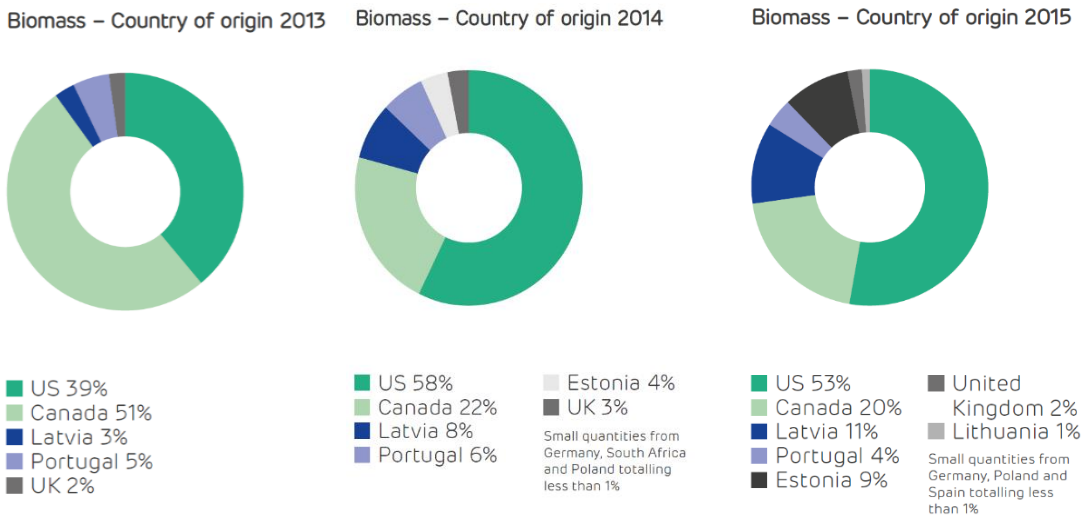


Figure 4.1. Drax Power Ltd. source of biomass 2013 – 2015 (Drax Power Ltd., 2015)

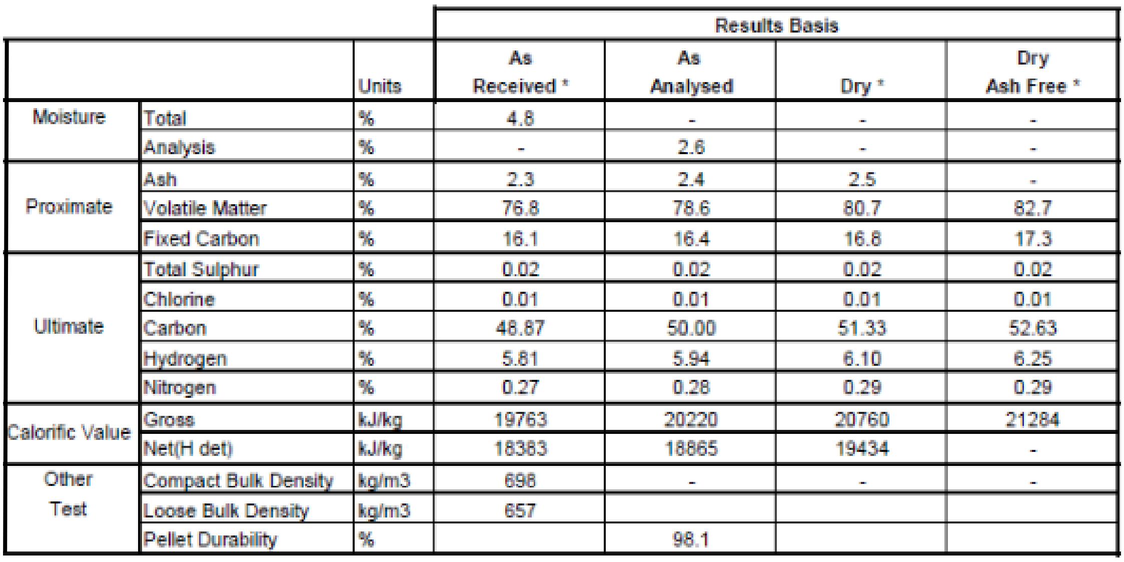
Data is audited on the basis of compliance year (1 April to 31 March) as part of Drax Power Ltd.'s reporting to the UK government. Data for 2013, 2014 and 1 January to 31 March 2015 has been audited. The data for 1 April to 31 December 2015 forms part of the audit for the current compliance year.

4.2. Biomass Test Samples

The following biomass samples types are used in this thesis:- Wood (Pine “White Wood”), Agricultural Residues (Miscanthus, Wheat or barley Straw), Torrefied pellets (Predominately mixed wood materials)

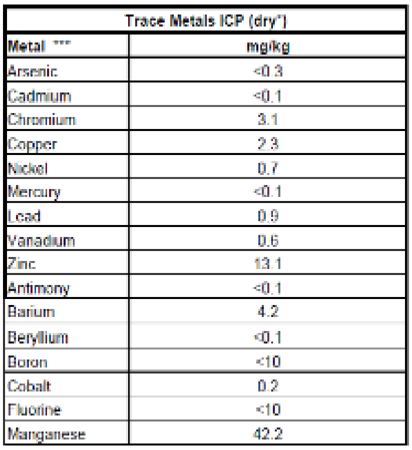
The main work has focused on compressed wood pellets and Agricultural Residues will only be used in some laboratory scale testing as a comparison to wood. The large scale storage of Agricultural Residues is not considered applicable to this thesis and work for Drax Power Ltd. Due to Drax Power Ltd. commercial sensitivities, only a typical un-referenced fuel analysis can be listed, as shown in Table 4.2 showing the main Ultimate and Proximate data along with moisture and calorific values. Table 4.3 shows typical elemental and oxide results. This typical results data is subcontracted as part of the general operations work at Drax Power Ltd.

Table 4.2. Typical Drax Power Ltd. biomass Ultimate and Proximate Analysis

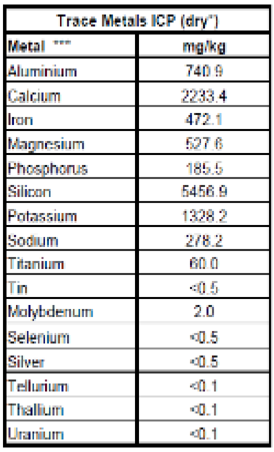


			Results Basis			
		Units	As Received *	As Analysed	Dry *	Dry Ash Free *
Moisture	Total	%	4.8	-	-	-
	Analysis	%	-	2.6	-	-
Proximate	Ash	%	2.3	2.4	2.5	-
	Volatile Matter	%	76.8	78.6	80.7	82.7
	Fixed Carbon	%	16.1	16.4	16.8	17.3
Ultimate	Total Sulphur	%	0.02	0.02	0.02	0.02
	Chlorine	%	0.01	0.01	0.01	0.01
	Carbon	%	48.87	50.00	51.33	52.63
	Hydrogen	%	5.81	5.94	6.10	6.25
	Nitrogen	%	0.27	0.28	0.29	0.29
Calorific Value	Gross	kJ/kg	19763	20220	20760	21284
	Net(H det)	kJ/kg	18383	18865	19434	-
Other Test	Compact Bulk Density	kg/m3	698	-	-	-
	Loose Bulk Density	kg/m3	657			
	Pellet Durability	%		98.1		

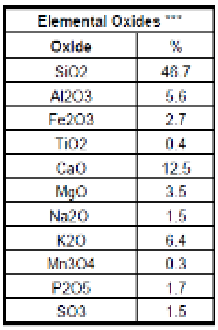
Table 4.3. Typical Drax Power Ltd. biomass Elemental and trace metals analysis



Trace Metals ICP (dry*)	
Metal ***	**mg/kg**
Arsenic	<0.3
Cadmium	<0.1
Chromium	3.1
Copper	2.3
Nickel	0.7
Mercury	<0.1
Lead	0.9
Vanadium	0.6
Zinc	13.1
Antimony	<0.1
Barium	4.2
Beryllium	<0.1
Boron	<10
Cobalt	0.2
Fluorine	<10
Manganese	42.2



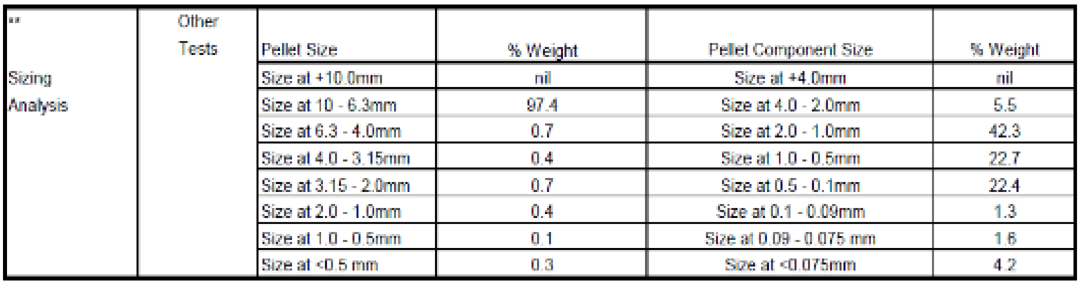
Trace Metals ICP (dry*)	
Metal ***	**mg/kg**
Aluminium	740.9
Calcium	2233.4
Iron	472.1
Magnesium	527.6
Phosphorus	185.5
Silicon	5456.9
Potassium	1328.2
Sodium	278.2
Titanium	60.0
Tin	<0.5
Molybdenum	2.0
Selenium	<0.5
Silver	<0.5
Tellurium	<0.1
Thallium	<0.1
Uranium	<0.1



Elemental Oxides ***	
Oxide	**%**
SiO2	46.7
Al2O3	5.6
Fe2O3	2.7
TiO2	0.4
CaO	12.5
MgO	3.5
Na2O	1.5
K2O	6.4
Mn3O4	0.3
P2O5	1.7
SO3	1.5

The physical dimensions of the pellets burned at Drax Power Ltd., are listed in Table 4.4. Pellet and component size distribution data. After transportation, the small amount of particles increases due to breakage and estimated as 2% below 1mm.

Table 4.4. Pellet and component size distribution data



**	Other Tests	Pellet Size	% Weight	Pellet Component Size	% Weight
Sizing Analysis		Size at +10.0mm	nil	Size at +4.0mm	nil
		Size at 10 - 6.3mm	97.4	Size at 4.0 - 2.0mm	5.5
		Size at 6.3 - 4.0mm	0.7	Size at 2.0 - 1.0mm	42.3
		Size at 4.0 - 3.15mm	0.4	Size at 1.0 - 0.5mm	22.7
		Size at 3.15 - 2.0mm	0.7	Size at 0.5 - 0.1mm	22.4
		Size at 2.0 - 1.0mm	0.4	Size at 0.1 - 0.09mm	1.3
		Size at 1.0 - 0.5mm	0.1	Size at 0.09 - 0.075 mm	1.6
		Size at <0.5 mm	0.3	Size at <0.075mm	4.2

CHAPTER 5. LABORATORY STUDIES

5.1. Experimental Methods

As stated in section 3.2.1, laboratory-scale experiments where performed in parallel to the experiments on the storage of pellets in temporary, off-site stores. These were undertaken to understand the changes taking place during storage and the reasons for the changes.

5.1.1. Elemental ICP/MS Analysis

In order to determine the levels of metals in biomass, the pellets were dried at 40°C for 8 hours to remove any moisture. The samples were then milled in to a fine powder, prior to microwave digesting using an Anton Paar Multiwave 3000. The samples were digested using ultra-pure concentrated nitric acid, hydrogen peroxide and hydrofluoric acid, and after digestion is completed the samples are returned to the microwave with the addition of boric acid to remove any complexes from free fluorides. The samples were then analysed using a Perkin Elmer Elan DRC é. This system had previously been calibrated for the elements shown in red in Figure 5.1:

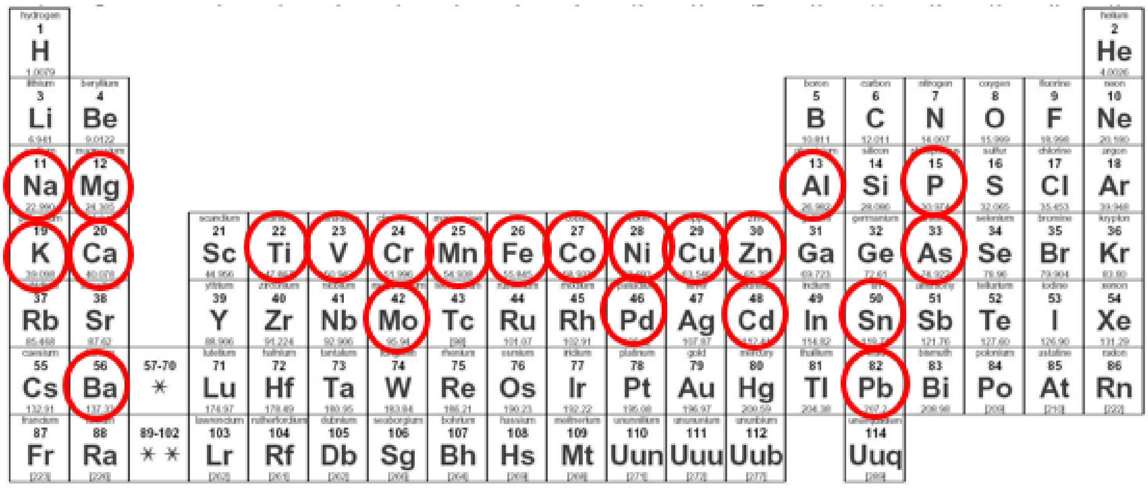


Figure 5.1. ICP-MS calibrated elements used in this thesis

5.1.2. Thermal Imagery

Using various types of biomass product, temperature change due to moisture addition were monitored using a FLIR model 6 infrared camera. Biomass samples including pellets, milled pellets and product pre pelletisation were weighed in to 1L polyethylene sample vessels. The weights used varied dependant on the volume of the test samples. Moisture was added in increasing volumes to create a profile of moisture contents ranging from 0 – 40% (w/v). After moisture addition, images were taken with the infrared camera monitoring the heating profile in each sample vessel for a period of 2 - 4 hours. An initial visible spectrum photograph was taken. All equipment and water was equilibrated at room temperature prior to the start of the experiment. Standard thermocouples were also be used to verify the internal temperatures of selected experiments and compare against the thermal image temperatures.

5.1.3. pH Measurements

Changes in pH due to contact with moisture was conducted using a Mettler Toledo Seven Multi pH meter. 10g of pelletised biomass was weighed in to a 100mL glass beaker, and the pH probe placed in to position. 50mL of room temperature demineralised water was then added to the beaker. pH measurements were then logged each minute until the sample had stabilised (20 – 30 minutes).

5.1.4. Microbiological Activity Measured Using Dip Slides

The microbiological content of biomass was ascertained using a leaching process followed by analysis using dipslides. 10g of milled biomass was weighed with 40mL of room temperature demineralised water in a 50mL centrifuge tube. This was then agitated for 2 minutes. The supernatant was then decanted on to the dipslides. Two types of dipslide were used, a sterile nutrient agar which grows bacteria, and another which grows fungi, bacteria and yeasts. These were then incubated for 48 hours (72 hours for yeast) at 30^{o}C. The results are then compared visually with the growth guide supplied with the dipslides shown in Figure 5.2

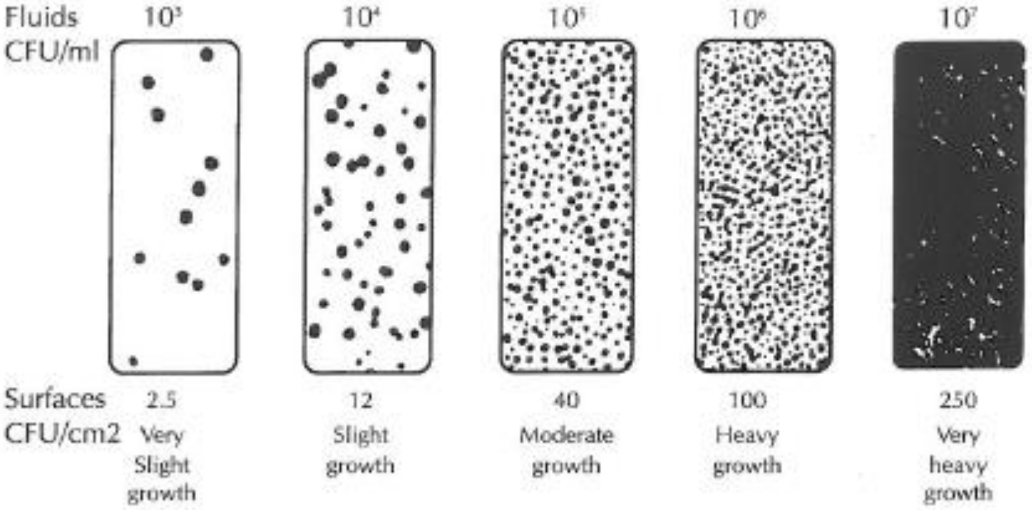


Figure 5.2. Comparison charts bacteria /yeasts

5.1.5. Thermogravimetric Analysis

Samples of biomass were analysed using thermogravimetric analysis (Perkin Elmer STA6000). The samples were analysed using a program with a temperature ramp between of 2 ^{o}C/min in nitrogen 30 – 900 ^{o}C. The samples were then held at 900 ^{o}C for 30 minutes in air. The traces were then plotted using derivative weight loss (%loss/min). This enabled the measurement of characteristic peak temperatures, and the estimation of apparent first order pyrolysis kinetics. At any temperature the apparent first order rate constant k, is given by:

$$k = (-1)/(wt - w\infty) - (dw/dt)$$

Equation 5-1

Where

Wt = mass of biomass at time t

W_∞ = mass of biomass at the end of pyrolysis

dW/dt = rate of weight loss

5.1.6. Nitrogen Injection Simulation (Laboratory Scale)

During development of the dome stores, it was necessary to understand the impact of inerting using nitrogen gas on pellet storage and self-heating.

A 10L container as shown in Figure 5.3, is fitted with a perforated mesh floor, approximately 20mm from the base of the container. This was sufficient to prevent fines falling through, but not to impede gas flow. Nitrogen gas was introduced to the container via a 1 stage pressure reducing regulator, set at a pressure less than 2 Bar, with the main factor was to maintain the required flow rate, which is adjusted via a needle valve with ball float. The container was equipped with 8 thermocouples in 2 layers, as shown in Figure 5.3. A thermocouple also measured the fixed external heat source at approximately 45°C (oven), which was used to simulate self-heating conditions. A RDXL12SD 12 Channel temperature recorder was coupled to the 9 K-Type thermocouples, with the ability to alter the sampling interval as required. The moisture content of the pellets before and after the experiment was also measure and also compared against a control batch in the oven with not nitrogen gas flow.

The purpose of this experiment was to validate CFD modelling results for inertion and if cooling of the pellets also occurs (See chapter 7). CFD data indicated that for dome normal operation gas flow = 750 m^3/h for ¼ floor surface area of dome, which equals 5 kg/m^2 h. The dome floor surface area = $3017m^2$, ¼ = $754m^2$= ~ $1m^3/h$ per m^2. Area of test rig = ~ $0.031m^2$ (20cm width), therefore the scaled flow rate = 0.52 l/min. Nitrogen cylinder volume = $9.48m^3$

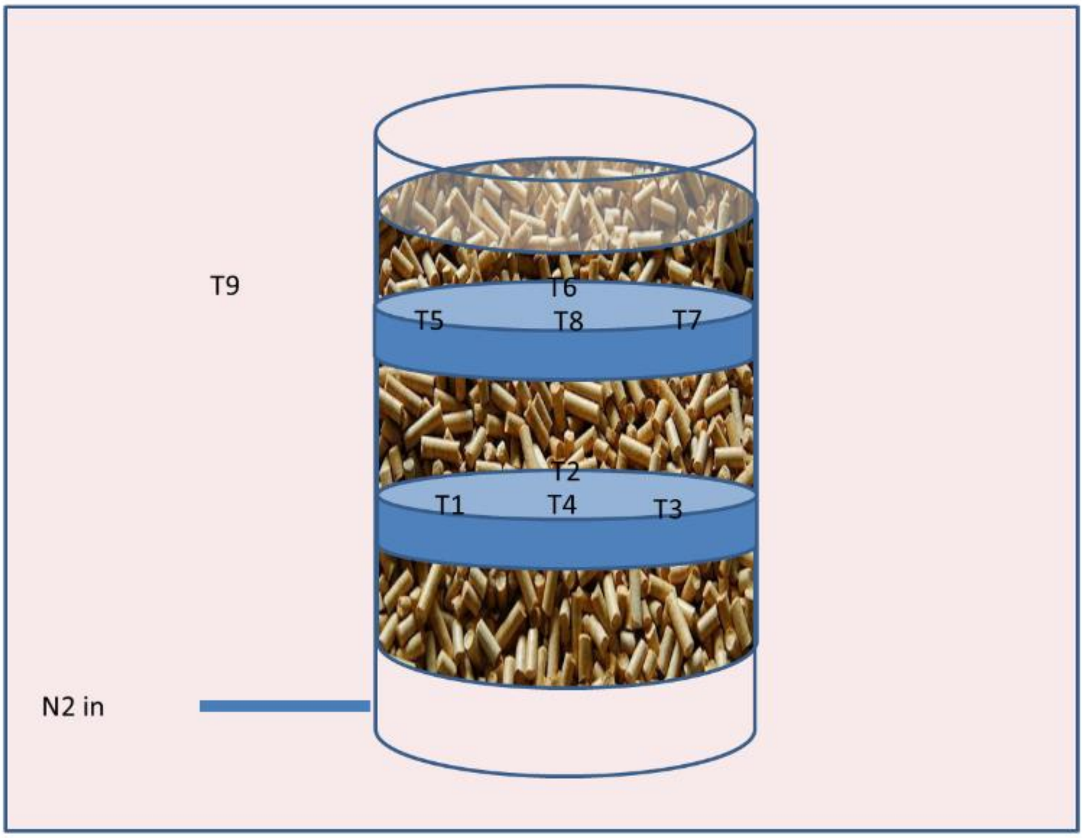


Figure 5.3. Nitrogen injection pilot test rig at 20L scale

5.2. Results And Discussion

5.2.1. Elemental Analysis

Data was obtained using an ICP/MS instrument (Perkin Elmer Elan DRC-e), Figure 5.4 shows the data obtained from average values of wood and Agricultural Residues. Figure 5.4 shows a very distinct difference between the two, with the Agricultural Residues materials showing the highest of the alkaline metals. This is one reason why the Agricultural Residues show less acidity than the woods.

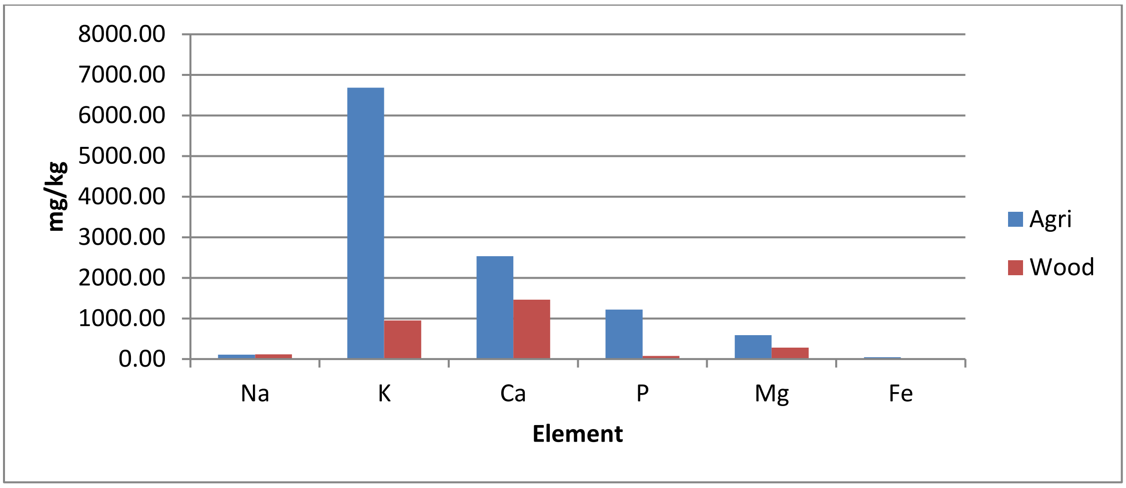


Figure 5.4. Key elemental analysis, wood and Agricultural Residues biomass pellets

Focusing on the heavy metals and comparing wood against Agricultural Residues biomass pellets, 5.5 shows the following differences. The Agricultural Residues materials contain nearly 70% versus the woods at approximately 30% on a like for like basis. Research by Harmsen P, et al (2010), suggested that the toxicity of heavy ions (e.g. Fe, Cr, Ni and Cu) may inhibit enzyme activity in the fermenting organism metabolism

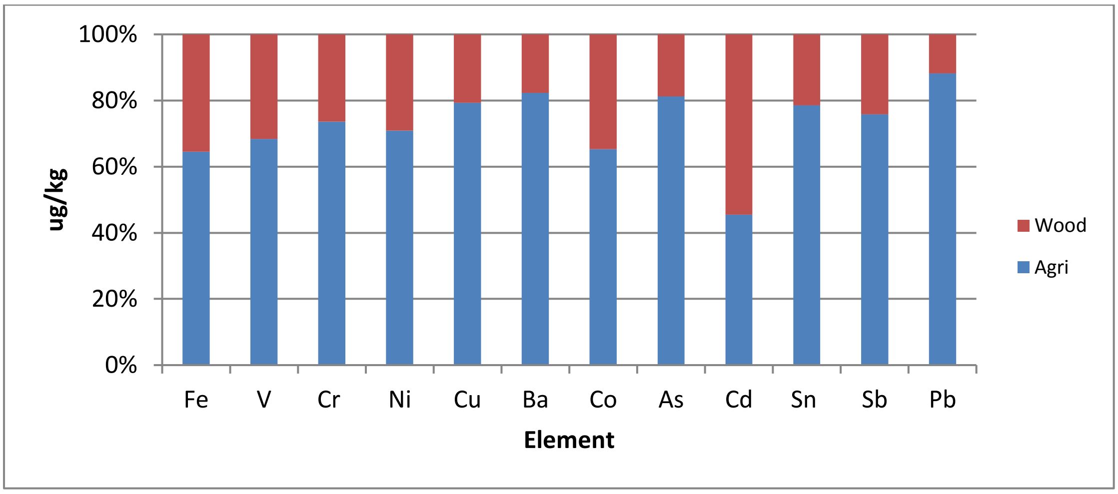


Figure 5.5. Heavy metal comparison, wood and Agricultural Residues biomass

5.2.2. Thermal Imagery

An initial visible spectrum photograph was taken as shown in Figure 5.6. After the water additions, images were taken at regular intervals using an Infra-red camera as shown in Figure 5.6

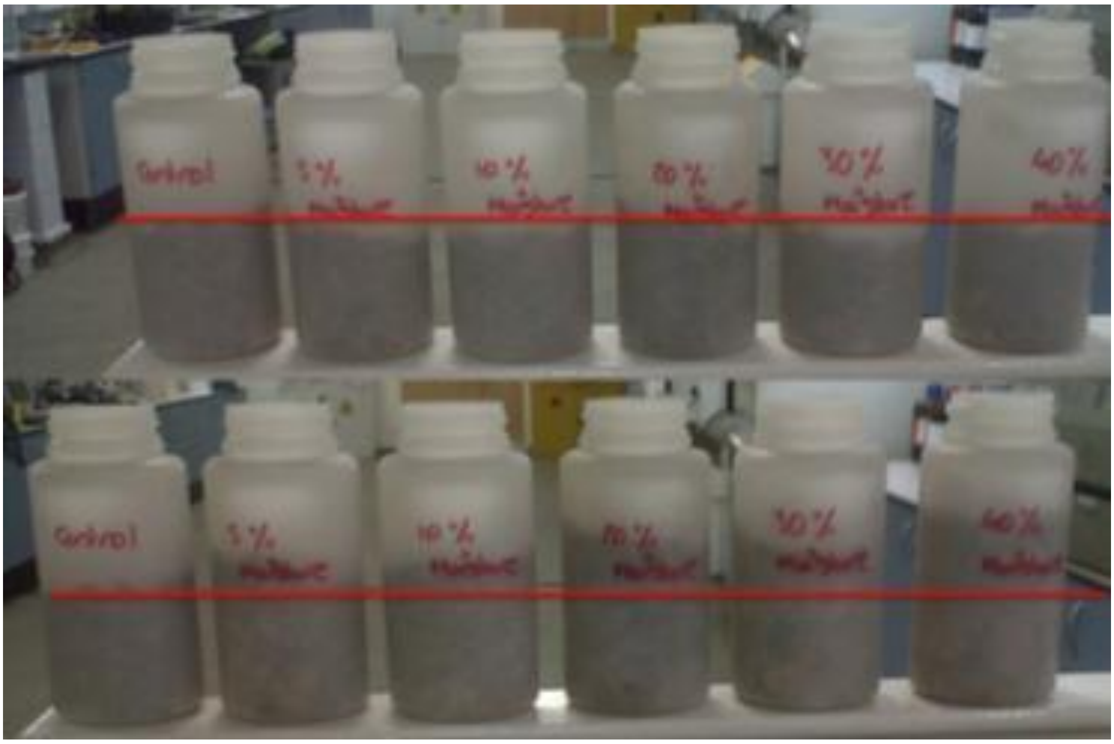
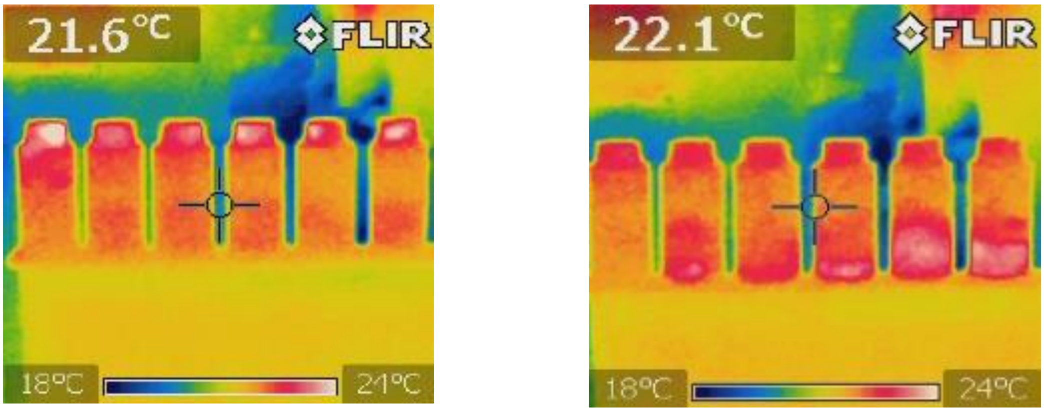


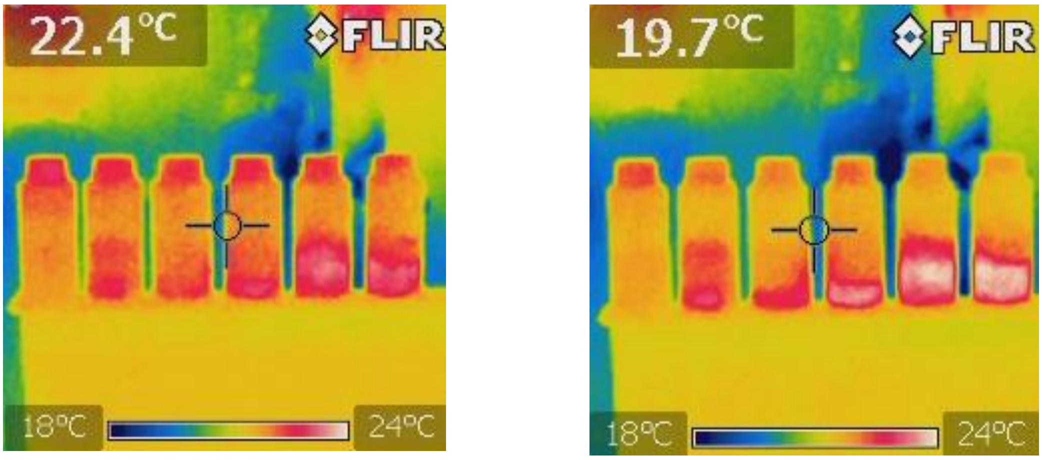
Figure 5.6. Photograph of water addition to pellets, before and after

Figure 5.6 also shows the physical change in volume of the wood pellets due to water addition. Swelling of the pellets is seen with even a 5%wt addition of water giving an increase of approximately 10% in volume. 40%wt addition of moisture yields an approximate 80% increase in volume as compared against control.

An infra-red view of Figure 5.6 is shown in Figure 5.7. This shows clearly after only 5 minutes temperature of approximately 24°C can be seen in all pots with a larger heated area corresponding to increased water addition. The total time from water addition to cooling back to room temperature was four hours with a maximum temperature achieved in wood pellets of 25°C. The experiment above was repeated using Agricultural Residues Straw but no temperature increase was visible from the infra-red camera



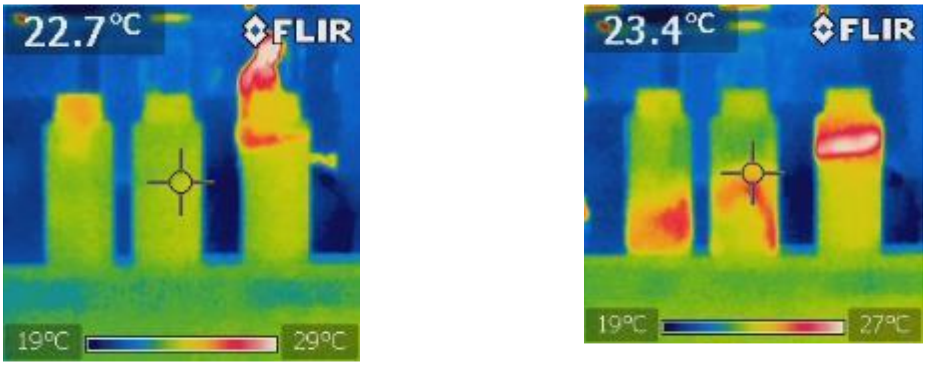
Time = 0 minutes Time= 5 minutes



Time = 15 minutes Time = 30 minutes

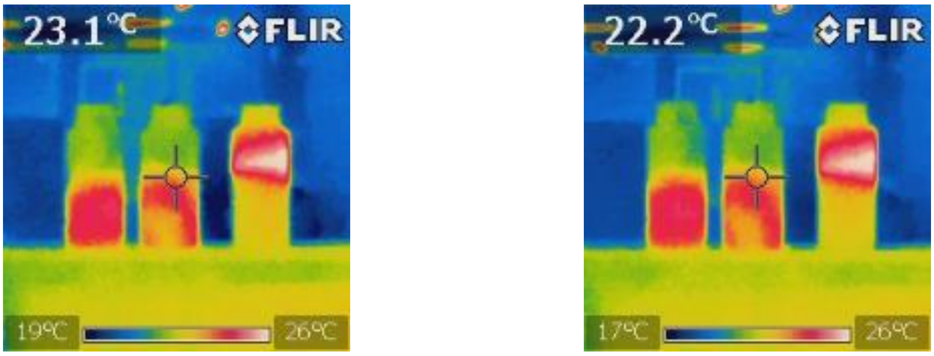
Figure 5.7. Thermal imaging of moisture addition to biomass pellet at time ranges from 0 to 30 minutes

A second experiment was completed using a new sample. The thermal images shown in Figure 5.8 from left to right, are whole pellets, pre-pelletized feed stock, and fine milled pellets. 30%wt moisture was added to each one simultaneously whist infrared images where taken along with a thermocouple located central within each pot of biomass. The noticeable difference from this test is the band of heated material at the top of the pot containing milled pellets. Compared to the whole pellets and pre-pelletized feed stock, the milled pellets heated rapidly and within this narrow band at the top. The relevance of this is in relation to quality of pellet production and amount of fines they produce. The temperature reach was the same as the previous tests of approximately 24°C as shown by the thermal image camera, but this temperature was achieved after only 60 seconds compared to 5 minutes. All samples heated, with the fine milled heating the fastest and producing the highest temperature. Figure 5.9 shows the plotted results from the thermocouples mounted centrally within each pot of biomass.



Time = 0 minutes

Time = 1 minutes



Time = 5 minutes

Time = 10 minutes

Figure 5.8. Thermal imaging of moisture addition to biomass pellets, broken down pellets and dust

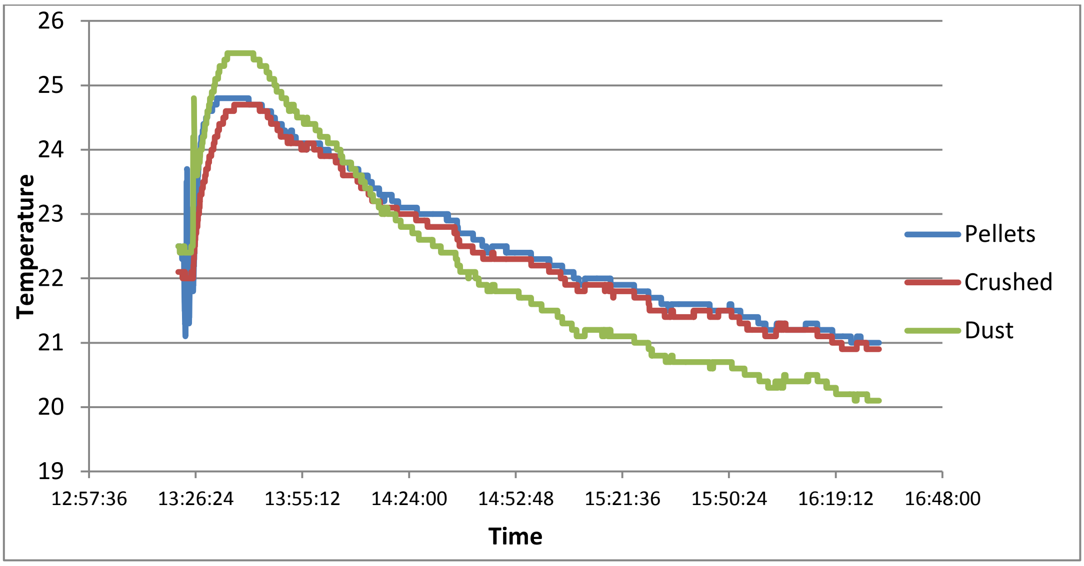


Figure 5.9. Thermocouple data of biomass dust

Using equations 2-1 and 2-2 from Chapter 2 for heat of wood wetting, Table 5.2 shows a range of possible temperature changes based on an initial starting moisture, and a change in moisture giving the resulting possible temperature change. Four different equations have been used, one from each of Kajita (1976), Manwiller (1976) and Volbehr (1896). This show theoretical temperature rise from water addition to wood. Summary of equations section 2.4.1.1

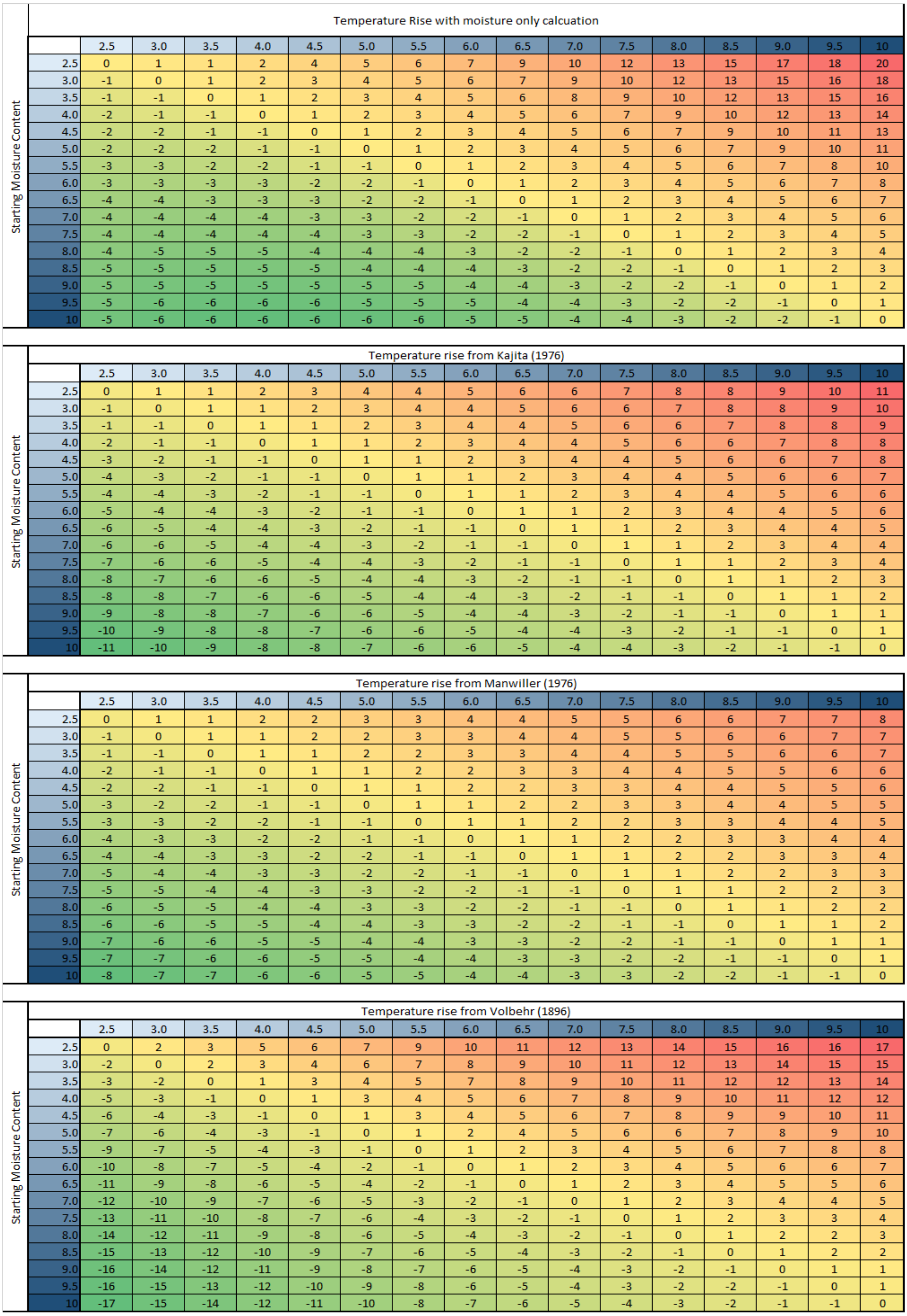
W_0 - heat of wetting of wood which is initially at zero moisture content

- Kajita (1976) Wo 0.5 + 0.67 M_f (cal/g of wood)
- Manwiller (1976) W0 = 4.64 + 0.480 M_f
- Volbehr (1896) W = 17.1 exp (-12.5m) (cal/g wood)
- Volbehr (1896) Qs = 214 exp(-12.5m) (cal/g water)
- Valid 2-10% moisture

Table 5.1. Heat of water wetting values

Heat capacity of pine	2 kJ/kg K
Heat capacity of water	4.2 kJ/kg K
1 calorie = 4.184 Joule	
1 calorie / g = 4.184 J / g	

Table 5.2 Calculated temperature rise for different moisture contents. Colour grading is just for a guide and not calibrated. Units in Degrees Celsius.



Temperature Rise with moisture only calcuation

Starting Moisture Content	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10
2.5	0	1	1	2	4	5	6	7	9	10	12	13	15	17	18	20
3.0	-1	0	1	2	3	4	5	6	7	9	10	12	13	15	16	18
3.5	-1	-1	0	1	2	3	4	5	6	8	9	10	12	13	15	16
4.0	-2	-1	-1	0	1	2	3	4	5	6	7	9	10	12	13	14
4.5	-2	-2	-1	-1	0	1	2	3	4	5	6	7	9	10	11	13
5.0	-2	-2	-2	-1	-1	0	1	2	3	4	5	6	7	9	10	11
5.5	-3	-3	-2	-2	-1	-1	0	1	2	3	4	5	6	7	8	10
6.0	-3	-3	-3	-3	-2	-2	-1	0	1	2	3	4	5	6	7	8
6.5	-4	-4	-3	-3	-3	-2	-2	-1	0	1	2	3	4	5	6	7
7.0	-4	-4	-4	-4	-3	-3	-2	-2	-1	0	1	2	3	4	5	6
7.5	-4	-4	-4	-4	-4	-3	-3	-2	-2	-1	0	1	2	3	4	5
8.0	-4	-5	-5	-5	-4	-4	-4	-3	-2	-2	-1	0	1	2	3	4
8.5	-5	-5	-5	-5	-5	-4	-4	-4	-3	-2	-2	-1	0	1	2	3
9.0	-5	-5	-5	-5	-5	-5	-5	-4	-4	-3	-2	-2	-1	0	1	2
9.5	-5	-6	-6	-6	-6	-5	-5	-5	-4	-4	-3	-2	-2	-1	0	1
10	-5	-6	-6	-6	-6	-6	-6	-5	-5	-4	-4	-3	-2	-2	-1	0

Temperature rise from Kajita (1976)

Starting Moisture Content	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10
2.5	0	1	1	2	3	4	4	5	6	6	7	8	8	9	10	11
3.0	-1	0	1	1	2	3	4	4	5	6	6	7	8	8	9	10
3.5	-1	-1	0	1	1	2	3	4	4	5	6	6	7	8	8	9
4.0	-2	-1	-1	0	1	1	2	3	4	4	5	6	6	7	8	8
4.5	-3	-2	-1	-1	0	1	1	2	3	4	4	5	6	6	7	8
5.0	-4	-3	-2	-1	-1	0	1	1	2	3	4	4	5	6	6	7
5.5	-4	-4	-3	-2	-1	-1	0	1	1	2	3	4	4	5	6	6
6.0	-5	-4	-4	-3	-2	-1	-1	0	1	1	2	3	4	4	5	6
6.5	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1	2	3	4	4	5
7.0	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1	2	3	4	4
7.5	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1	2	3	4
8.0	-8	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1	2	3
8.5	-8	-8	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1	2
9.0	-9	-8	-8	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1	1
9.5	-10	-9	-8	-8	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0	1
10	-11	-10	-9	-8	-8	-7	-6	-6	-5	-4	-4	-3	-2	-1	-1	0

Temperature rise from Manwiller (1976)

Starting Moisture Content	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10
2.5	0	1	1	2	2	3	3	4	4	5	5	6	6	7	7	8
3.0	-1	0	1	1	2	2	3	3	4	4	5	5	6	6	7	7
3.5	-1	-1	0	1	1	2	2	3	3	4	4	5	5	6	6	7
4.0	-2	-1	-1	0	1	1	2	2	3	3	4	4	5	5	6	6
4.5	-2	-2	-1	-1	0	1	1	2	2	3	3	4	4	5	5	6
5.0	-3	-2	-2	-1	-1	0	1	1	2	2	3	3	4	4	5	5
5.5	-3	-3	-2	-2	-1	-1	0	1	1	2	2	3	3	4	4	5
6.0	-4	-3	-3	-2	-2	-1	-1	0	1	1	2	2	3	3	4	4
6.5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1	2	2	3	3	4
7.0	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1	2	2	3	3
7.5	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1	2	2	3
8.0	-6	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1	2	2
8.5	-6	-6	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1	2
9.0	-7	-6	-6	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1	1
9.5	-7	-7	-6	-6	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0	1
10	-8	-7	-7	-6	-6	-5	-5	-4	-4	-3	-3	-2	-2	-1	-1	0

Temperature rise from Volbehr (1896)

Starting Moisture Content	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10
2.5	0	2	3	5	6	7	9	10	11	12	13	14	15	16	16	17
3.0	-2	0	2	3	4	6	7	8	9	10	11	12	13	14	15	15
3.5	-3	-2	0	1	3	4	5	7	8	9	10	11	12	12	13	14
4.0	-5	-3	-1	0	1	3	4	5	6	7	8	9	10	11	12	12
4.5	-6	-4	-3	-1	0	1	3	4	5	6	7	8	9	9	10	11
5.0	-7	-6	-4	-3	-1	0	1	2	4	5	6	6	7	8	9	10
5.5	-9	-7	-5	-4	-3	-1	0	1	2	3	4	5	6	7	8	8
6.0	-10	-8	-7	-5	-4	-2	-1	0	1	2	3	4	5	6	6	7
6.5	-11	-9	-8	-6	-5	-4	-2	-1	0	1	2	3	4	5	5	6
7.0	-12	-10	-9	-7	-6	-5	-3	-2	-1	0	1	2	3	4	4	5
7.5	-13	-11	-10	-8	-7	-6	-4	-3	-2	-1	0	1	2	3	3	4
8.0	-14	-12	-11	-9	-8	-6	-5	-4	-3	-2	-1	0	1	2	2	3
8.5	-15	-13	-12	-10	-9	-7	-6	-5	-4	-3	-2	-1	0	1	2	2
9.0	-16	-14	-12	-11	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	1
9.5	-16	-15	-13	-12	-10	-9	-8	-6	-5	-4	-3	-2	-2	-1	0	1
10	-17	-15	-14	-12	-11	-10	-8	-7	-6	-5	-4	-3	-2	-1	-1	0

Table 5.2. supports up the thermal images showing the temperature rise simply due to water additions.

Therefore an amendment to the original graph by Meier and Gast (2007) shown in Figure 2.2, creates the following graph shown in Figure 5.10.

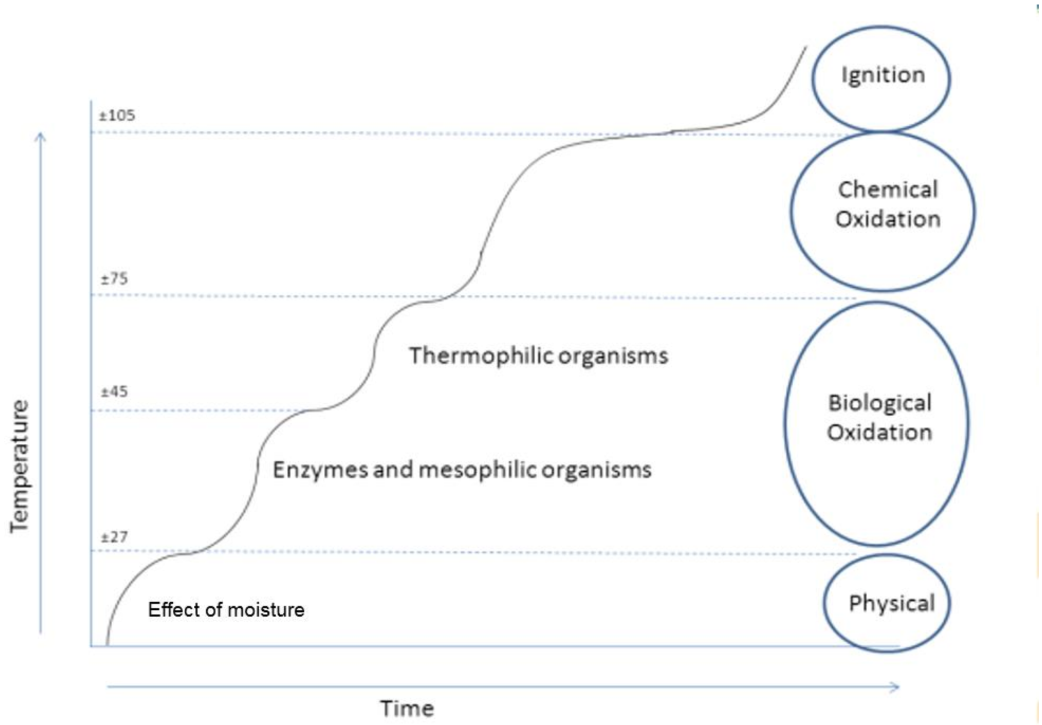


Figure 5.10. Revised reactions in biomass

This result is important when considering pellet particle size specification, as not only for a spark/static ignition, but also for potential self-heating of high percentages of fines through their ability to heat faster and hotter than pellets on their own.

5.2.3. Effects Of Moisture On pH

The acid nature of the pellets has been seen repeatedly in the large-scale biomass piles, where galvanised tubes have been inserted to aid in releasing trapped moisture and heat (shown in Figure 5.11). On the internal surface of the tube was found a thin film of mildly weak acid condensate, assumed to be from the vapours that have been released from the inside of the pile. The galvanisation of the internal surface of the tube had virtually all been removed by the acidity of the biomass vapours.

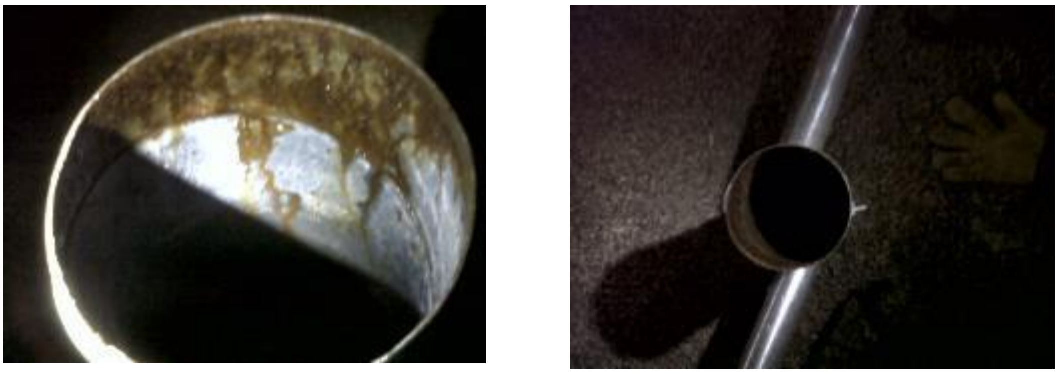


Figure 5.11. Vent pipes used to exhaust off-gassing within the biomass piles, showing corrosion.

Figure 5.12 shows the laboratory scale measured pH and temperature changes when moisture is added to wood and Agricultural Residues (Miscanthus) pellets. It is seen that the pH drops over a period of a few hours to different values depending upon the biomass. The, torrefied biomass, and some of the store samples show an equilibrium pH value of 4.5-5.5, while Miscanthus reaches a constant value of pH 7. The Straw sees only a small drop in pH, from pH 9 to pH 8.0. The results are discussed in 5.2.5

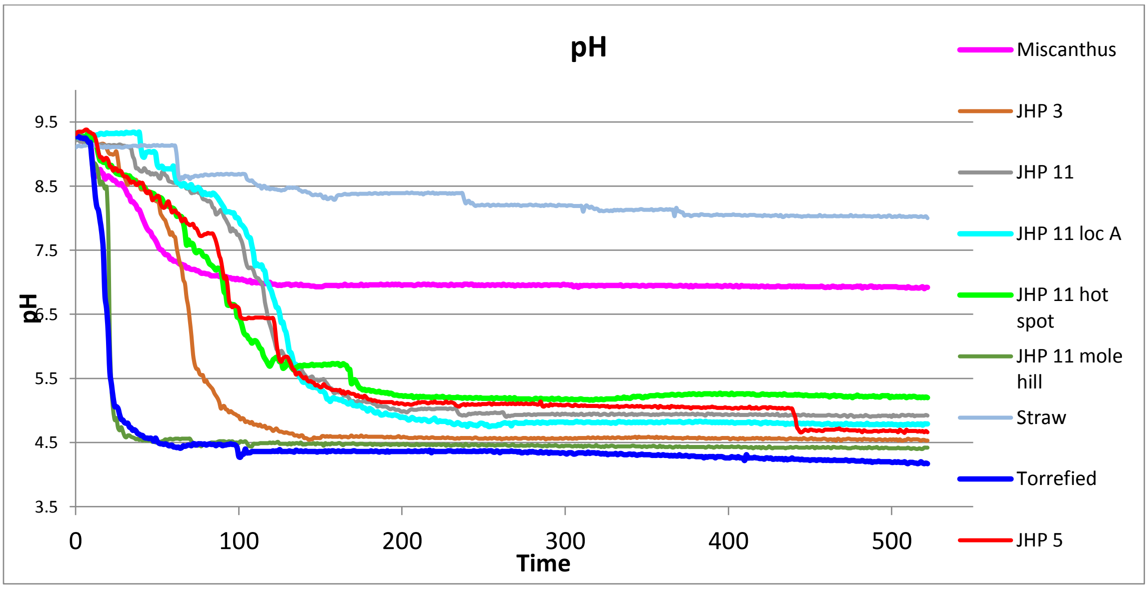


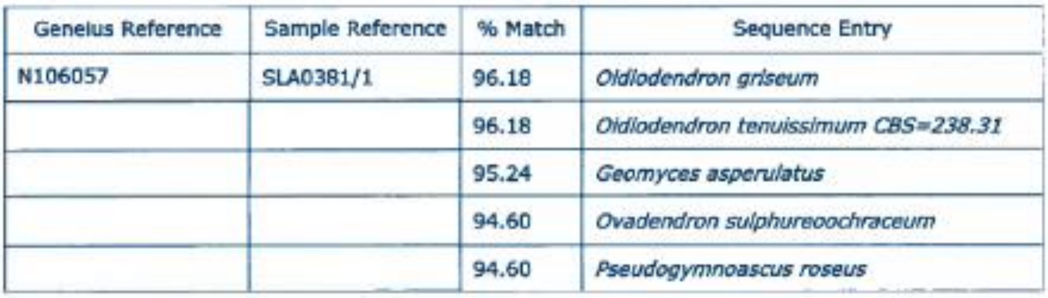
Figure 5.12. laboratory scale measured pH and temperature changes when moisture is added to wood and Agricultural Residues (Miscanthus) pellets. Time in minutes.

5.2.4. Microbiological Measurements

Moulds have been seen in the stores where heating has occurred along with high humidity and poor ventilation. The moulds have been identified as Amorphotheca resinae (also known as Cladosporium resinae described by (Parbery, 1969), The results are shown in Table 5.3.

The asexual state of Cladosporium resinae is considered to be very variable, a number of forms arising from the one hypha although all forms apparently have the same perfect state Amorphotheca resinae. Parbery, suggesting that many different strains of the fungus possibly exist. Dubbed by Hendey (1964) the “kerosene fungus’, it lives on plant resin and various petroleum products such as creosote, kerosene, diesel and aviation fuel. Known for the last century, it was best known from wood impregnated with creosote or coal tar, which the fungus uses as a source of carbon. The carbon utilisation of Cladosporium resinae is well illustrated by the growth pattern on creosoted timber; the growth stops on reaching that section of the timber not treated with creosote.

Table 5.3. Microbiological identification



Geneius Reference	Sample Reference	% Match	Sequence Entry
N106057	SLA0381/1	96.18	*Oidiodendron griseum*
		96.18	*Oidiodendron tenuissimum CBS=238.31*
		95.24	*Geomyces asperulatus*
		94.60	*Ovadendron sulphureoochraceum*
		94.60	*Pseudogymnoascus roseus*

Further work utilising pre-made agar slides shown in Figure 5.13; comparing stores not heating (shown on lower slides) versus stores showing signs of heating (upper slides). The microbial activity is visually evident from the stores showing signs of heating.

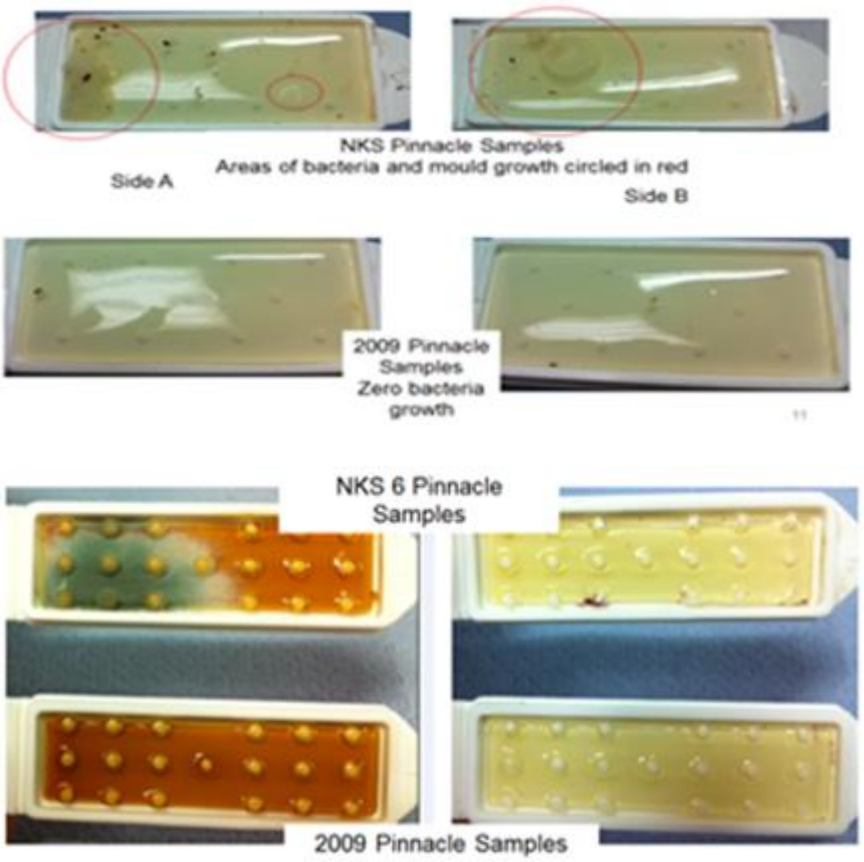


Figure 5.13. Microbial activity dip slide of NKS

5.2.5. Lignocellulosic Effects

Using a TGA – (Perkin Elmer STA6000) traces were produced comparing wood, wheat Straw, Miscanthus and torrefied pellets as shown in Figure 5.14. No set particle size is used, only suitable small original components of the pellet construction that will fit in the TGA cup. The lignocellulosic areas have been identified, as hemicellulose, cellulose and finally lignin. The largest proportion of hemicellulose was found in the Agricultural Residues materials (Straw and Miscanthus), with wood having considerably less. Torrefied material has zero hemicellulose, assume to be removed as part of the torrefaction process.

According to Kubler (1982), when the temperature in wood piles reaches 60-70°C, a chemical reaction occurs in which the acetyl groups present in hemicellulose molecules break, forming acetic acid. This reaction produces heat and raises the acidity of the wood pile. Therefore based on the above finding the

Agricultural Residues materials should have the highest acidity, but Drax Power Ltd. results, (both laboratory) and full scale does not show this.

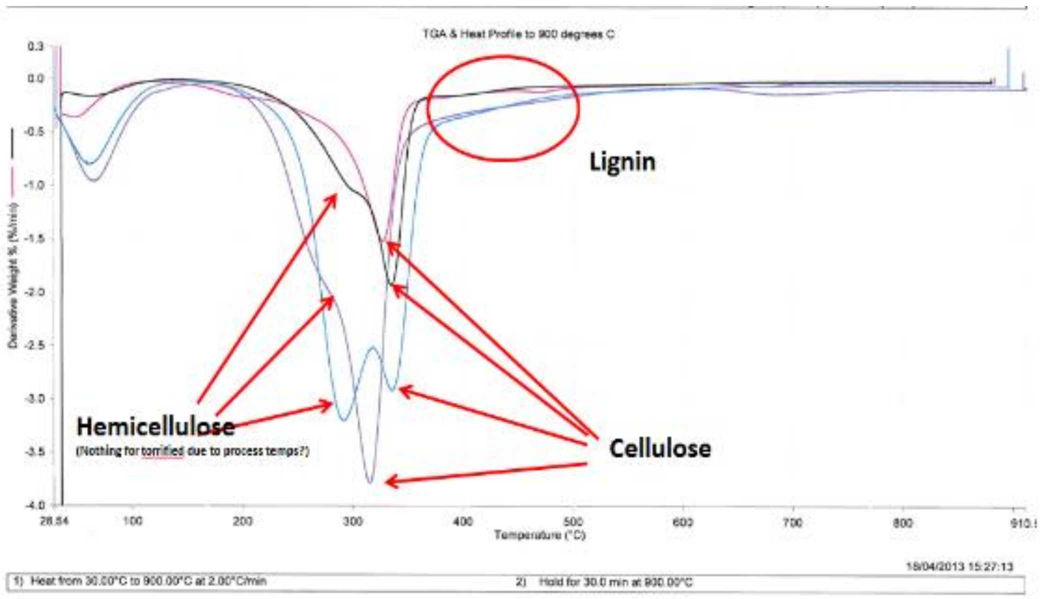


Figure 5.14. Thermogravimetric graphical results showing Lignocellulosic effect. Key- Black = wood, Pink = Torrefied, Purple = Straw, Blue = Miscanthus

5.2.6. Nitrogen Simulation Experiments

5.2.6.1. Thermogravimetric Analysis

The impact of inerting on biomass decomposition was explored using TGA. Figure 5.15 shows the TGA traces obtained using varying nitrogen gas concentrations. The concentrations were 100% nitrogen, 95, 90 and 85% nitrogen. Even with 100% nitrogen, there is still an indication of combustion because the material contains chemically bound oxygen which is released on heating, therefore nitrogen gas can only be used for control of fire and not extinguishing. The percentage of chemically bound oxygen is approximately 45-50%. The typical composition is as follows. (Element % dry weight) carbon 45.0, oxygen 48.0, hydrogen 5.0, ash 1.0, and nitrogen >0.5. However, the reactions become less exothermic as the level of nitrogen increases as evident from the

DTA trace (heat flow), and at 100% N_2 there is only a very small exotherm on the decomposition data.

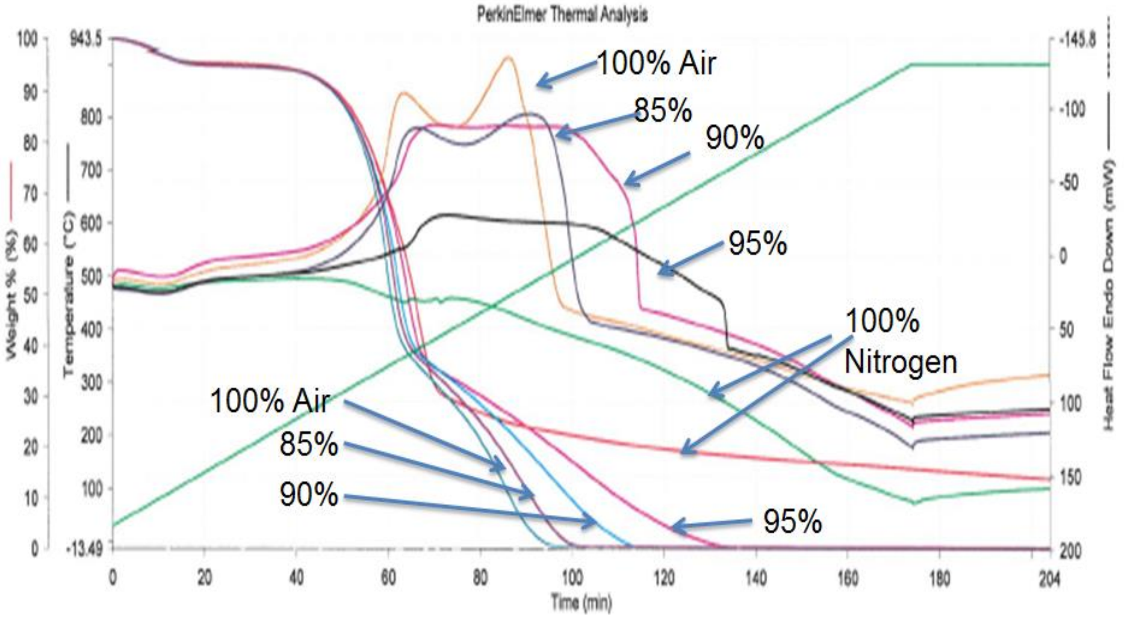


Figure 5.15. Thermogravimetric results showing mass of wood biomass measured against time under varying nitrogen concentrations

A second experiment was completed this time using carbon dioxide as the inerting gas. Figure 5.16 shows the same wood biomass sample, measured using the TGA with 100% carbon dioxide gas for inerting; this simulates the introduction of the carbon dioxide into the dome under fire conditions. The wood sample shows some combustion/gasification has taken place under CO_2 atmosphere, and this becomes very important at temperatures above 700°C

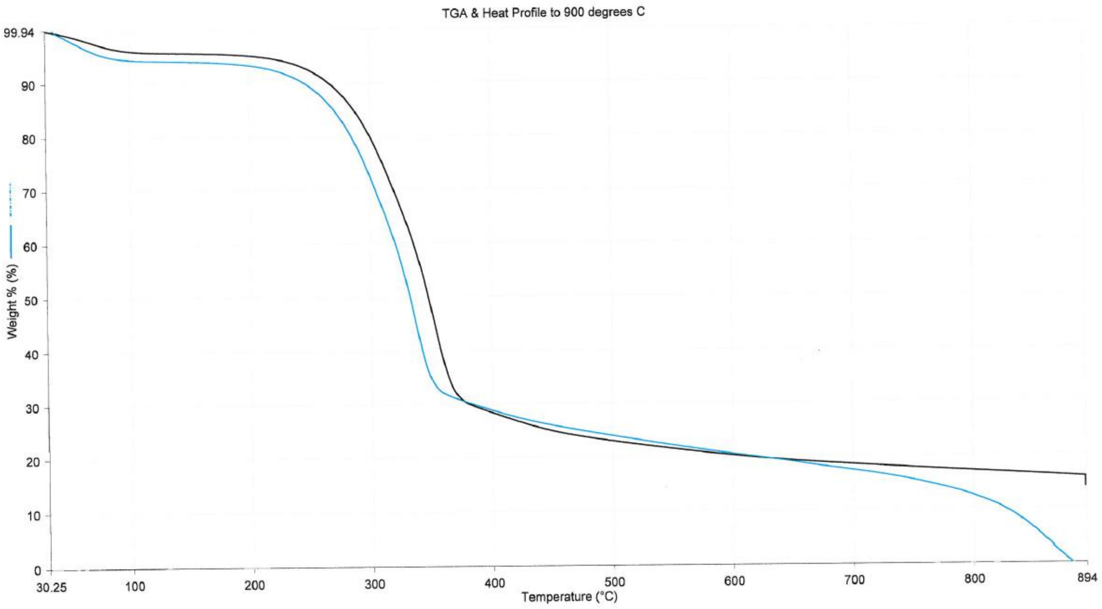


Figure 5.16. Thermogravimetric analysis showing mass of wood biomass measured against temperature under carbon dioxide

For both the nitrogen and carbon dioxide TGA data, values were obtained for T Max, volatile matter (Vm) and char along with Tbo (Temperature total burn out). Peak areas for both Vm and char were also obtained, as shown in Table 5. It is seen that the Tvm is lowest in air, and that it increases as the amount of inerting increases, showing that the reaction rate is slower when inerting is present. The Tvm in a CO_2 atmosphere is comparable to that seen between 90-95% N_2. Tchar also decreases as the level of inerting decreases in the N_2/O_2 mixtures. However, the char is less reactive in CO_2 than it is in air, as seen from a higher value of Tmax.

Table 5.4. Temperature and peak area data

	T Max			Peak area
	Vm	char	Tbo	Vm
100% Air	323.6	461.9	515	-42.33
100% N_2	359	-	505	-54.87
95% N_2	339.07	551.93	700	-47.89
90% N_2	332.49	517.3	595	-44.12
85% N_2	327.36	484.65	530	-42.52
CO_2	336.62	850.23	-	-52.86

Apparent first order kinetic values where calculated using the Arrhenius equation ($k=A e(-E/RT)$) for the nitrogen TGA ranging from 100% air to 100% nitrogen, with values also at 95,90 and 85% nitrogen gas concentrations and the range used was from ~95 – 90% wt. Results are summarised in table 5.5. This data clearly shows the suppression effect of the nitrogen on the combustion of the biomass pellets.

Table 5.5. Tabulated E and A data values against varying nitrogen concentrations

	E J/mol	A s-1
100% nitrogen	68849.9	1221.091
95% nitrogen	72001.73	2523.999
90% nitrogen	73565.6	3908.074
85% nitrogen	75401.33	5877.578
100% air	75415.46	6137.667

Utilisation of the Arrhenius equation (k=A e(-E/RT)) to calculate decomposition as a function of time for any temperature alpha = e^{-kt}. Temperature values relevant to industry of 40,60 and 100°C have been utilised. These have been calculated for the nitrogen concentrations used and plotting the impact of nitrogen on decomposition, gives the graphs shown in Figures 5.17-5.21.

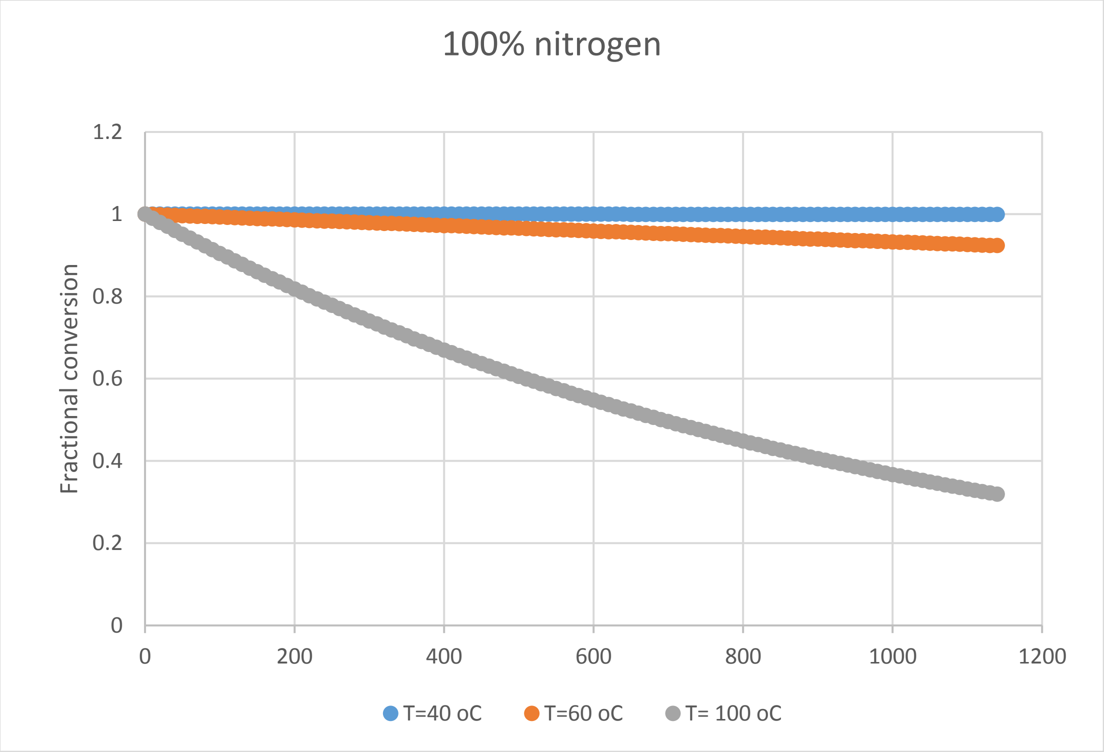


Figure 5.17. Decomposition as a function of time.100% nitrogen at 40,60 and 100°C

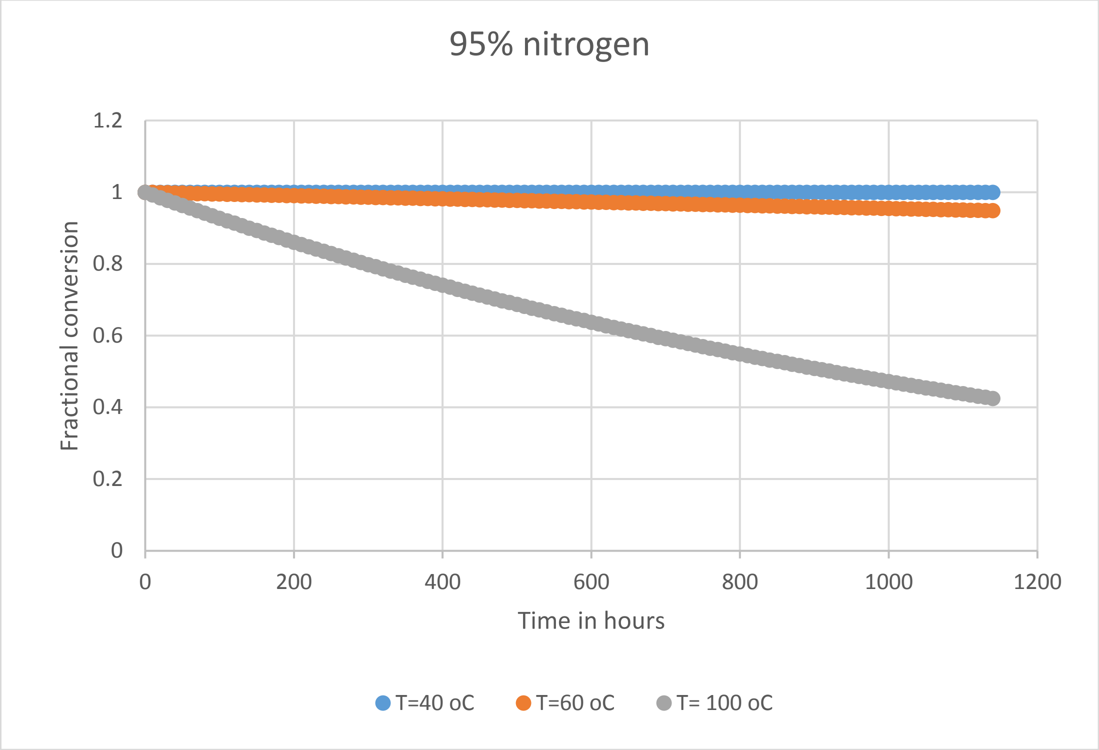


Figure 5.18. Decomposition as a function of time.95% nitrogen at 40,60 and 100°C

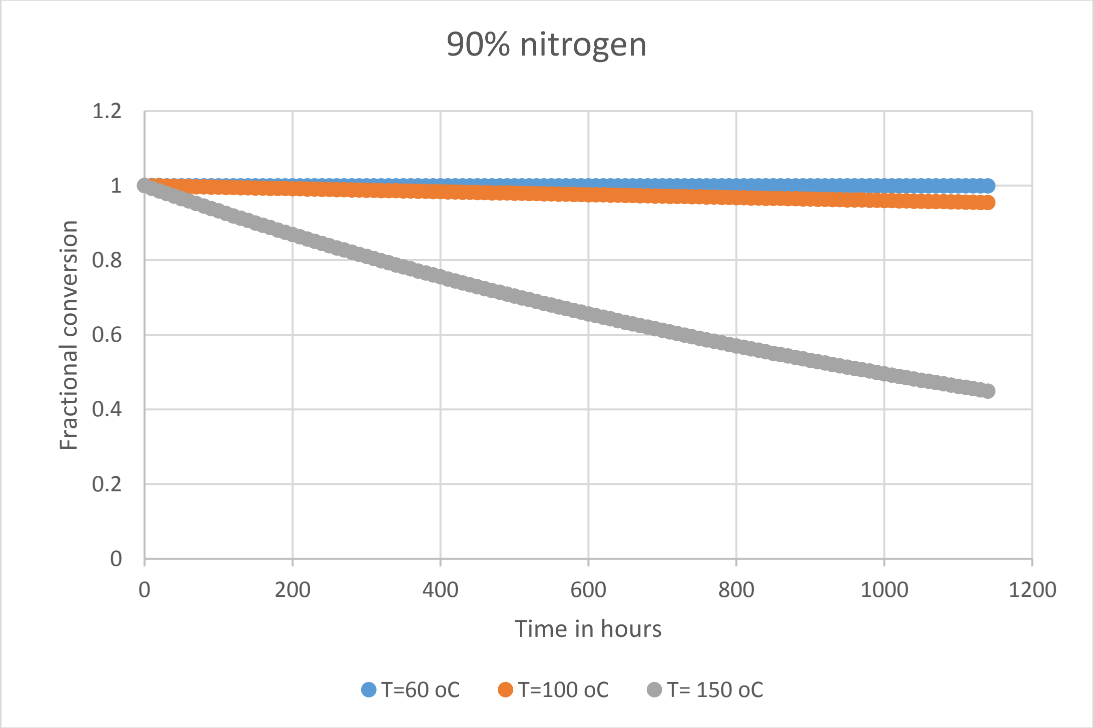


Figure 5.19. Decomposition as a function of time.90% nitrogen at 40,60 and 100°C

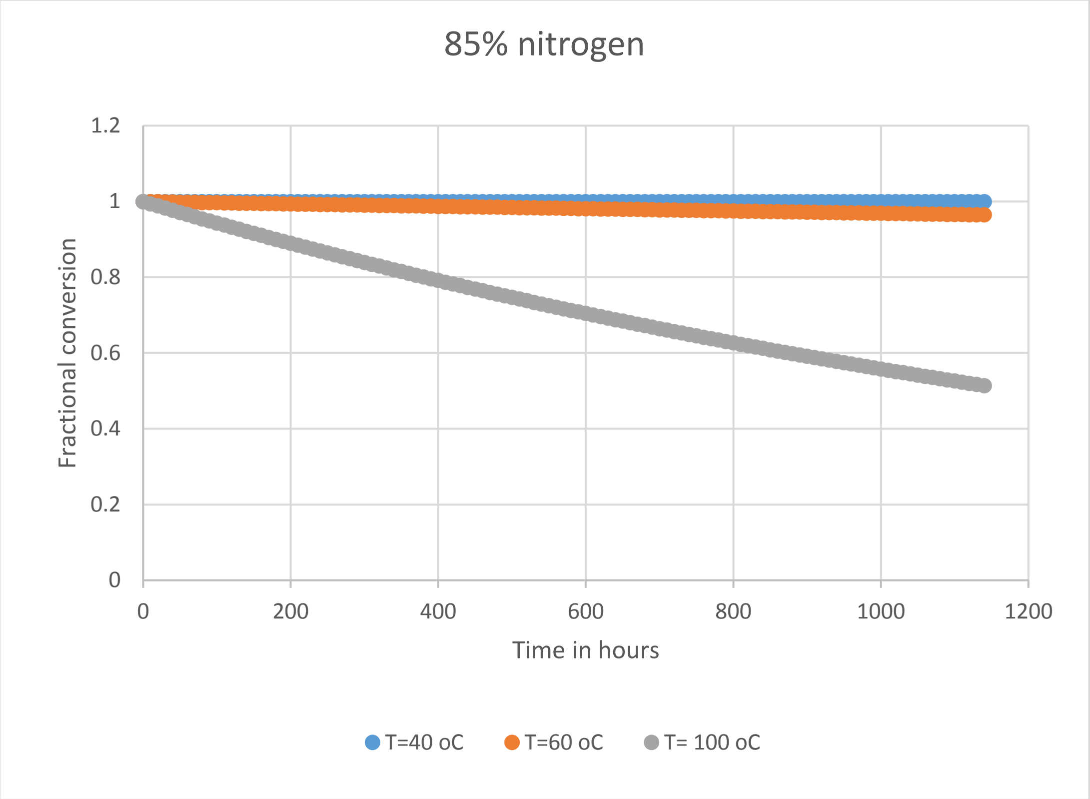


Figure 5.20. Decomposition as a function of time. 85% nitrogen at 40,60 and 100°C

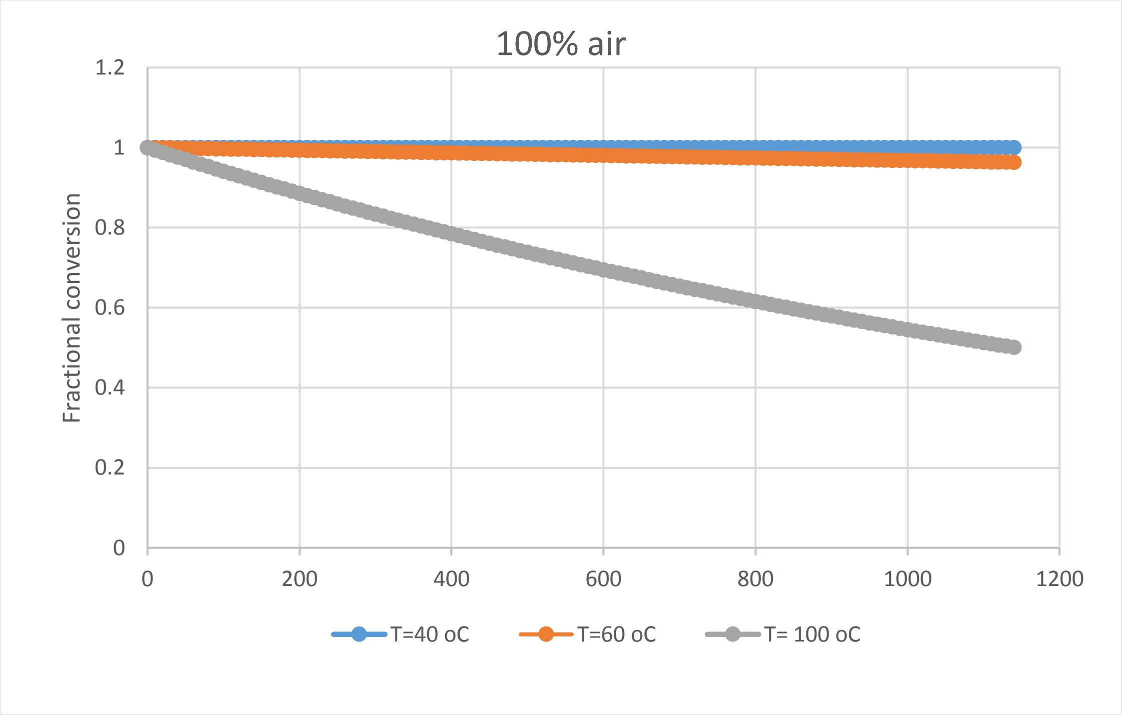


Figure 5.21. Decomposition as a function of time. 100% air at 40,60 and 100°C

Figures 5.17 to 5.21 for temperatures of 40,60 and 100°C show an increasing decomposition rate, which is not consistent with Figure 5.15 which shows nitrogen slows the composition rate (but never stops it). These temperatures were selected based on large scale industrial storage values. However, if you calculate temperatures at above 150°C then there is a cross over, and increasing oxygen accelerates the decomposition rate shown in Figure 5.22. Therefore once a certain critical temperature is reached, oxygen concentration will affect the reaction rate.

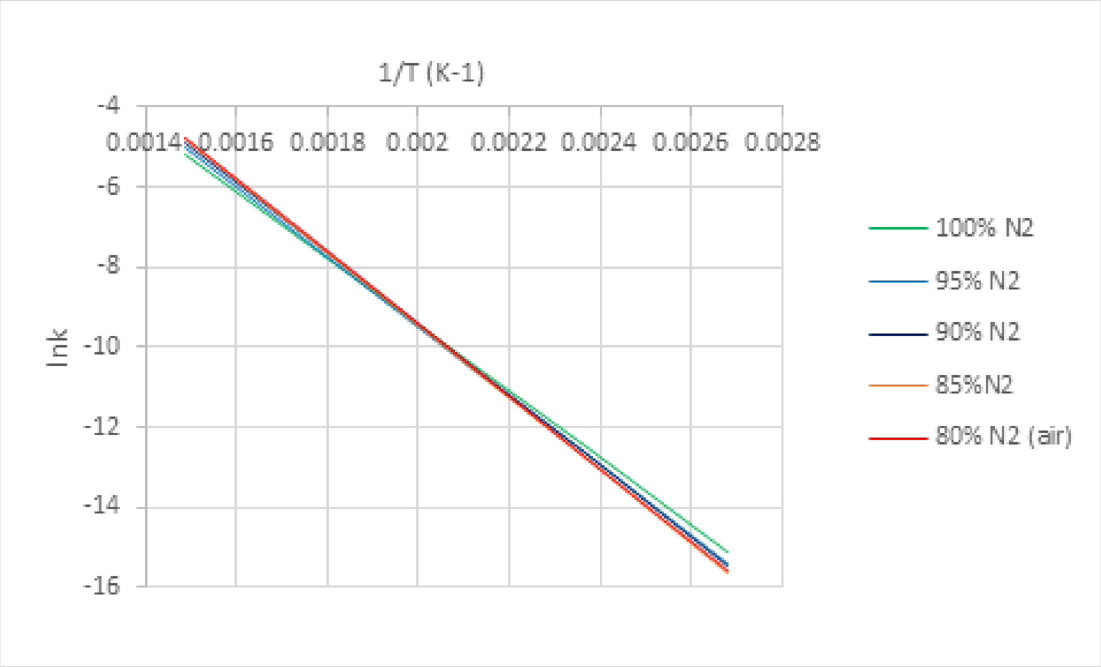


Figure 5.22. Decomposition rate at 150°C showing crossing point.

An hypothesis for the difference between the rate of decomposition at different temperatures is that at lower temperatures, the chemically bound oxygen is the preference for the rate of decomposition and therefore the nitrogen has little effect on this, but at temperatures greater than 150°C, the chemically bound oxygen and volatiles have reduced and surrounding atmospheric oxygen with have a greater effect, therefore in an increasing nitrogen content atmosphere the oxygen content is reduced therefore reducing the rate of decomposition.

5.2.6.2. Nitrogen Injection Simulation Within The Biomass Pile At 20 L Pilot Scale

Figure 5.23 shows the results from the 10L nitrogen test rig, used to examine the impact of nitrogen flow through biomass sitting at elevated temperature in an oven at 45°C. Although there are some anomalies in the data in relation to the oven temperature fluctuations, the effect of the increasing gas flow rate can still be seen, whereby the biomass is cooled to well below the oven temperature, and the degree of cooling increases as the flow rate of N_2 increases.

Scaling down for the dome flow rate of 5kg/h/m^3, equates to a scaled flow rate of 0.5L/min. A cooling effect of ~1˚C was noted over this time range of approximately 24 hours. The initial effect of the cooling was observed on the lower thermocouples, which are closest to the gas flow, with the upper thermocouples showing a slight increase in temperature. This is assumed to be the transfer of the heat from the lower thermocouples region. The maximum reduction of temperature occurred over the flow rate of 3.0L/min, which was nearly 6°C

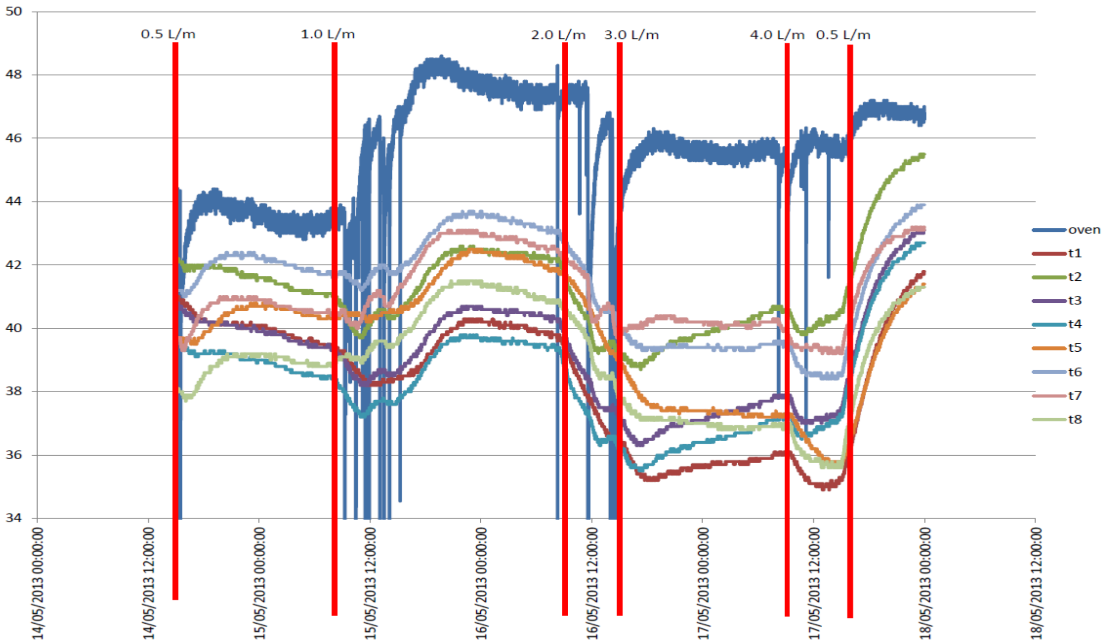


Figure 5.23. Temperature effects due to nitrogen gas at varying flow rates

Figure 5.24 shows USB loggers in vent showing humidity increasing as moisture is driven off from pellets. This would indicate that on this scale, the nitrogen gas is causing air/gas movement within the pellets which might aid in cooling and drying the pellets in large scale storage.

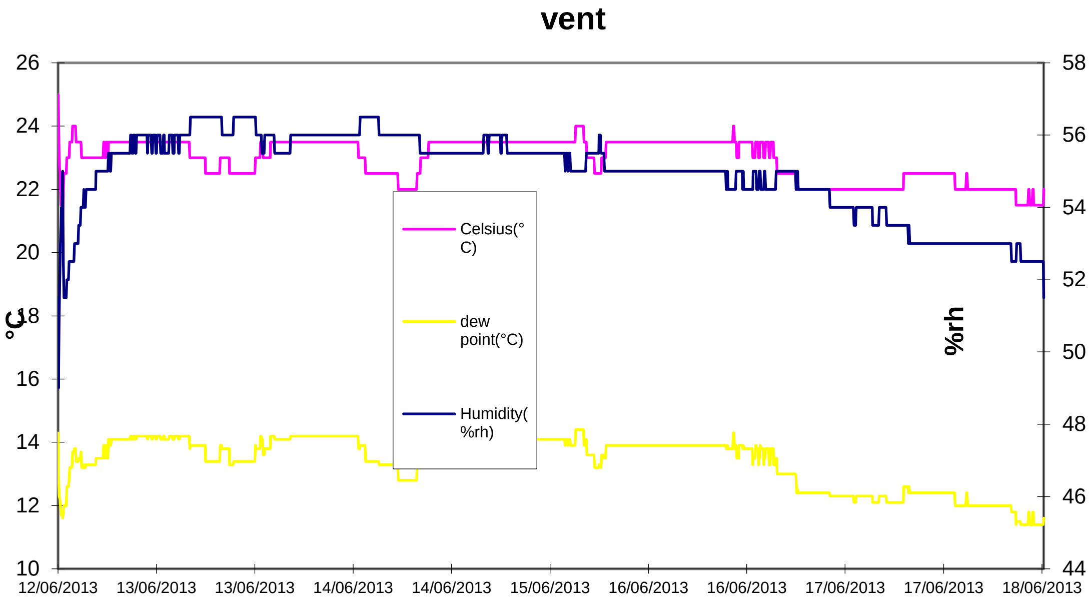


Figure 5.24. Humidity change in head space of pilot scale nitrogen test rig

On completion of the experiment, the moisture content of the pellets was analysed again and compared against their original moisture. The control batch of pellets without nitrogen gas was also analysed again for moisture. The results are tabulated in Table 5.6.

Table 5.6. Tabulated values of pellet moisture content in percent. Comparing before and after exposure at 45°C along with the effect of nitrogen gas flow or not.

	% Moisture of pellets	
	Before	After
Nitrogen gas exposure	7.2	7.1
Control with no nitrogen gas	7.5	7.5

5.3. Conclusions

It has been shown that there are differences between the storage of wood pellets and Agricultural Residues. The reasons why Agricultural Residues have not shown the same tendencies to self-heat to the extent of woods, have been explored through the laboratory research to be linked to the pH effects of moisture on the biomass and the effect to the lignocellulosic components. Upon storage the pH in Straw drops less than it does in woody biomass, and this is thought to be due to the acidic nature of the Straw coming from the formation of acetic acid. Additionally there is a potential influence of higher heavy metals concentrations in the Agricultural Residues and this may introduce toxicity effects on enzyme growth, thus restricting temperature rise. Research by Jones, et al 2015 on “Low temperature ignition of biomass” using small scale laboratory studies have been made to rank the risk factors, and they show that milled particles of Agricultural Residues having high risk than ground particles of wood. The large scale work carried out in this thesis that shows that pellets of agricultural residues have a lower self-heating potential than woods. As stated in section 4.2, the large scale storage of Agricultural Residues is not considered applicable to this thesis and for Drax Power Ltd. due to the relatively low production rates and fast turnaround of storage of this material compared to wood biomass.

The initial data from the TGA has shown some distinct differences in possible structural groups between woods and Agricultural Residues and stores that are heating and not heating. But at this stage in this research, the relevance of this data cannot be conclusive. Thermogravimetric analysis has shown that due to the inherent chemical oxygen content of the biomass pellets, even 100% nitrogen will only slow/reduce the combustion of biomass (once heating has started). There is evidence of a slight exothermic reaction during pyrolysis in nitrogen, which indicates that some heat development could still occur in this atmosphere.

Kinetic data modelled from the TGA analysis using different nitrogen concentrations of 100, 95, 90 and 85% show the increasing time for pyrolysis at low temperatures as nitrogen concertation increases. The is the inverse seen at temperatures at and above 150°C- this will help examine the impact of inerting on biomass decomposition.

The dew point of nitrogen gas (-70^{o}C) results in a natural affinity for moisture acquisition and transposition as the gas percolates upwards through the biomass storage. This has shown to give an approximate 2% reduction in pellet free surface moisture compared to the control (zero gas flow) of 0.5% moisture reduction. Based on previous work, which has shown that moisture is an initial catalyst for self-heating, this would appear to be a positive benefit through control and reduction of moisture within the pellets and pile. The moisture migration has been tracked on the small scale test-rig, and shown to have exited the pile. On the full scale dome, given the depth, this moisture might not exit the pile before it has condensed and this may result in higher concentrations of moisture in the upper levels of the biomass store.

CHAPTER 6. STUDY OF TEMPORARY STORAGE OF BIOMASS AT SCALES UP TO 40,000 TONNES

6.1. Experimental Methods

The temporary store project ran from 22/10/2013 to 17/12/2013, and various parameters were monitored. To enable a vertical start-up on the 2nd April 2013 following the conversion of the first unit at Drax Power Ltd. to 100% biomass, a number of temporary storage facilities were pre-filled by Drax Power Ltd., prior to the completion of the whole logistics systems (ports, rail and permanent on-site storage). The temporary storage facilities were located close to the main shipping ports used by Drax Power Ltd., with the majority (215,000 tonnes) of the storage within 50 km of Drax Power Ltd. This is shown on Figure 6.1. Drax Power Ltd. Biomass storage. Drax Power Ltd.'s location is shown by the red dot.

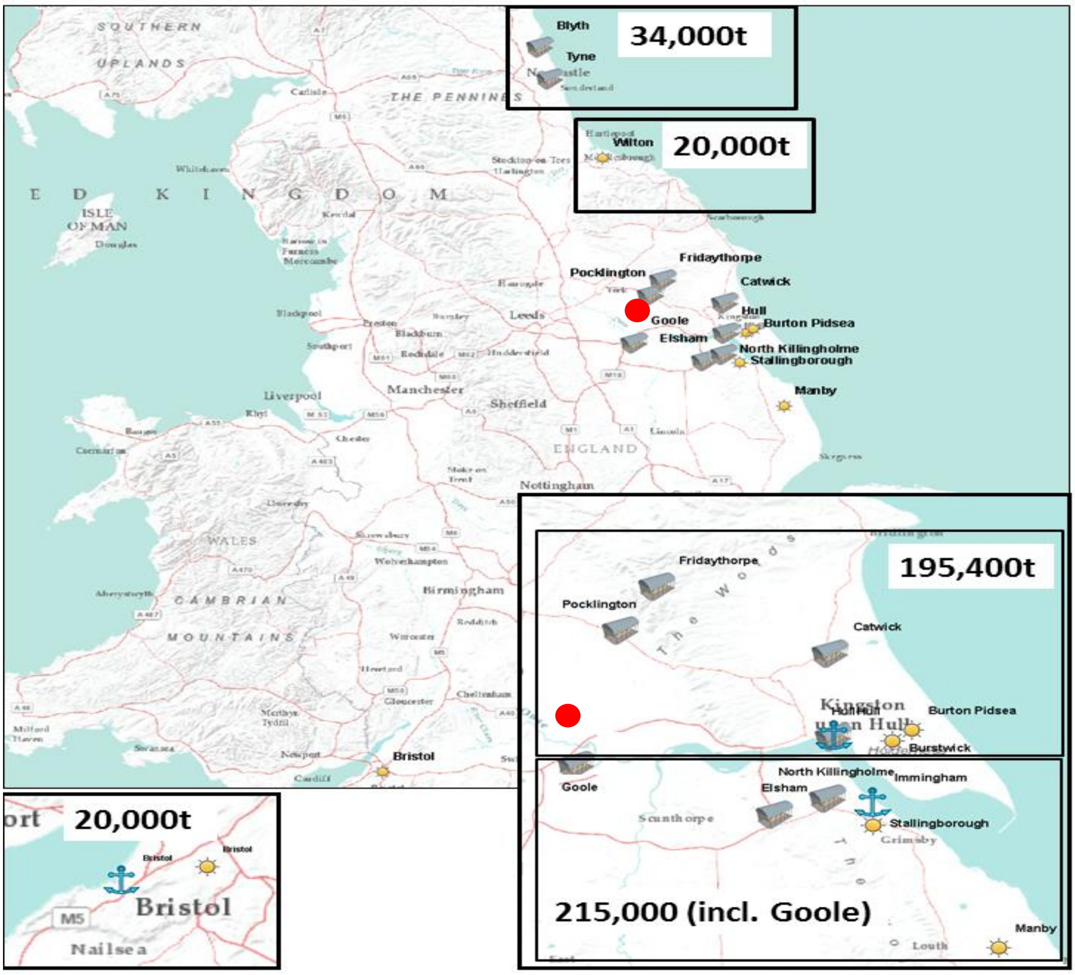


Figure 6.1. Drax Power Ltd. Biomass storage location in England and storage capacity

The pellets arrive in the UK via bulk cargo ships of a similar type to the shown in Figure 6.2 Typical cargo volumes are 40-50,000 tonnes which is segregated over typically 5 holds. It has been noted that some initial heating can occur in the ships hold for two reasons;

- The hold nearest to the engine room is usually warmer due to the heat from the engine
- Generally the ships that originate on the western side of the USA/Canada that have transited via the Panama Canal are usually warmer cargos than East Cost transits.

Figure 6.2 shows the progress of the cargo as it is discharged with quay cranes and grabs, via hoppers, to bulk tipping road transport vehicles, immediately after which the cargo was delivered, via the weighbridge to the storage shed. The discharge of the ship can take 5-7 days operating round the clock, with stoppages due to weather (rain or wind). The stores are typically filled to an even depth of 8 -10m, but some can reach heights of 15m.

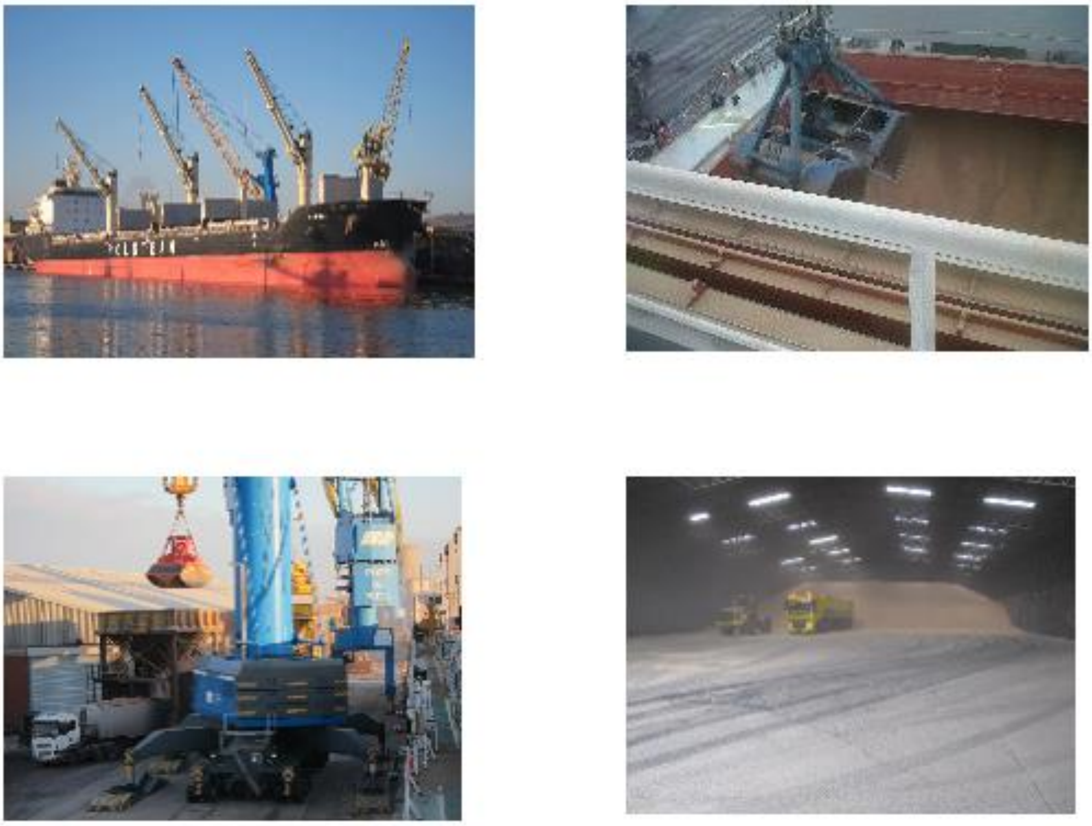


Figure 6.2. Biomass off-loading, ship to store and loading into storage

The main focus of this thesis has been on the storage facilities of JHP Storage Ltd., Brigg, in North Lincolnshire. An aerial view of the storage facility is in Figure 6.3, and the stores identified, which are named JHP 1, 3, 5, 9 and 11.

Figure 6.3. Aerial view of JHP biomass stores, identifying stores utilised in this study

Figure 6.4 and Figure 6.5 are simplified schematic aerial views of the stores JHP9 and 11 respectfully. Points shown on the aerial schematic of the stores are the monitoring points referred to in the results. The total capacity of JHP9 was approximately 40,000 kg and monitoring points were at a depth 6-8m over the monitored area. JHP11 also stored approximately 40,000 kg and monitoring points were at a depth of 8-10m. The red line shows the edge of the biomass heap for each store. The biomass is filled in the stores to an even depth on all 3 sides of the stores and forms the natural angle of repose for biomass down to the red line (approximately 60°). For both stores a monitoring point was included, in the store, but not on the heap. JHP9 this was point 12, and JHP11 this was point 1. An additional point, point 13, was selected outside JHP9 to be an external ambient monitoring point. The numbering order was selected randomly.

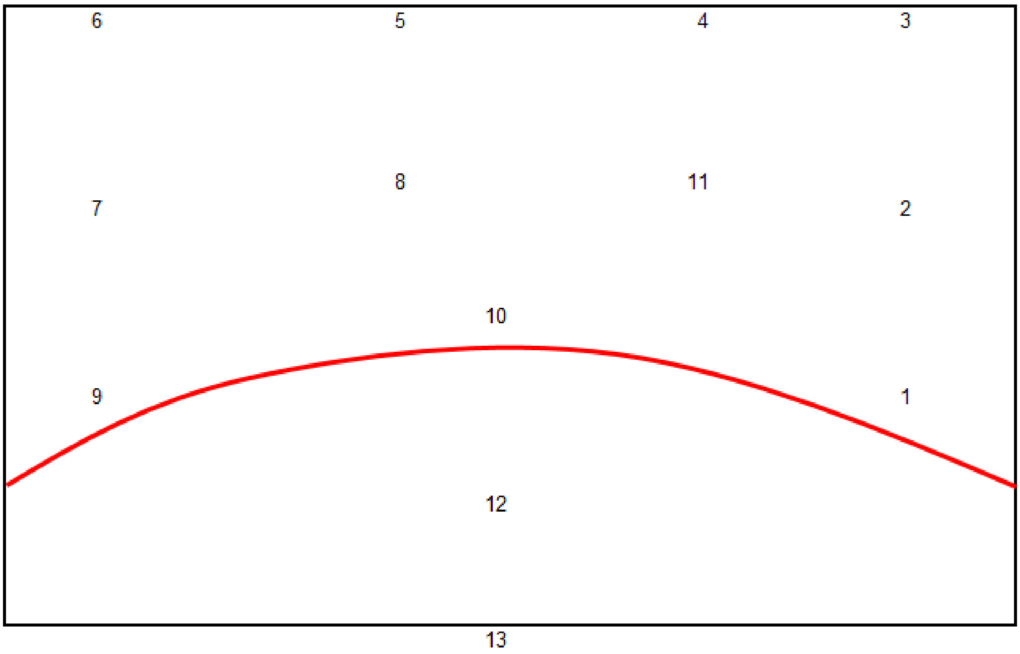


Figure 6.4. JHP9 simplified store aerial view, 40,000 tonnes. Depth – 6-8m over monitored area. The red line shows the edge of the biomass heap for each store

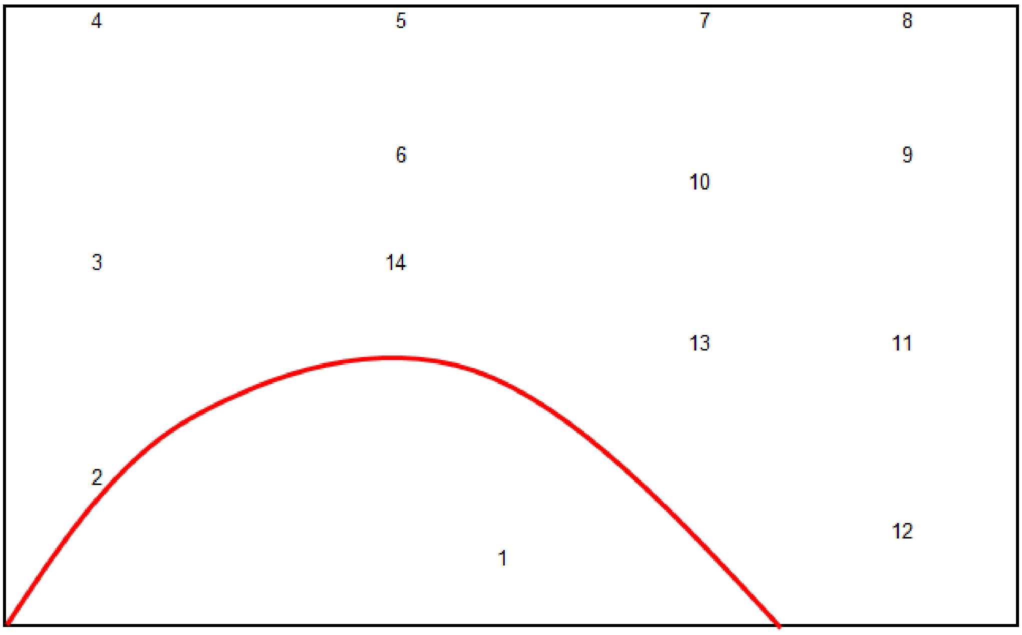


Figure 6.5. JHP11 simplified store aerial view, 40,000 tonnes. Depth – 8-10m over monitored area. The red line shows the edge of the biomass heap for each store

6.1.1. Building Construction

When selecting building to store biomass a number of factors were considered to ensure the building was of suitable construction to store biomass pellets. Many of the off-site storage facilities are purposely built bulk handling or grain stores designed specifically for long and short term storage of loose granular materials, these types of stores contain load bearing walls which allow biomass to be stocked to the height of the load bearing walls. Some stores were not specifically designed to hold loose granular products, and in these biomass had to be stocked away from the walls or temporary concrete load bearing walls of a suitable design were installed.

To minimise the risk of fire from decomposing biomass, the storage facility needed to be of such a design that biomass could not enter voids within the building i.e. behind pre-cast temporary concrete walls (Stellcons) or voids within cladding. Any material trapped within these areas was removed prior to the store being accepted for deliveries of biomass. Biomass pellets degrade rapidly when wet, therefore all the building needed to be water tight and the surrounding area was assessed for suitable drainage to prevent rain water entering the building. As part of the weekly stock monitoring process the stock pile were inspected for any signs of water contamination and any water ingress was reported .

Operational electrical equipment within the store must meet legislative requirements and be in a serviceable condition. The heat generated from exposed light fittings has the potential to ignite deposited biomass dust unless the concentration in the air is above the flammability limit. All store lamps were fitted with a lens cover to prevent biomass dust coming into contact with the lamp. Any electrical equipment deemed redundant and therefore not maintained was isolated from electrical supplies. Operatives carrying weekly stock monitoring also reported any apparent defects with lighting or electrical equipment. Wherever possible electrical systems such as lighting were turned off when not required.

A Dangerous Substances and Explosive Atmosphere Regulations Risk (DSEAR) Assessments was in place for each store and a copy provided to Drax Power Ltd. If the store operator has concluded that activities associated with storing biomass in their facility do not fall within the requirements of the DSEAR, then documented evidence explaining the rationale underpinning the decision was provided to Drax Power Ltd. Mobile plant and delivery wagons are a potential source of ignition within the store. In particular mechanical loading shovels that operate for considerable periods within areas containing biomass dust are prone to catching fire due to a build-up of combustible dust within the engine bay of the machine. The store operator needed a procedure in place to ensure that mobile plant was cleaned regularly to minimise the risk of vehicle fire.

6.1.2. Atmosphere Monitoring Above The Stored Biomass Pile

6.1.2.1. Humidity And Temperature Measurements Above The Stored Biomass Pile

An OM-EL-USB USB data logger was utilised for temperature and temperature/relative humidity within the head space of the domes. The USB data logger is set-up and the stored data downloaded by plugging the module into a PC's USB port and running the included software. Software-selectable setup parameters include logging rate, start-time, high/low alarm settings, and temperature units (°C or °F). Data was then exported to Excel. These devices where located in each store at a position of approximately 1m above the surface of the pellets.

6.1.2.2. Volatile Organic Compound Measurements Above The Stored Biomass Pile

Volatile organic compounds in ambient air was analysed from the pile surface in locations shown in Figure 6.4 and Figure 6.5 using a Rae systems ppbRae3000 gas detector. This was situated in various positions in the sampling area in order to obtain a stable result and the reading recorded manually.

6.1.2.3. Non-Condensable Gas Measurements Above The Stored Biomass Pile

Concentration of CO, CO_2, O_2, SO_2 and flammable gases were analysed using a Drager XAM7000 with a pump unit. This was used to measure gas concentrations from ambient air, at locations shown in Figure 6.4 and Figure 6.5, in order to obtain a stable result and the reading recorded manually.

6.1.2.4. Condensable Gas Measurements Above The Stored Biomass Pile

Condensable gases where analysed from within the dome using sampling tubes for acetaldehyde, formaldehyde, hexanal, pentanal, furfural and glutaraldehyde (flow rate 0.3L/min for 45mins) and charcoal tubes for turpentine, acetone, and butanoic and octanoic acids (flow rate 0.2L/min for 60min)) which were attached to a pump unit and exposed for the specified period extracting via the tube. Analysis was performed by a sub-contractor.

6.1.2.5. Microbial Content Measurement Above The Stored Biomass Pile

Microbial content in air samples were determined using a Sartorius Airport MD8 portable air sampler. Total viable bacteria count (TSA) and Fungi (Sabourguard) agar plates were used for sample collection. The pump was set at 125mL/min for 4 minutes. The plates were then subcontracted for analysis, incubated at 22^{o}C for 3 days and the results provided in cfu/plate for bacteria and no/plate for fungi.

6.1.2.6. Personal Dust Measurements Above The Stored Biomass Pile

Inhalable dust levels were determined using a Casella TUFF Plus pumped unit set a 2mL/min. Filter papers were dried and weighed prior to use, then the dust pumps were worn for the period spent exposed to biomass dust. These filter papers were then dried and reweighed, and exposure was calculated for particles greater than 10 microns.

6.1.2.7. Ambient Dust Measurements Above The Stored Biomass Pile

Dust levels in air were quantified using a GRIMM 11-R dust monitor. This measures in real time the respirable dust levels in the ambient air for particles greater than 10 microns.

6.1.3. Measurements Within The Stored Biomass Pile

To enable measurements from within the pile at varying depths, a number of extraction tubes and thermocouples were constructed to form "bundles" shown in Figure 6.6

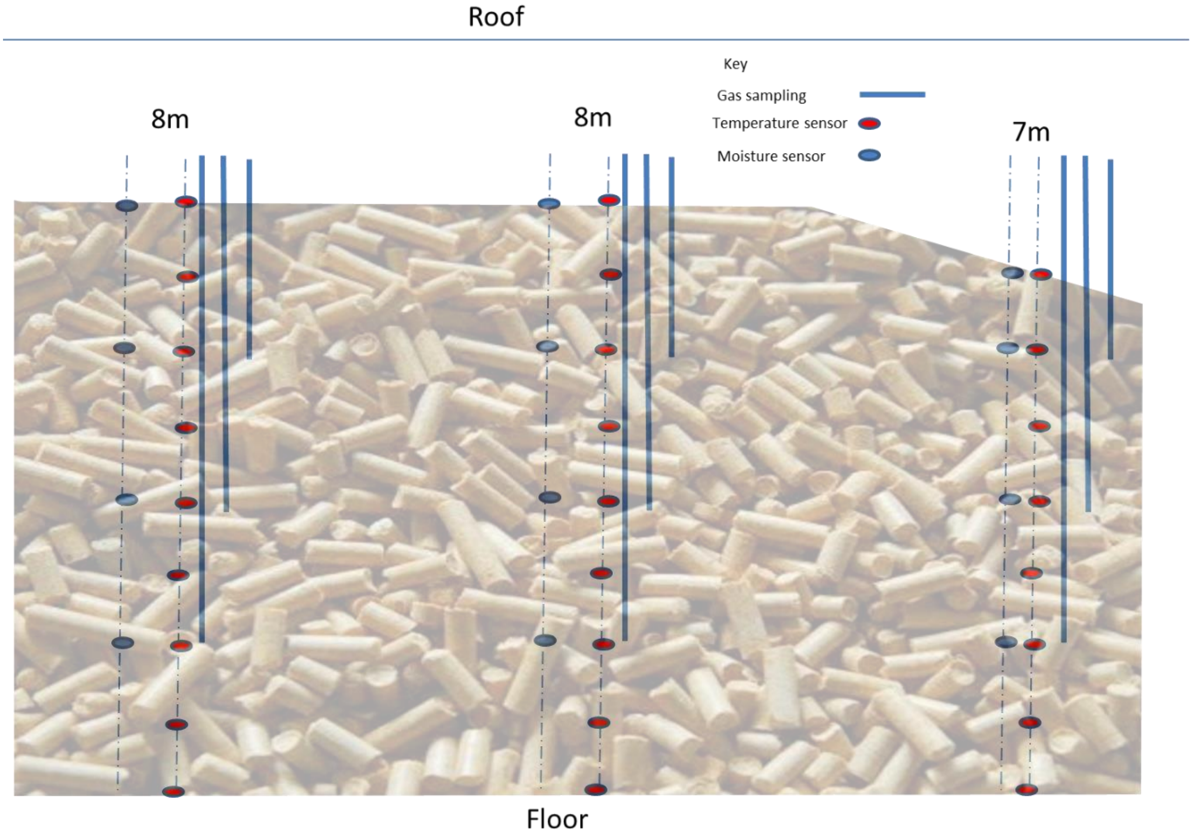


Figure 6.6. Cross section of a JHP store showing instrumentation within the biomass pile. Consisting of thermocouples every 1m and gas sampling extraction every 2m through the stored biomass pile.

Each bundle consisted of a K–type thermocouple every 1m connected to a thermocouple recorder. The first thermocouple measured point was at floor level

(0m). Extractive gases (condensable and non-condensable) were to be measured via 5mm internal diameter clear PVC tubing at 2m intervals starting 2m from the pile floor. A bundle was located in JHP9 at location 11 and JHP11 at location 13 as shown in Figure 6.6. The heights of the piles were 6m in JHP9 and 9m in JHP11.

6.1.3.1. Volatile Organic Compound Measurements Within The Biomass Pile

Volatile organic carbon from within the pile was analysed using a Rae systems ppbRae3000 gas detector. The gas detector was connected to each of the sampling tubes on the bundle within the pile. Reproducible results were obtained and the reading recorded manually.

6.1.3.2. Non-Condensable Gas Measurements Within The Biomass Pile

Concentration of CO, CO_2, O_2, SO_2 and flammable gases were analysed using a Drager XAM7000 with a pump unit. The gas detector was connected to each of the sampling tubes on the bundle within the pile. Reproducible results were obtained and the reading recorded manually.

6.1.3.3. Condensable Gases Measurements Within The Biomass Pile

Condensable gases where analysed from within the pile using sampling tubes (2, 4 DNPH tube for acetaldehyde, formaldehyde, hexanal, pentanal, furfural and glutaraldehyde (flow rate 0.3L/min for 45mins) and charcoal tubes for Turpentine, acetone, and butanoic/octanoic acids (flow rate 0.2L/min for 60min) were attached to a pump unit and exposed for the specified period extracting via the tube bundles at the 2m level. Analysis was performed by a sub-contractor.

6.1.3.4. Dry matter loss Measurement Of Long-Term Stored Biomass

Over a period of nearly 12 months, selected shipments of biomass will be accurately weighed into and out of stores. The length of time in storage will be will range from a minimum of 4 months to a maximum of 12. The difference between the two weights will be recorded and differences (+ve or –ve).

6.1.3.5. Nitrogen Injection Simulation Within The Biomass Pile At 40,000 Tonne Scale

Prior to filling with wood biomass pellets, the test store (JHP11), was equipped with temperature thermocouples and gas sampling/ injection tubes in 3 locations in the centre of the store as described in Figure 6.7. Three locations were selected within the store, utilising the building stations to fix the equipment to, thus enabling temperature measurements (vertically through the pile) every metre and gas sampling/injection every two. This equipment is shown in Figure 6.7 being installed and the store part filled. Figure 6.7 shows the monitoring equipment used which will be a 12 Channel RDXL112SD temperature data logger and Dragger XAM7000 gas monitor.

The nitrogen 15 cylinder pack was supplied by BOC, as shown in Figure 6.8 (bottom left photograph). Temperature and off-gassing data collection start immediately after the store has been filled and results collected manually approximately every 10 days. For this thesis only, the tube 2m from the base of the pile floor (approx 8m from the surface), will be utilised for injection of nitrogen gas to this location, whilst the thermocouples are used for data logging temperature changes.

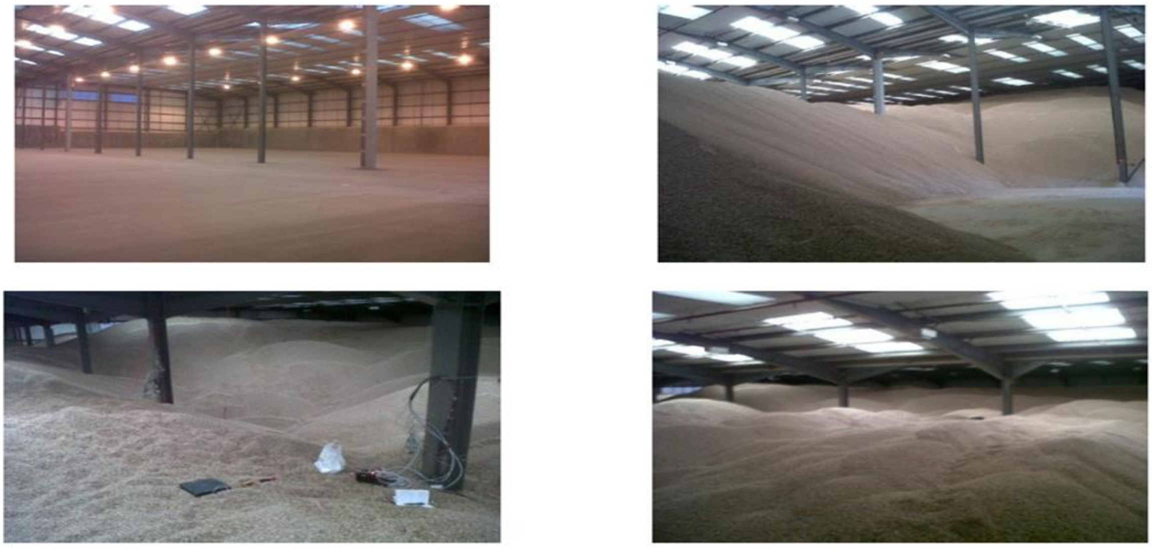


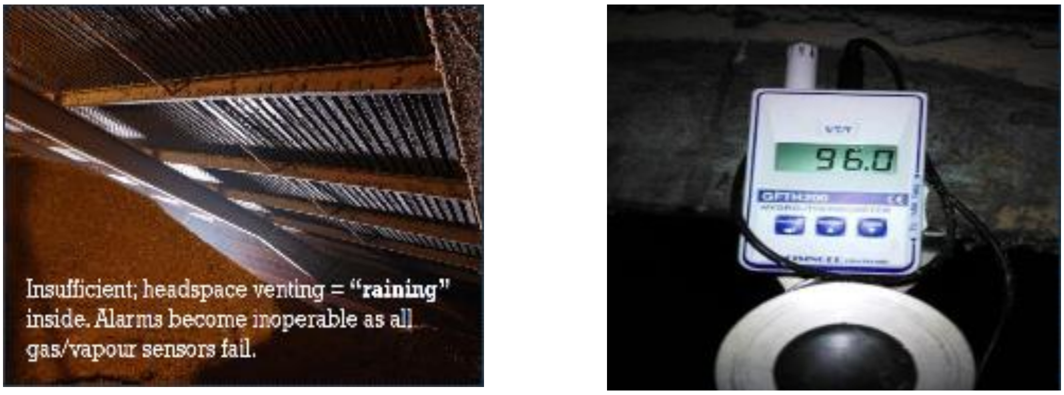
Figure 6.7. Installation of temperature and gas monitoring within the stores at JHP. Showing the store empty for scale and then examples of onsite monitoring

Figure 6.8. 12 Channel RDXL112SD temperature data logger and Dräger XAM7000 gas monitor measuring temperature and gas concentration within the stored biomass pile. Nitrogen bottle pack shown in bottom left photograph, with total volume of 142m^3 of gas.

6.2. Results And Discussions

6.2.1. Condensation And Humidity Within A Biomass Store

The self-generation of and release of moisture from within the biomass store is accepted, but the control and monitoring of this moisture has shown to be critical in the effect on the stores progression towards self-heating, but how this moisture is vented is critical to prevent absorption and heat generation.



Insufficient; headspace venting = "**raining**" inside. Alarms become inoperable as all gas/vapour sensors fail.

Figure 6.9. JHP3 - High humidity inside store

Figure 6.10. Images of moisture accumulation and venting off from the stored biomass

As a comparison, one shipment of material has been split equally between two stores. JHP3 and 5. JHP3 was found to reach a temperature of approximately 65 °C at which point action was taken as per Drax Power Ltd. management instructions of remove and spread out material, Figure 6.9 which shows the internal humidity >90%. These extremes of humidity, at times, lead to effectively "rain" on the inside of the store as shown in Figure 6.9 and Figure 6.10.

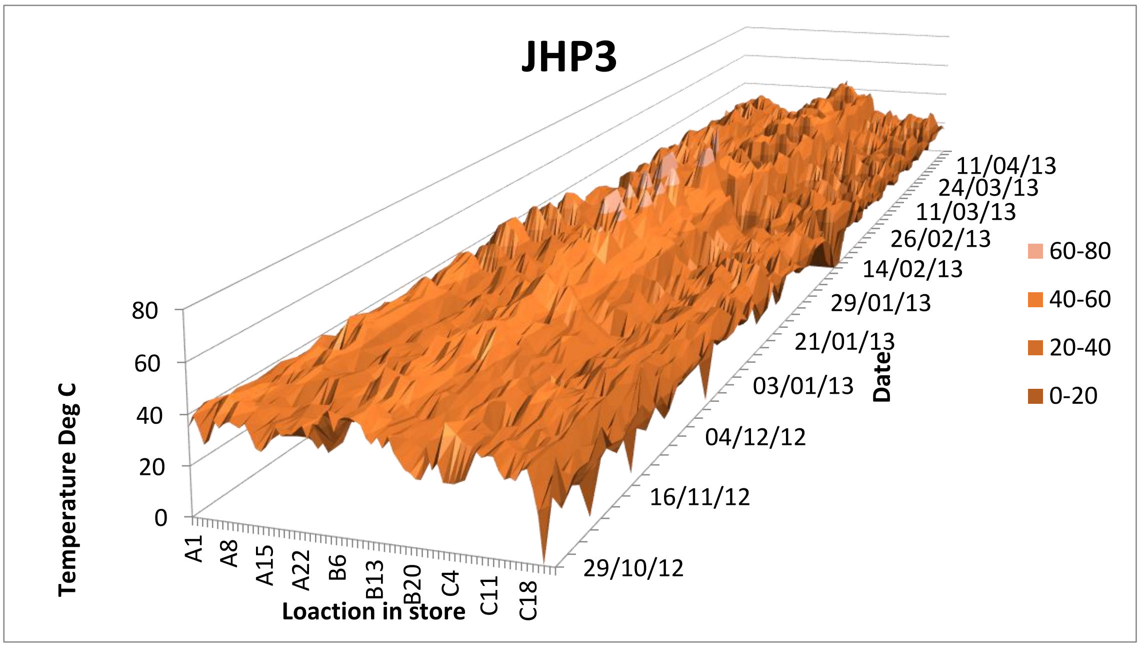


Figure 6.11 JHP3 3D Temperature graph

The water, formed on the internal roof sheets due to condensation of the cold, un-insulated metal panels. The water then dripped off the internal roof, leading to concentration of water in specific locations on the store surface as shown in Figure 6.10. This compares to the identical biomass pellets in JHP5, where the temperature never exceeded 35 °C, shown in Figure 6.12

Figure 6.12 JHP5 3D Temperature graph

The only discernible differences are in the construction and design of the stores. JHP3, is a single skinned un-insulated store with minimal ventilation. Additionally the material was filled to less than 2m from the internal roof height. JHP5 is a double skinned insulated store, with considerable cross ventilation. The height from the surface of the material to the internal roof height is approximately equal to the pile heights in both stores (10m).

Chapter 5 showed the increased in temperature due to water addition both theoretically and measured using a thermal image camera, this has now shown to occur in normal operation in stored biomass at depths of up to 10m and 40,000 tonnes.

JHP9 was monitored for humidity in the head space approximately 1m above the pellet surface. Figure 6.13 shows the results of increasing of humidity, but unlike JHP3 no condensation was seen inside JHP9. This was attributed to its good ventilation and insulated sore walls and roof. In certain climatic conditions condensation can form if the roof space of bulk stores. The type of the building, presence of ventilation systems and insulation in the store are the factors that affect the control and formation of condensation. Over time this condensation can concentrate in particular areas within the roof structure and subsequently water can fall onto the stock pile. It is therefore important that individuals monitoring the condition of the stock piles look to identify wet biomass due to condensation. Where wet biomass is identified the Store Operators must take measures to reduce condensation forming and manage any areas of wet biomass.

In some stores it is possible to utilise ventilation systems vents and fans to remove moisture from the air space above the biomass. Where these systems aren't present opening doors to allow natural ventilation can have a positive effect. Where condensation has caused damp or wet biomass the main two ways of dealing with the biomass is to either remove it from the store or spread it thinly across the top of the stock pile and allow the biomass to dry naturally. Where wet biomass due to condensation is identified, the Store Operator will agree with Drax Power Ltd. Power what action is to be taken.

Drax Power Ltd. have used a minimum figure of 5% moisture normally but some supplies have been coming in at <4.5% (Max 10%). The minimum acceptable moisture should not fall below 4%. Where moisture contents fall between 4 and 4.5% there will be an increased risk of self-heating to the point of spontaneous combustion from long term storage, to the increased potential of moisture thermal increase as shown in chapter 5.

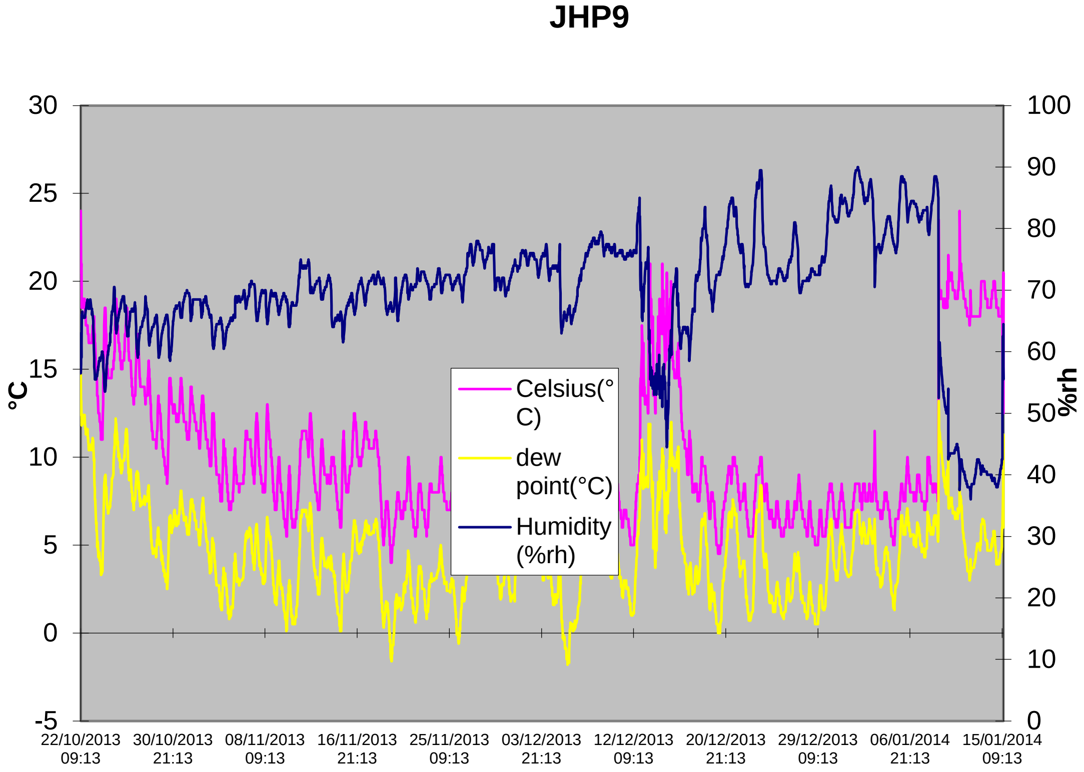


Figure 6.13. JHP9: measured humidity data, including temperature and dew point.

6.2.2. Temperature Measurements Results Of Biomass Stored At Up To 9m Depth, And 40,000 Tonnes

Temperature was measured using vertical thermocouples through the pile at 1m intervals. Original data is tabulated in Appendix 6-5 and 6-6. The heights of the piles were 6m in JHP9 and 9m in JHP 11. JHP9 Figure 6.14 showed a maximum temperature of 38.8°C in week 4 at a depth of 2m from the bottom. This temperature was sustained throughout the study with little fluctuation.

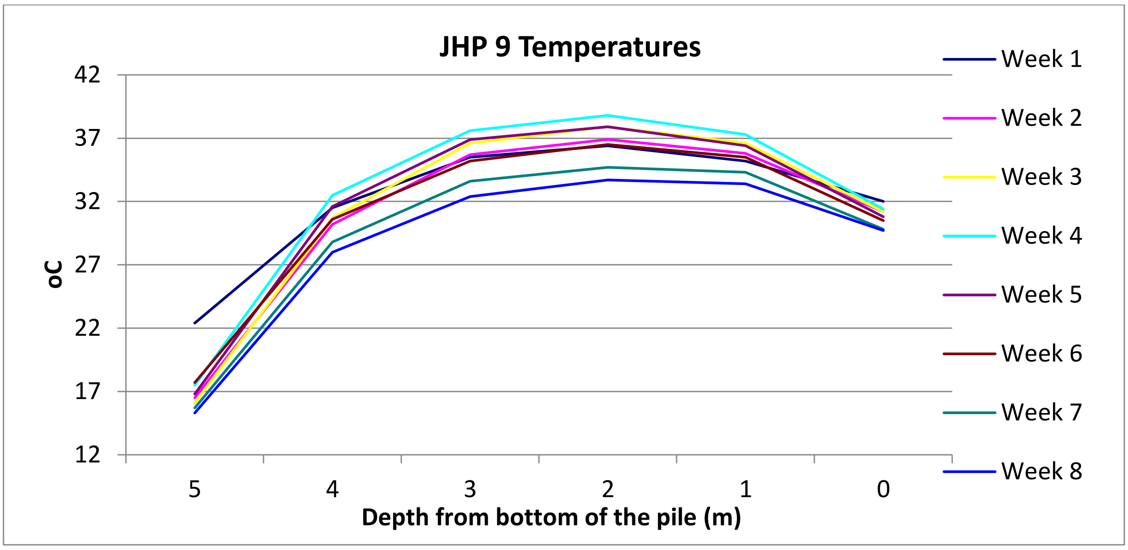


Figure 6.14. JHP9: Temperature profile through the stored biomass pile at 1m intervals

In JHP11 Figure 6.15 showed a maximum temperature of 45.8ºC in week 5 at a depth of 3m from the bottom. However a steady increase was seen to this temperature then it slowly cooled back to a temperature comparable to JHP9. The depths of these hottest spots differed due to the total mass of the pile.

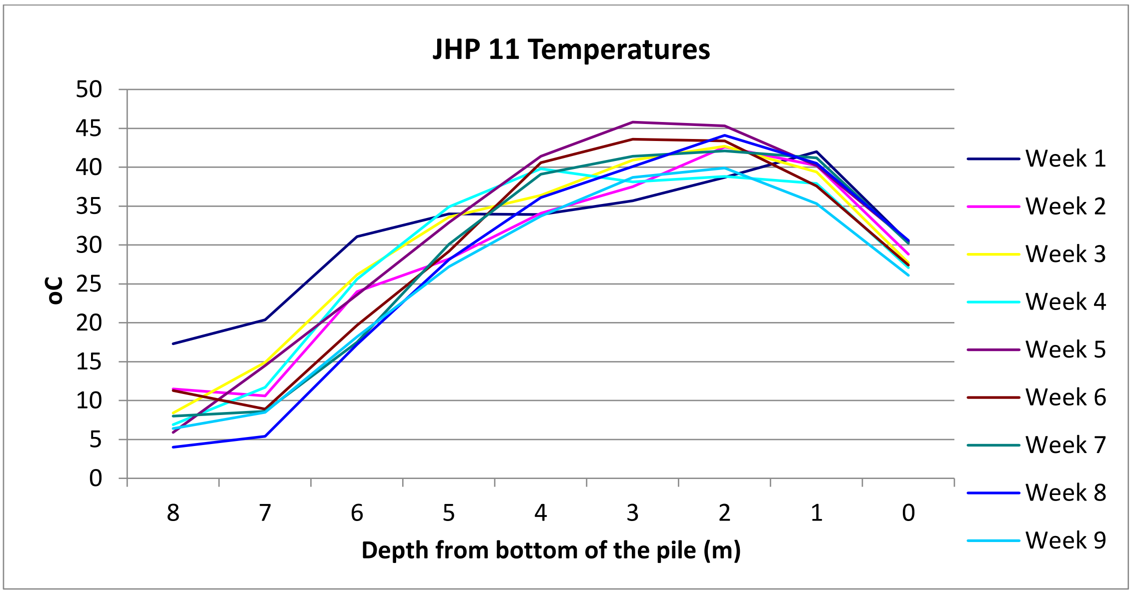


Figure 6.15. JHP11: Temperature profile through the stored biomass pile at 1m intervals

The coolest spots for each pile were 5m from the bottom in JHP9 and 8m from the bottom in JHP11. These were the thermocouples nearest the surface;

however it was found in JHP11 that this reading was less than the ambient temperature in the store showing a possible error. Based on the above information a procedure for temperature monitoring has been established see pages 124 and 125.

Temperature monitoring is important since it gives information on the complex way the temperature changes in the silo. Research by Hughes, et al (2017) who used a one-dimensional model to present numerical and analytical results on the propagation of combustion waves, driven by competing exothermic and endothermic chemical reactions in parallel with water evaporation, as shown in Figure 6.16. The research was motivated by the phenomenology of emulsion explosives comprising a mixture of fuel and an ammonium nitrate (AN)–water solution. An extensive programme of computational modelling has covered a range of important physical influences, particularly the water fraction and the ambient pressure, on which the endothermic effect of evaporation is critically dependent. A substantial, and not immediately obvious, influence of the evaporation, through its effect on the temperature, is on the fraction of the AN consumed, respectively, by the competing exo- and endothermic reactions, which are controlled by differing, temperature-sensitive kinetics. Self-sustaining travelling combustion waves are initiated for a wide range of parameter values. They are usually oscillatory, regular for small water content and become highly irregular, sometimes causing extinction for larger water content. The numerics are complemented by a brief theoretical analysis, which throws light on the complex and subtle interplay of the two chemical reactions and the evaporation, expressed in the form of a highly convoluted integral over the whole time and space extent of the process.

Similar effects are seen in this work and are shown in Figures 6.23 and 6.24.

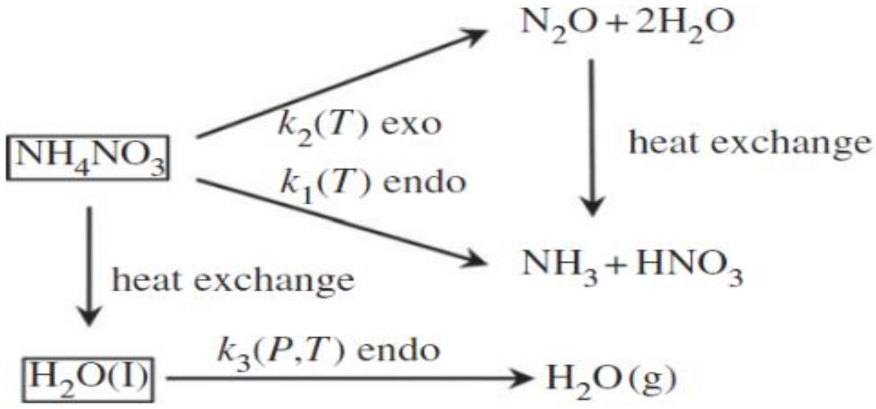


Figure 6.16. Schematic of the competing system processes, (Hughes, Brindley McIntosh 2017)

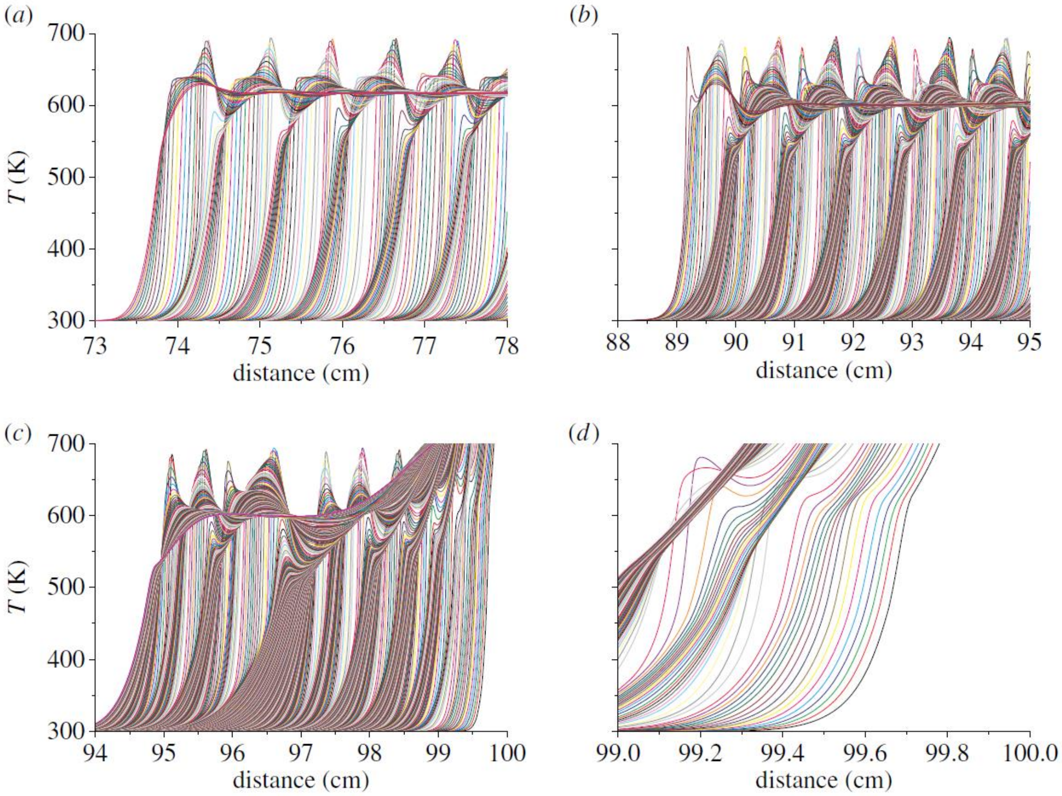


Figure 6.17. Temperature profiles at successive time intervals of the travelling AN combustion front at ambient pressure of 10 atm: (*a*) 5%water, (*b*) 10%water, (*c*) 15%water and (*d*) 20%water. (Hughes, Brindley McIntosh, 2017)

The biomass fuel temperature are monitored on delivery and no fuel will be accepted above 50°C. The store operator will carry out weekly temperature checks and the results of the checks will be supplied to Drax Power Ltd. The temperature measurements will take place in accordance with a store plan that details a matrix of zones. A Drax Power Ltd. representative will carry out independent temperature checks on a weekly basis taking measurements in the same zones. The results of the temperature checks will be reviewed on receipt, collated, entered in to a data-base and trended.

If the temperature of biomass reaches 50°C and the monitoring trends suggest the temperature will continue to increase or there is evidence that biomass is decomposing, more frequent checks must be carried out at a frequency agreed with Drax Power Ltd. Temperature probes should be routinely calibrated in line with manufacturers recommendations The biomass store temperature monitoring reports provided by the Store Operators and the independent representative will be collated centrally at Drax Power Ltd. The data from the temperature monitoring reports will be entered into a data-base or spreadsheet that will graphically plot the temperature trend of each storage facility. The data will be analysed on receipt by a nominated person. Where there is evidence of the temperature increasing overtime or approaching the action level of 50^{o}C the Drax Power Ltd. Technical Section Head must be informed.

If the temperature of biomass in storage exceeds 50^{o}C the frequency of temperature monitoring in the affected area must be increased. Where it becomes evident that the temperature is continuing to rise beyond 50^{o}C with no signs of a temperature plateau more detailed monitoring should take place. The monitoring should take into account the temperature, CO, levels, visible appearance of the biomass pellets, smells or other indicators that the biomass may be unstable and likely to continue to self-heat or catch fire. If detailed monitoring of the affected zone identifies the temperature of the biomass is continuing to increase measures must be taken to reduce the temperature in the affected area of the biomass pile. The most effective means of reducing the temperature of overheating biomass is to remove the biomass from the stock pile with mobile plant and lay out the biomass in an alternative dry well ventilated storage area at the facility or transport to an alternative store.

If the biomass within the store reaches 70ºC the affected area of biomass must be removed from the stock pile and taken out of the store. If the affected area is localised it may not be necessary to empty the full store, however it is critical a detailed assessment is carried out of the remaining biomass to establish that the remaining material temperature is at an acceptable level and there are no signs of smouldering or burning biomass. If there are any doubts as to whether the remaining biomass is in a safe state then the whole store should be emptied.

6.2.3. Dust Monitoring Results Of Both The Biomass Store And Also Personnel Within The Store

Dust levels were monitored using a Grimm dust monitor which was positioned in each store as shown in Figures 6.18 and 6.19. Original data is tabulated in appendix 6-17 and 6-18. It showed throughout the study that JHP11 (Figure 6.19) had a higher level of dust consistently than JHP9 (Figure **6.**6.18), and a peak was seen in both stores on week 7 due to extremely windy external conditions. The levels were highest at the start of the project and slowly reduced to a consistent level.

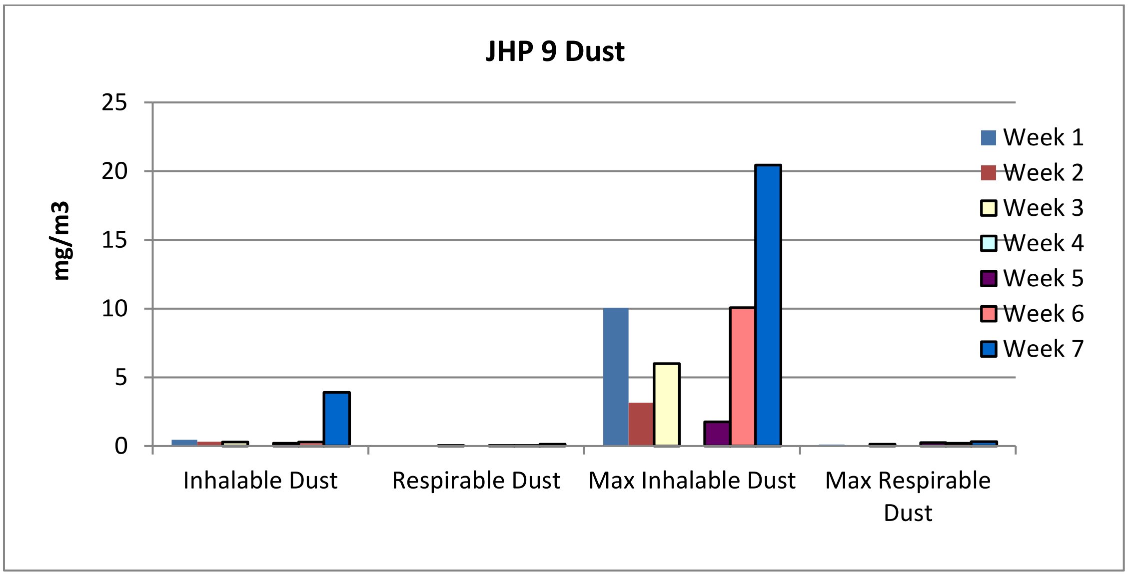


Figure 6.18. JHP9: air quality dust results measured within the biomass store

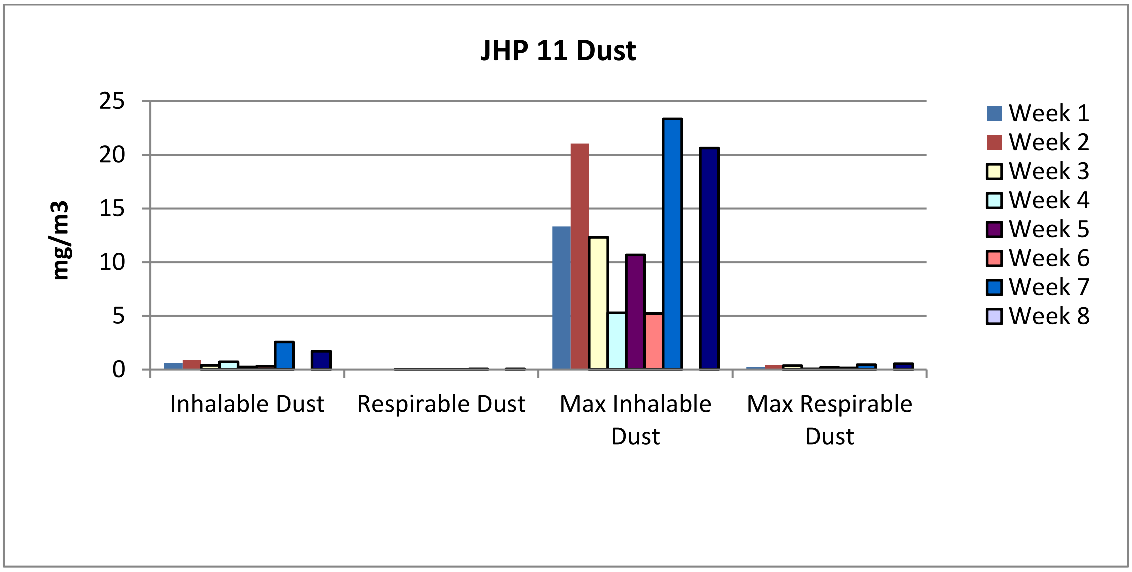


Figure 6.19. JHP11: air quality dust results measured within the biomass store

Personal dust was also monitored shown in Figure 6.20. The highest level showed a 6.34 mg/m^3 8 hour total weighted average (TWA).

Drax Power Ltd. Power Ltd, recognises it's duties under Health and Safety and is committed to minimising the risk to health from wood dust in its premises. Both hardwood and softwoods dusts have a Workplace Exposure Limit (WEL) of 5mg/m^3, which must not be exceeded. These are limits placed on the amount of dust in the air over an eight–hour shift. However the Control of Substance Hazardous to Health Regulations 2002 (as amended) requires exposure to wood dust to be "As low as reasonably practicable" (ALARP).

Drax Power Ltd. Power Ltd manages exposure to wood dust to as low as reasonably practicable. The primary means of preventing exposure, is by containment of wood dust within the materials handling and processing plant. Dust control equipment such as Local Exhaust Equipment (LEV), will be used in conjunction with handling and processing plant to ensure that dust levels are kept to as low as is reasonably practicable.

For certain operational and maintenance tasks it is necessary to use additional procedural controls to ensure that the risk of exposure to wood dust are managed effectively The site standard at Drax Power Ltd. is a dust mask with designation filtration specification of FFP3, therefore Drax Power Ltd. will designate this as a mandatory dust mask area with a rating of FFP3, thus giving 20 times reduction to biomass wood dust, effectively reducing the exposure to the equivalent of 0.25 mg/m^3 .

During the windy external conditions on week 7, very low personal dust levels were found which a contrast to the Grimm monitor reading. In general dust readings were very low unless the biomass pile surface was disturbed.

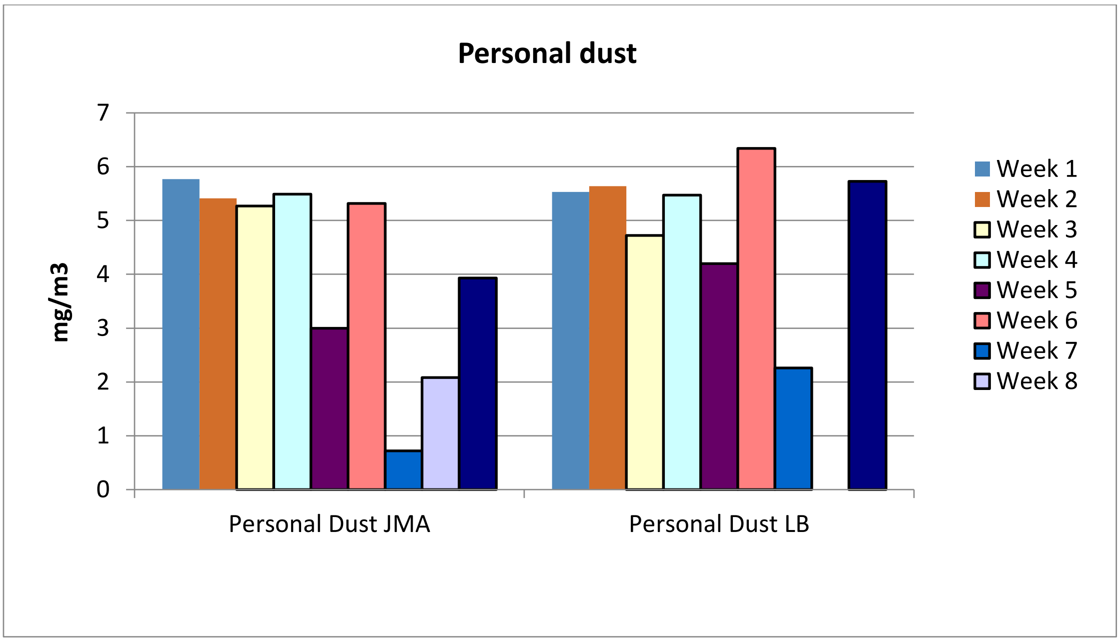


Figure 6.20. Personal dust monitoring results from James Ashman (JMA) and Laura Barlow (LB)

6.2.4. Microbiological Measured Results For The Store

Tests were conducted using a high flow rate pump (500L at 125L/min) with agar plates. Original data is tabulated in appendix 6-14 and 6-15. Total viable bacterial count and yeasts/fungi plates were used. The level of growth obtained was proportional to the level of dust found.

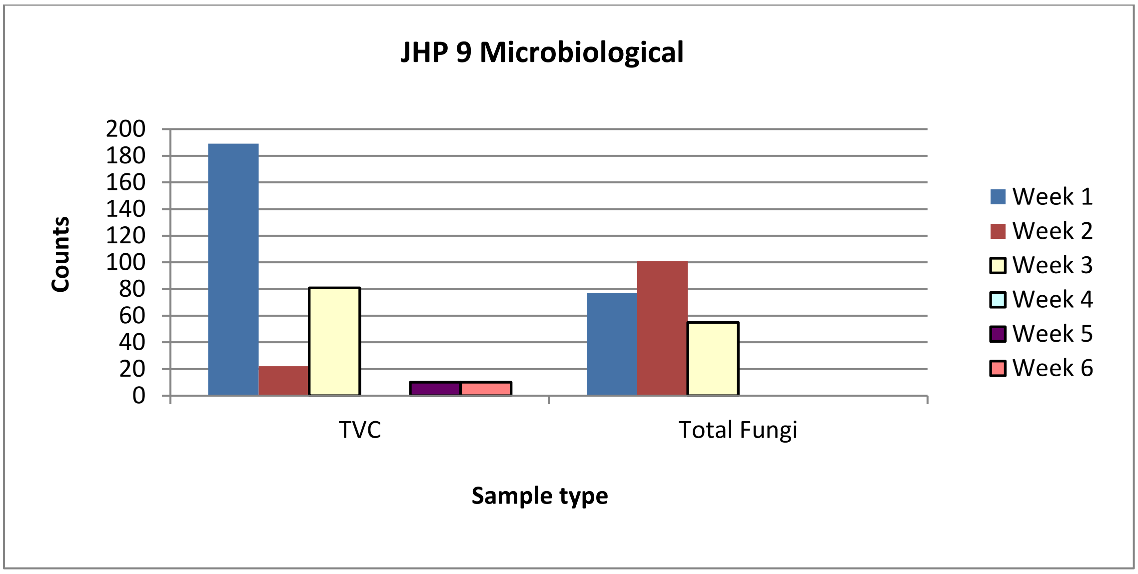


Figure 6.21. JHP9: Microbiological grows as measured above the stored biomass

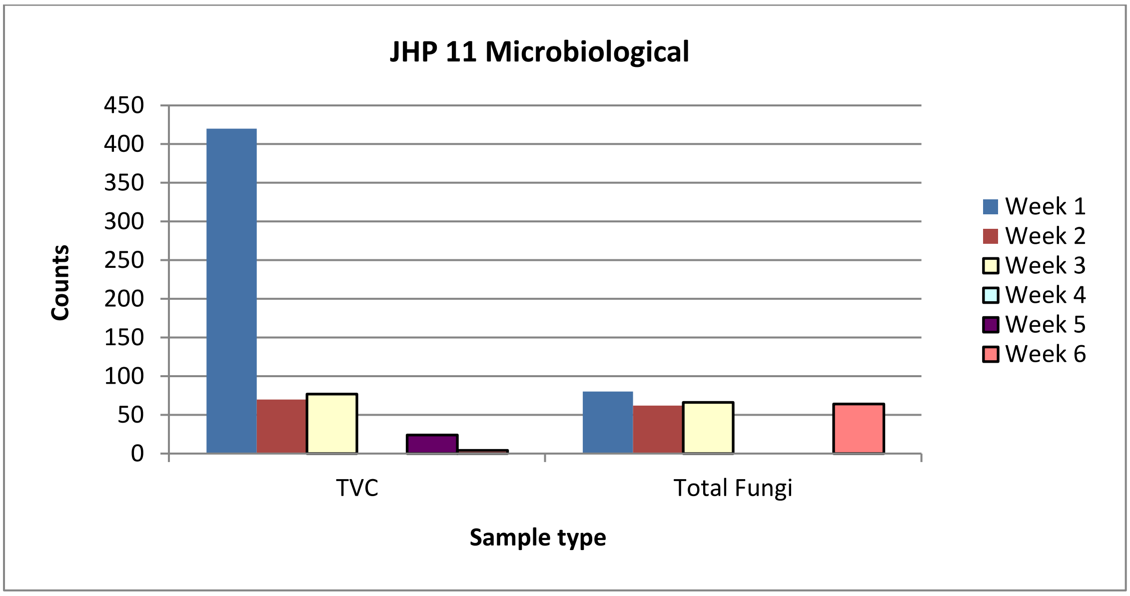


Figure 6.22. JHP11: Microbiological grows as measured above the stored biomass

All values are below World Health Organisation (WHO) guidance) of 500 colony forming units per m^3 (cfum^3) shown in Table 2.7.

Bacteria and fungi may produce aerially dispersed spores and chemical metabolites which can cause health effects if inhaled. In addition, skin contact with some types of moulds may result in toxic effects. Human reactions to exposure can vary greatly depending on length of exposure, virility and viability of the organism, personal susceptibility, route of exposure, etc. Health effects may include allergic reactions (asthmatics may be particularly susceptible) and toxic or irritative effects such as non-specific respiratory symptoms, flu-like symptoms, headaches, impaired immune functions, tiredness, skin irritation, fungal infection, etc.

Airborne concentrations of microorganisms are extremely variable and are affected by many factors including species, season, local environment conditions, etc. In addition, because there are so many different species which may produce a range of symptoms, or no health effects at all, in exposed personnel there is lack of information about the dose response relationship for most of the organisms which may be present in the atmosphere. There is, therefore, a lack of a good scientific basis for the setting of exposure limits or the determination of ‘no observed effect levels’. Guidance issued by various organisations indicates that, with regard to fungal species:

- the indoor levels expressed as colony forming units per cubic metre of air should be less than the external level
- airborne levels should be less than 500 ($cfum^3$) (World Health Organisation (WHO) guidance)
- types of species present (especially with respect to moulds) should be similar to those present in the outdoor air.

The Advisory Committee on Dangerous Pathogens (ACDP) produces ‘The Approved List of Biological Agents’ and provides the approved classification of biological agents as referred to in COSHH. The list is produced to aid the development of risk assessments for personnel who work with biological agents; however, it can be considered useful guidance with regard to the potential health effects of exposure to species identified during air sampling.

The high temperature seen during the pelleting process kills off most other fungi and bacteria present in the biomass in its unprocessed state. However, following processing the biomass pellets suffer 'reinfection' from fungi and bacteria such that the biomass may start to decompose through biological oxidation as a result of microbial activity. The pace of this process depends on the fines and moisture content of the pellets. This oxidation process produces heat and gases such as carbon monoxide (CO) and carbon dioxide (CO_2). It is therefore normal for biomass to produce off-gas.

As the biomass temperature reaches 75°C, a chemical oxidation process starts which increases the temperature further and kills off the microbial activity. The starting temperature for this process varies with moisture content. The chemical oxidation process results from the breakdown of chemicals within the biomass such as fats and it also produces carbon monoxide and carbon dioxide, but in addition flammable compounds such as formaldehyde, acetaldehyde, methanol and ethanol are produced as the temperature increases to 105°C.

As Biomass is an organic matter, it is prone to bug infestation. Infestation can occur due to various reasons:

- Poor building construction / building maintenance i.e. roof leaks, condensation causing material to heat up attracting bugs and promoting eggs / larvae development.
- The vehicles used to transport the material are not cleaned down properly and could carry bugs from previous loads.
- Adjacent buildings could have infestation problems allowing spread
- Pelleting plants / manufacturing systems – In particular older plants which cannot maintain a totally bug free environment, so bugs/infestation arrive within the product.

Regular temperature monitoring is the best indicator of product stability, any rise in temperature could indicate the presence of bug activity. The best method of control is to keep product temperatures below $10^{o}C$. Bugs are not active at this temperature. This is generally difficult to achieve, so alternatives such as fumigation need to be employed, this has a short term impact but for longer term storage fumigation will not solve the problem. Once a product is infested and with a temperature above 10 ^{o}C bugs are very difficult to eradicate. It is essential that buildings are weather and condensation proof.

As long as the correct chemical fumigation is used, the treatment should not have any detrimental effect on biomass products. Depending on the severity, if a bug infested product has broken down to an extent where it has turned to dust then the product will be unusable. In the worst case scenario if an infestation problem goes unnoticed, with increasing temperatures and moisture levels then a product can eventually self- combust, so destruction of product and buildings could occur.

6.2.5. Dry Matter Loss Results Of Long-Term Stored Biomass

Over a period of nearly 12 months, 14 shipments of wood biomass totalling just over half a million tonnes, were monitored for weight change over a period of up to 9 months in storage. The results are shown in Table 6.1. The difference in weights of each shipment was evaluated and the maximum gain in weight was found to be 888 tonne of a 47,006 tonne shipment. This equates to 1.89% of the shipment. The greatest loss was 237 tonne of a 26,042 shipment. The total of all shipments was found to be only a 101 tonne gain which is only 0.16% change. There was shown to be no correlation to time in store to weight change.

The main reason for these such stable values is attributed to the tight quality control at production and specification limits for moisture of a maximum of 10% in pellet and minimum of 4% in pellet. Others have conducted experiments on much smaller (less than 5,000 tonne) piles and shown loses of >20% or more, but these have always been conducted on chips or “green” material.

Table 6.1. Dry matter losses comparing time in storage against weight change

		Tonnage				
Date	**Ship**	**Start**	**End**	**Change (T)**	**% change**	**Time in storage (months)**
02/02/2013	Star Norita	35646	35636	-10	-0.03	7
05/02/2013	ID MERMAID	23924	24272	348	1.45	9
05/03/2013	Star Athena	46887	46878	-9	-0.02	6
21/04/2013	Astarea	47006	47894	888	1.89	7
22/04/2013	Hermann Schoening	26042	25804	-237	-0.91	8
30/05/2013	TN Dawn	47221	47698	477	1.01	9
13/06/2013	Northern Dancer	26369	26191	-179	-0.68	7
19/06/2013	Spar Mira	46639	46770	131	0.28	6
12/07/2013	Star Athena	46821	46768	-53	-0.11	5
18/08/2013	Genco Pyrenees	46755	47024	269	0.58	4
09/09/2013	Sandpiper Bulker	46014	45897	-117	-0.25	7
16/09/2013	Lowland Breeze	49025	49411	385	0.79	8
10/10/2013	CMB Boris	27359	26668	-691	-2.52	9
05/11/2013	Lucy Oldendorff	25772	25980	207	0.80	7
		541,480	542,891	101	0.16	
		Total Tonnage		Averages		

6.2.6. Gases In Atmosphere Measured Above The Stored Biomass

Monitoring was carried out at set positions in each store using a multi-gas detector for CO, CO_2, O_2, LEL and SO_2 and a volatile organic compounds (VOC) detector. Original data is tabulated in appendix 6-1 to 6-4. Ambient results were obtained for both stores for CO_2, O_2, LEL and SO_2. Higher levels of volatile organic compound were found in JHP9 (see Figure 6.23). The highest result found was in JHP9 at 13.6ppm during week 6 (average 6ppm). The highest result obtained in JHP11 (Figure 6.24) was 8.6ppm (average 2.4ppm) during week 6. Higher levels of CO were also found in JHP 9 (Figure 6.23). The highest result found was in JHP 9 at 31ppm during week 2 (average 12ppm). The highest result obtained in JHP11 was 22ppm (average 6ppm) during week 3.There was no trend for each of the monitoring locations in both stores, however generally the highest readings were found at the back of each store. Very low results were found when the external conditions were windy. This was due to the increased ventilation and air flow. JHP11 was generally lower than JHP9 due to the improved ventilation.

Detection of carbon monoxide (CO) within the store could be the early indication that the biomass may be self-heating and is beginning to smoulder or burn. Although the storage facilities are not fitted with online CO monitoring systems, all personnel entering the stores must carry a personal CO monitor for their own safety. If CO levels above that normally expected are identified the store operator is made aware and the details recorded in the weekly store report submitted to Drax Power Ltd. CO monitors must be calibrated and maintained in line with the manufactures recommendations. Because of the noxious fumes given off, it is therefore imperative that suitable control measures are in place to protect staff.

Natural ventilation or forced ventilation is likely to evacuate any toxic gases that may arise. Where possible stores ventilation systems should be deployed to minimise the risk of noxious fumes building up within the store; In particular prior to staff entering the stores vents should be opened and ventilation systems operated. Where these systems aren't present doors should be opened to create natural ventilation. As a precautionary measure all staff entering the store must have a personal CO monitor and if a CO level of 35 ppm is identified then inform Drax Power Ltd. Technical Section Head. If 100 ppm and rising, withdraw from the store immediately and inform Drax Power Ltd.

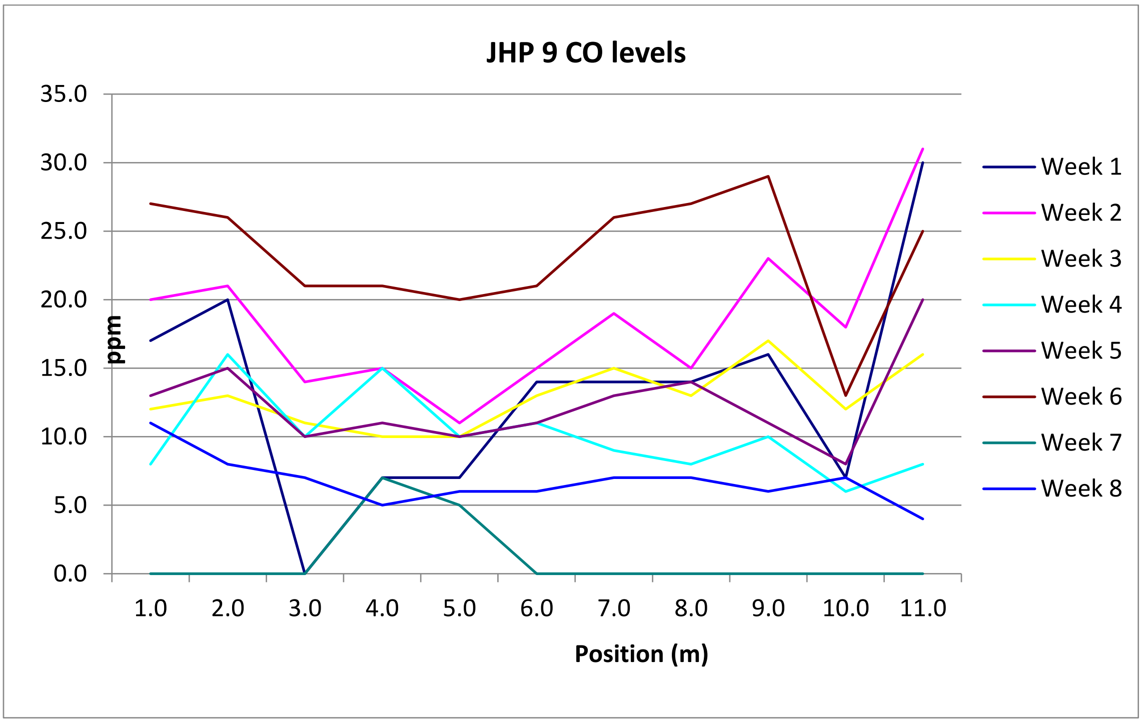


Figure 6.23. JHP9: carbon monoxide measurement results from above the stored biomass pile

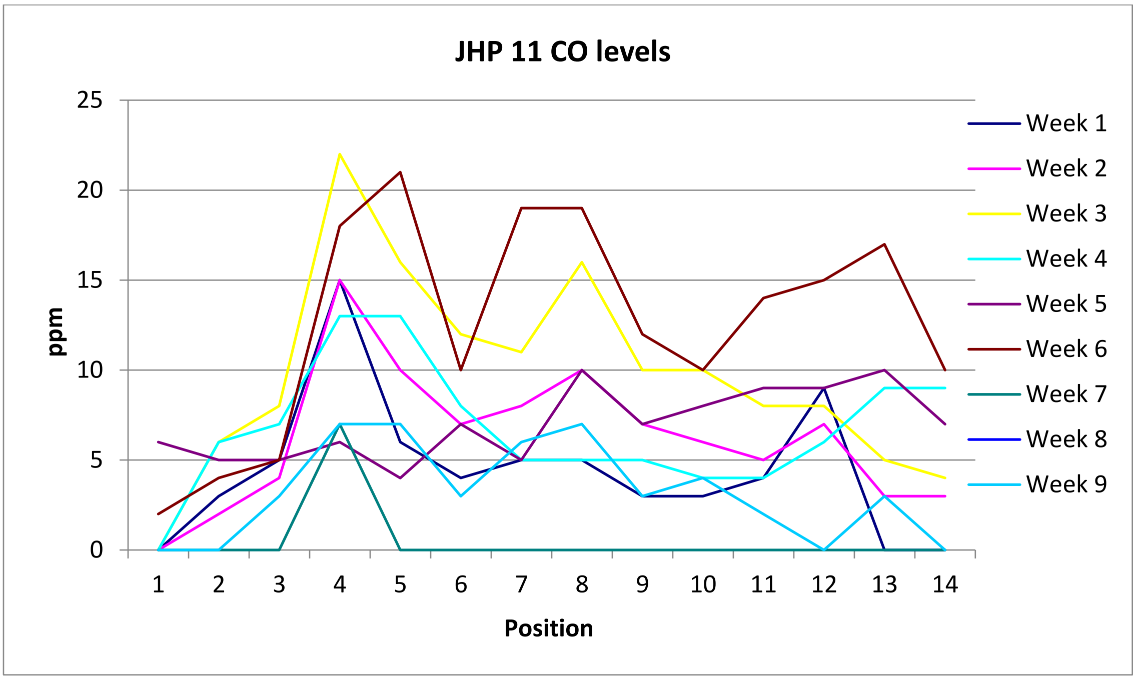


Figure 6.24. JHP11: carbon monoxide measurement results from above the stored biomass pile

The oscillating behaviour is as predicted by the model developed by Hughes et al (2017) which is described in see section 6.2.2. The carbon monoxide emission results from the periodic change in temperature and hence reaction leading to its formation. A similar effect occurs with other temperature related products such as volatile organic compounds shown in the next figure (Figure 6.25)

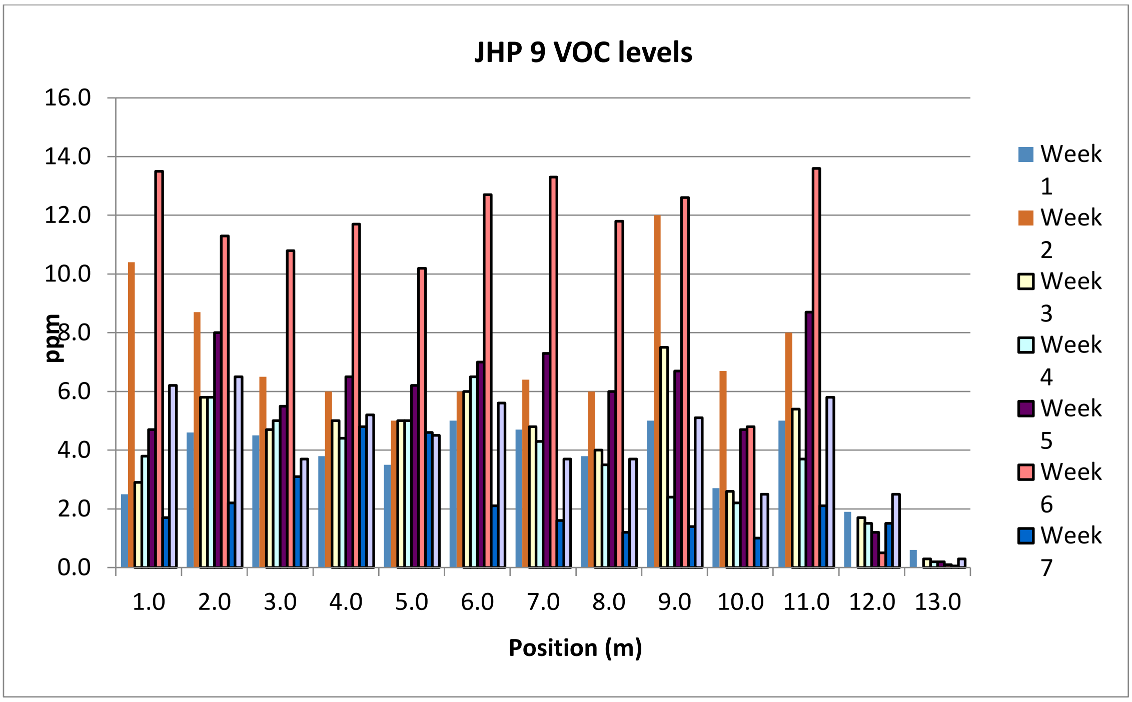


Figure 6.25. JHP9: volatile organic compound measurement results from above the stored biomass pile

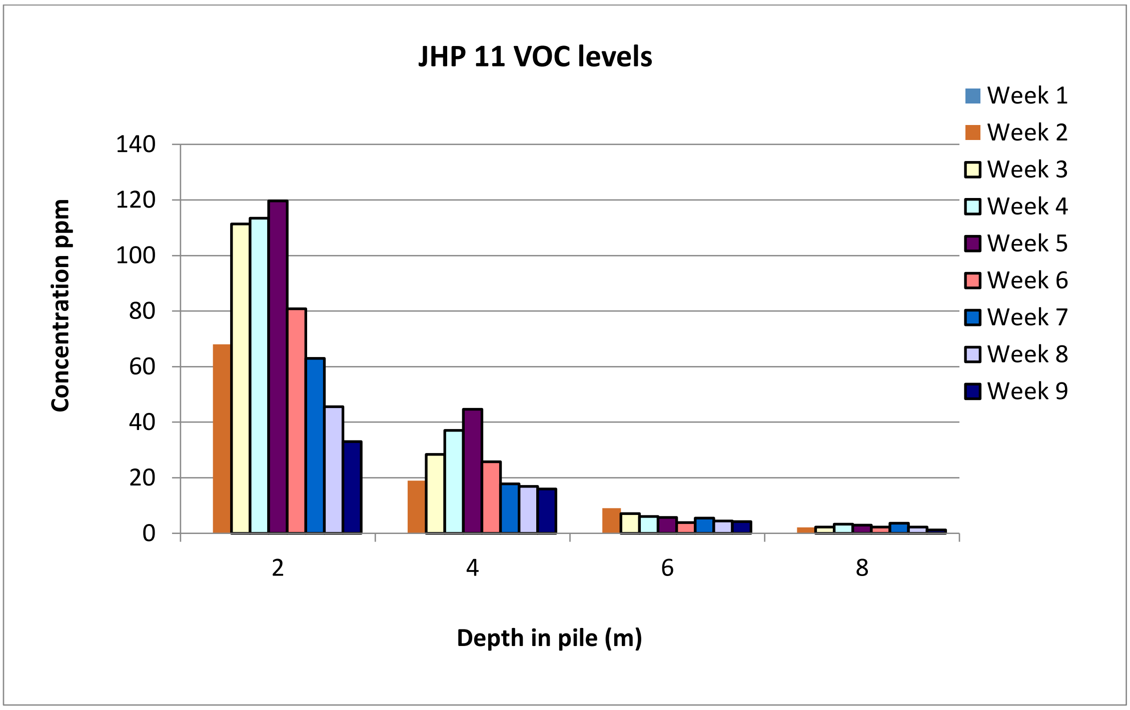


Figure 6.26. JHP11: volatile organic compound measurement results from above the stored biomass pile

6.2.7. Non-Condensable Gas Results Measured From Within The Stored Biomass Pile

Gas measurements were taken using a multigas detector (CO, CO_2, O_2, LEL and SO_2) and a volatile organic compounds (VOC) detector through vertical gas pipes through the pile at 2m intervals. Original data is tabulated in appendix 6-6 to 6-13. It was found that in JHP9 the CO (Figure 6.27) and VOC (Figure 6.31) levels showed a steady decrease over the monitoring period. O_2 levels were depleted when the pile was fresh, however by week 6 the level had returned to normal. All highest results were at the 2m from bottom level with a peak of 260ppm CO in week 1, 20ppm VOC in week 2 and the lowest O_2 level was 20.4% in week 2.

JHP11 the CO (Figure 6.28) showed a steady decrease over the monitoring period similar to JHP9. The highest level found was at the 2m from bottom level with a peak of 500ppm CO in week 1. This is a higher result than JHP9 and is mostly likely due to the increased mass and depth of the pile. However VOC levels peaked in week 5 at 120ppm. This coincides with the highest temperatures found within the pile. After this point the levels slowly decrease. O_2 levels were also depleted when the pile was fresh down to 19.8% in week 1, however by week 4 the level had returned to normal. Again all highest results were at the 2m from bottom level. Therefore this shows that level of gases given off in the pile depends on the volume of pellets, depth of the pile and the internal pile temperature.

The rate of the chemical oxidation process increases exponentially with temperature until eventually the biomass will self-ignite in areas of localised concentration of the flammable compounds. It is important to understand this chain of events, recognise the risks involved and take action to control what is a natural process. An increase in off-gassing can be an indication of acceleration in the decomposition of the biomass and the onset of chemical oxidation with its higher rate of self-heating. Monitoring the levels of carbon monoxide present in the storage facilities is therefore a useful indicator of the stability of the biomass.

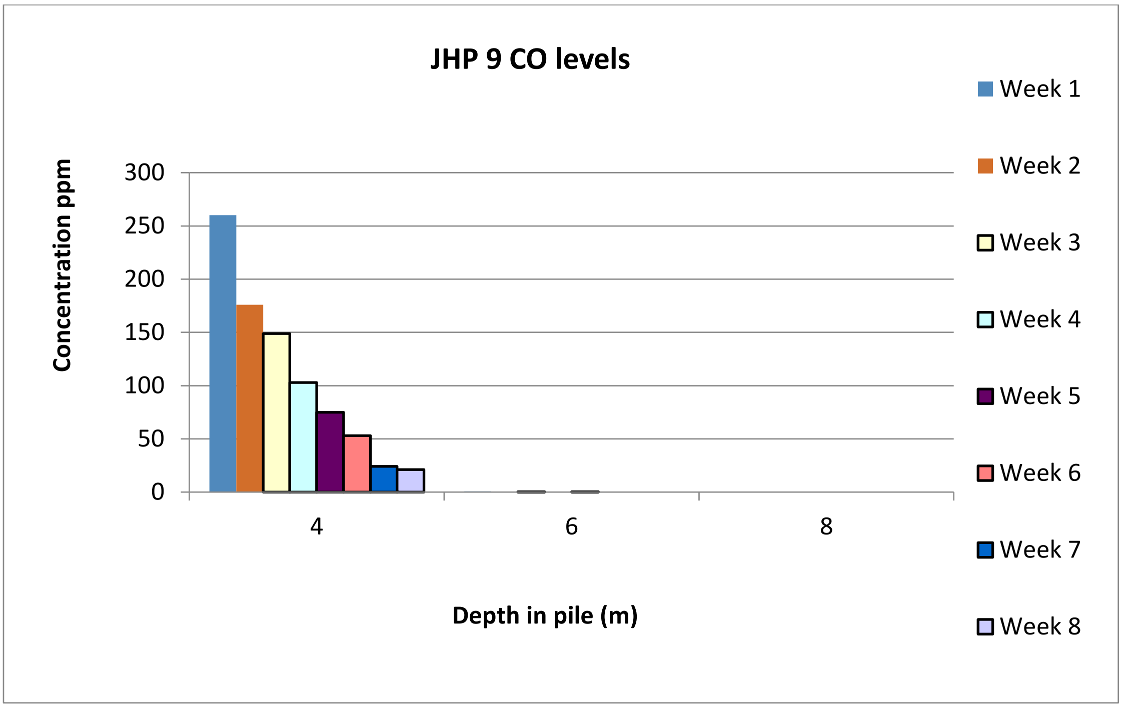


Figure 6.27. JHP9: carbon monoxide measurement results from within the stored biomass pile

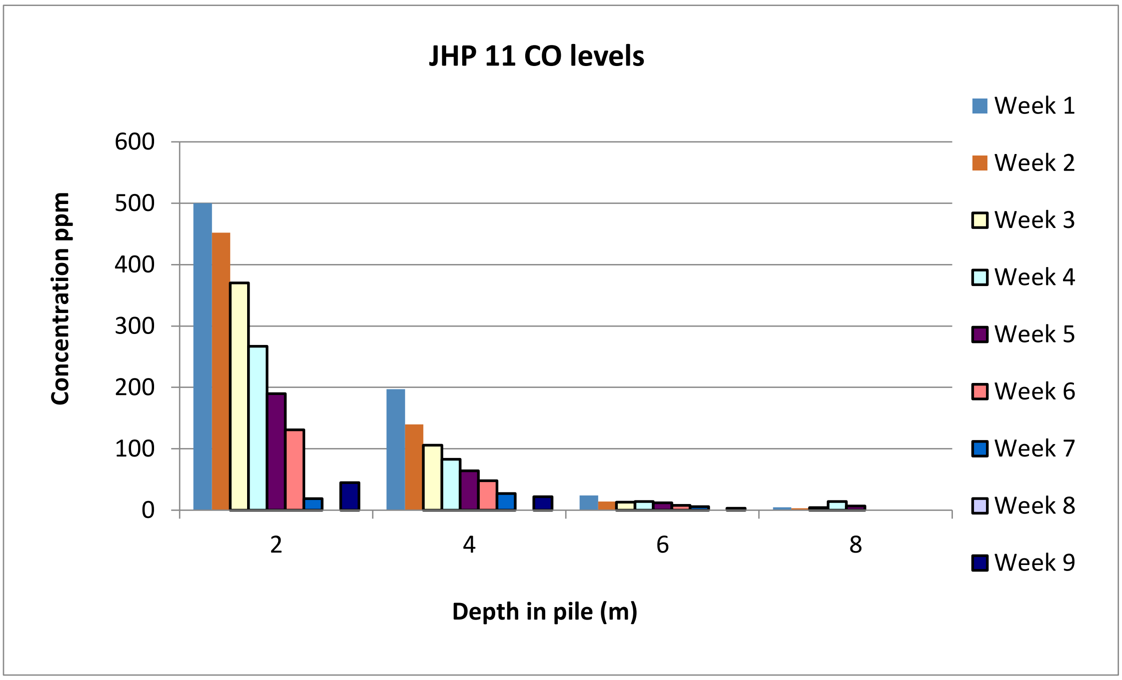


Figure 6.28. JHP11: carbon monoxide measurement results from within the stored biomass pile

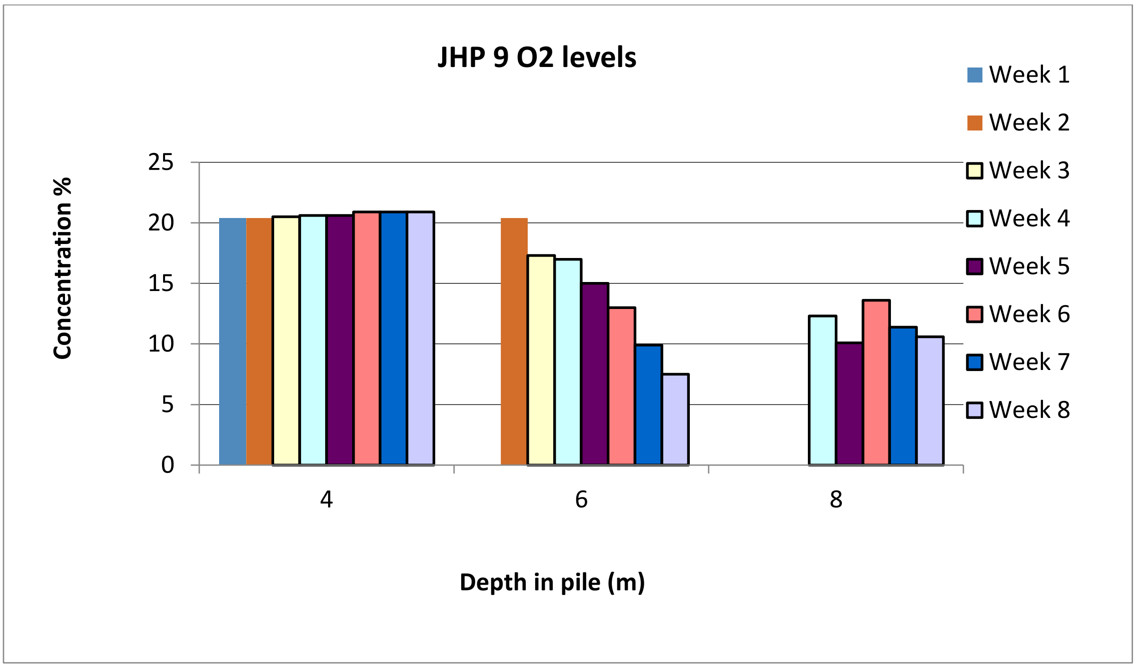


Figure 6.29. JHP9: oxygen measurement results from within the stored biomass pile

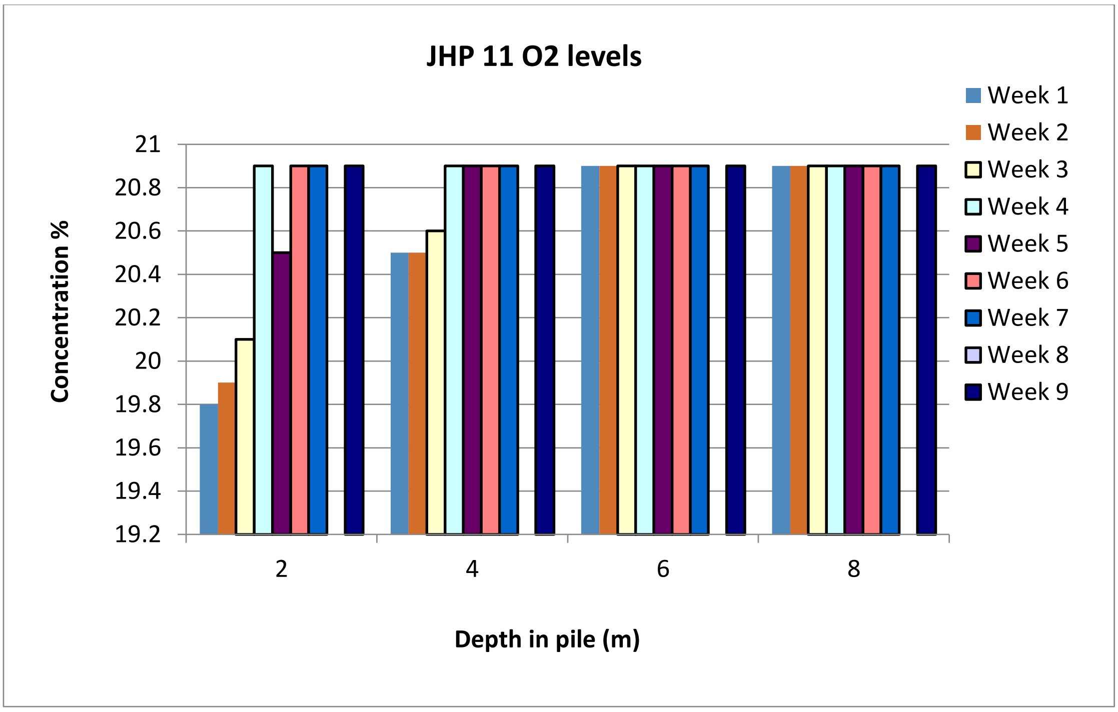


Figure 6.30. JHP11: oxygen measurement results from within the stored biomass pile

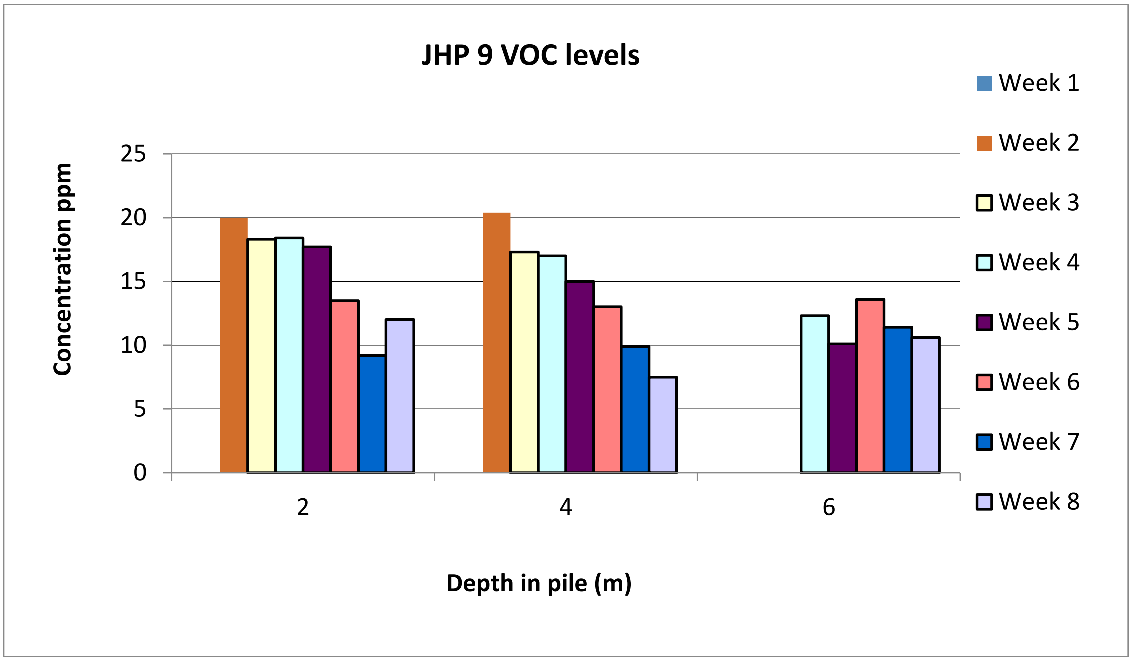


Figure 6.31. JHP9: volatile organic compound measurement results from within the stored biomass pile

6.2.8. Volatile Organic Compound Results Measured In Air Above The Stored Biomass, Within The Store.

Samples were taken using charcoal sampling tubes with a pump at a flow rate of 12L/hour. Original data is tabulated in appendix 6-19 to 6-20. This draws the air through the tube and parameters of interest are adhered to them. These samples were then subcontracted for analysis for specific aldehydes and ketones. All values found in both stores were below the occupational work exposure limit. Overall the results in JHP9 showed higher levels than JHP11 even though the pile mass was much less. This is due to the poor ventilation in JHP9 and therefore the gases are retained within the building. Appendix shows data for other Volatile organic compound analysed, again all values higher in JHP9 than 11.

Table 6.2. EH40/2005 Workplace exposure limits for compounds monitored

Substance	CAS Number	Workplace exposure limit			
		Long-term exposure limit (8 hr TWA reference period)		Short-term exposure limit (15 minute reference period)	
		ppm	mg/m^3	ppm	mg/m^3
Acetone	67-64-1	500	1210	1500	3620
Formaldehyde	50-00-0	2	2.5	2	2.5

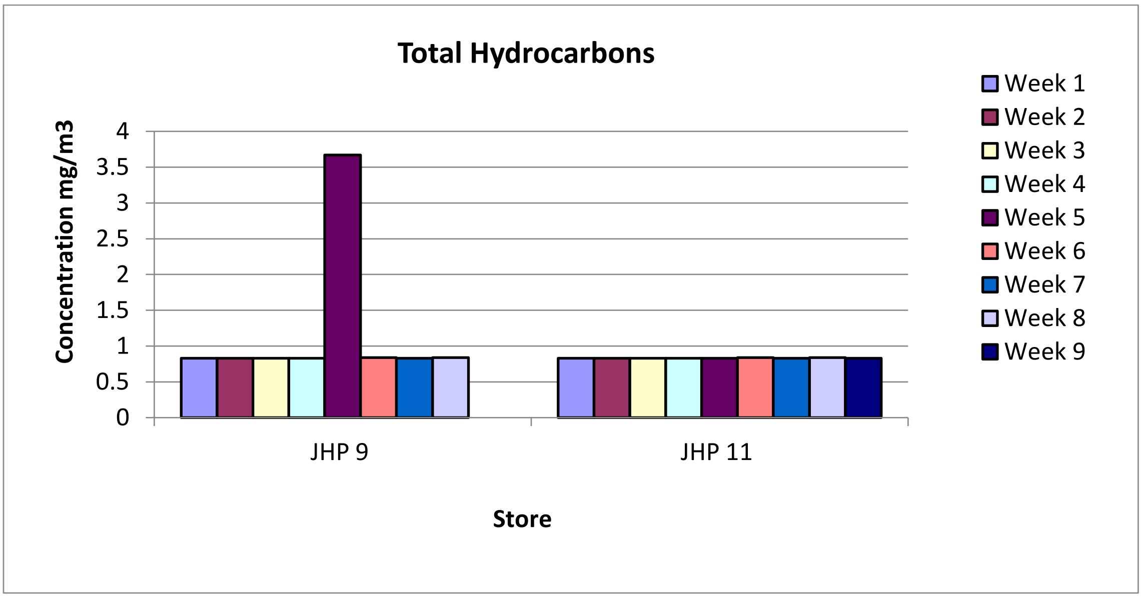


Figure 6.32. JHP9 and 11: total hydrocarbons in atmosphere above pile

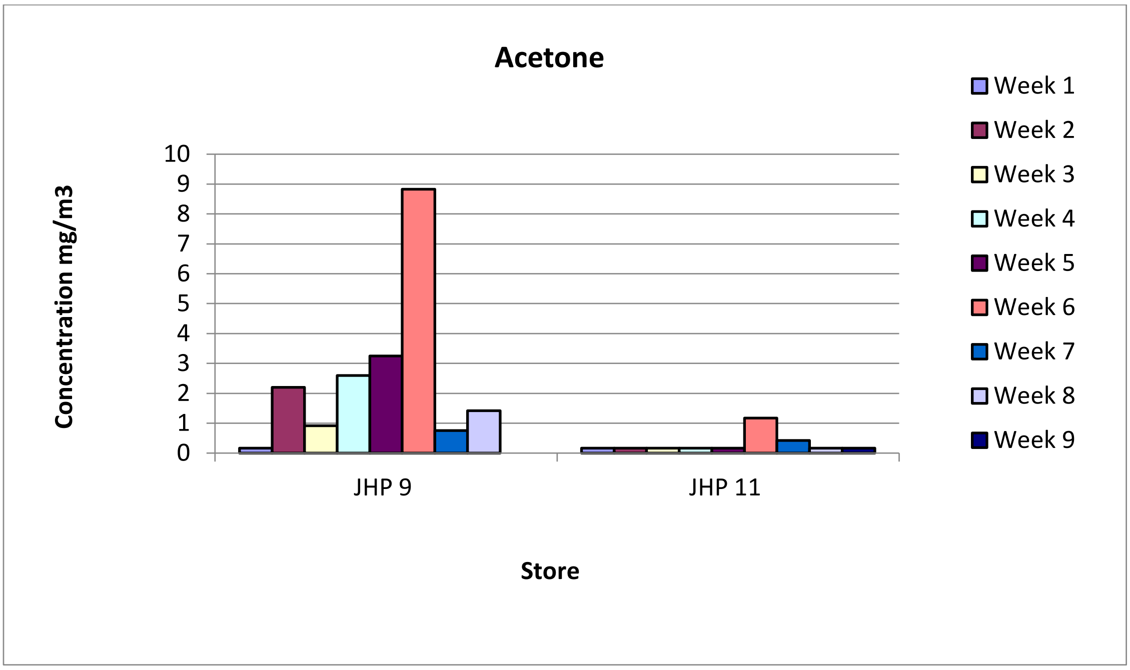


Figure 6.33. JHP9 and 11: Acetone in atmosphere above pile

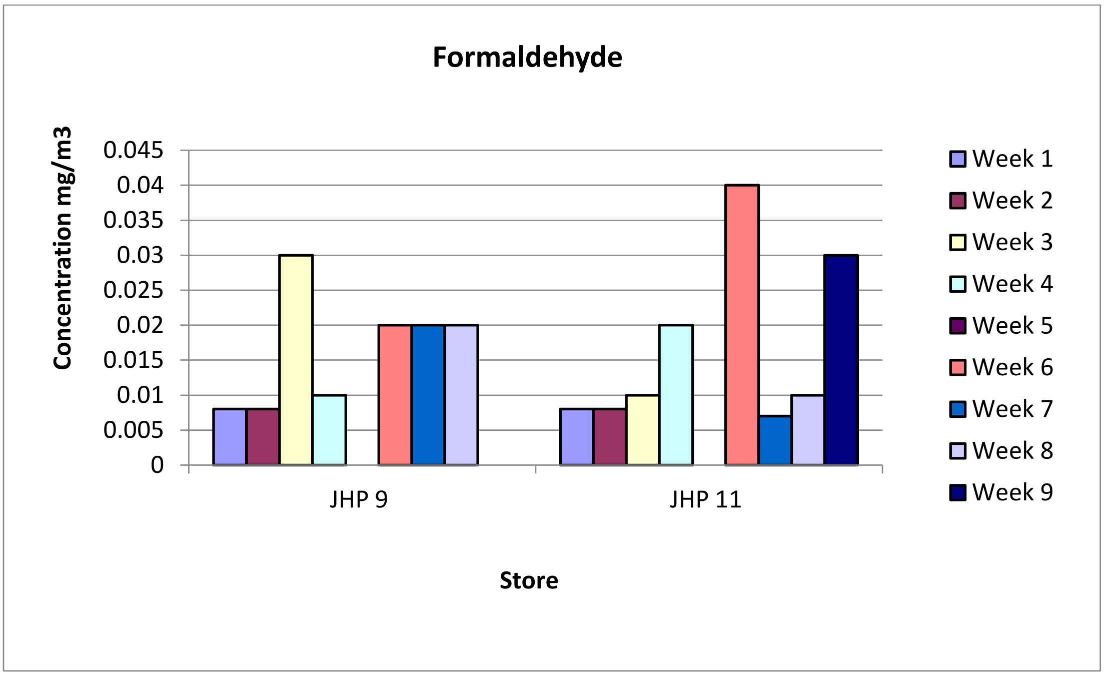


Figure 6.34. JHP9 and 11: Formaldehyde in atmosphere above pile

6.2.9. Volatile Organic Compound Results Measured within The Stored Biomass

The same technique was used to sample the gases present in the pile. Original data is tabulated in appendix 6-21 to 6-22. Sampling was conducted at the 2m level as this was the deepest/hottest area and therefore would show the highest results. Both stores show similar levels being given off. However acetone level in JHP11 showed a higher result than what was found in JHP9.

The other difference was the presence of limonene in JHP9. JHP11 consistently showed a result less than the limit of detection (0.08mg/m^3), whereas JHP9 showed a maximum result of 1.6mg/m^3. The higher level could possibly be due to the elevated temperatures in JHP11. At temperatures above 25^{o}C and increased acidity, limonene begins to break down to isoprene (Diels Alder reaction), which would not be detected from the tests that were conducted. Therefore it could possibly be an explanation for the low results in JHP11 as this had a higher temperature of 45 ^{o}C.

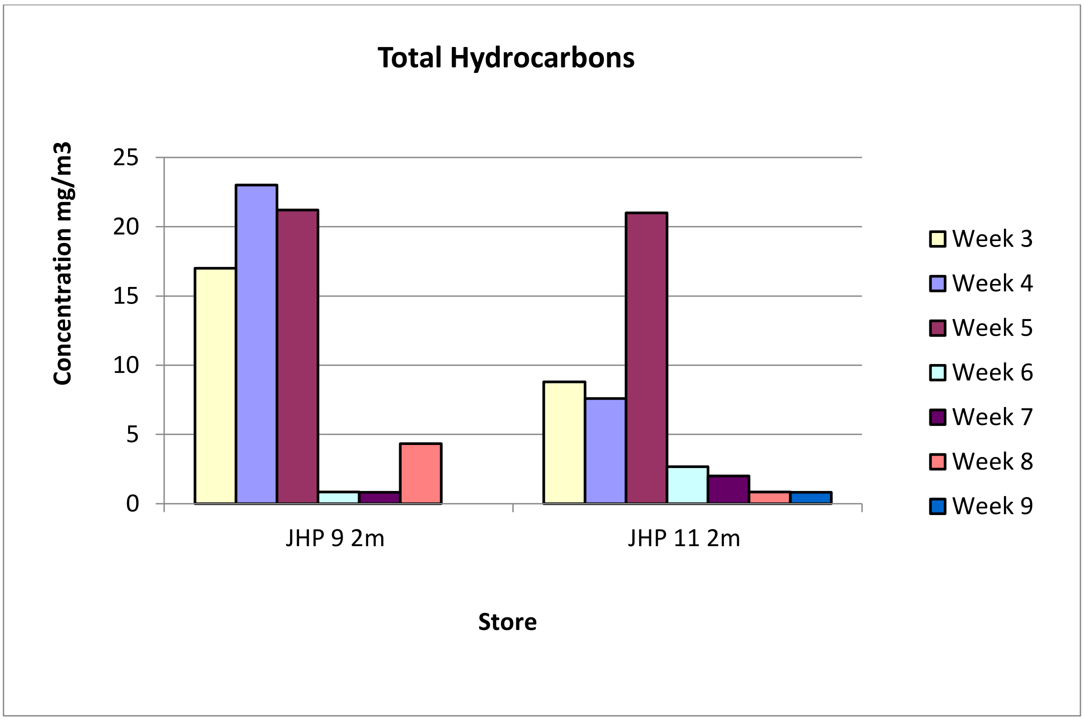


Figure 6.35. JHP9 and 11: total hydrocarbons in-pile

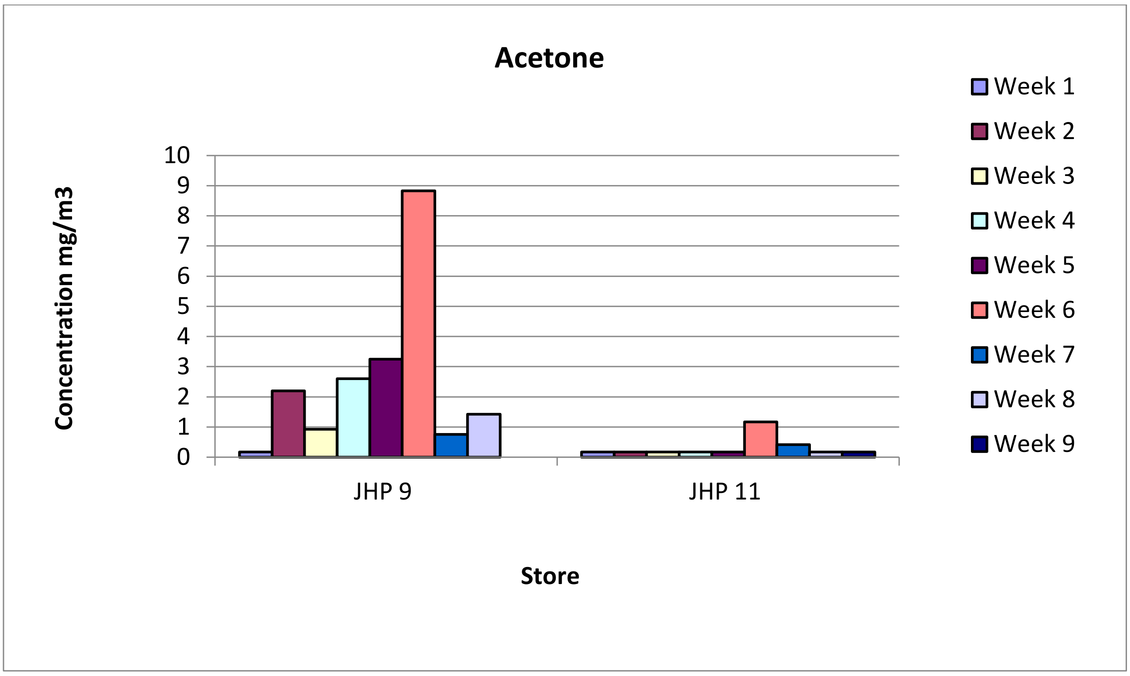


Figure 6.36. JHP9 and 11: total acetone in-pile

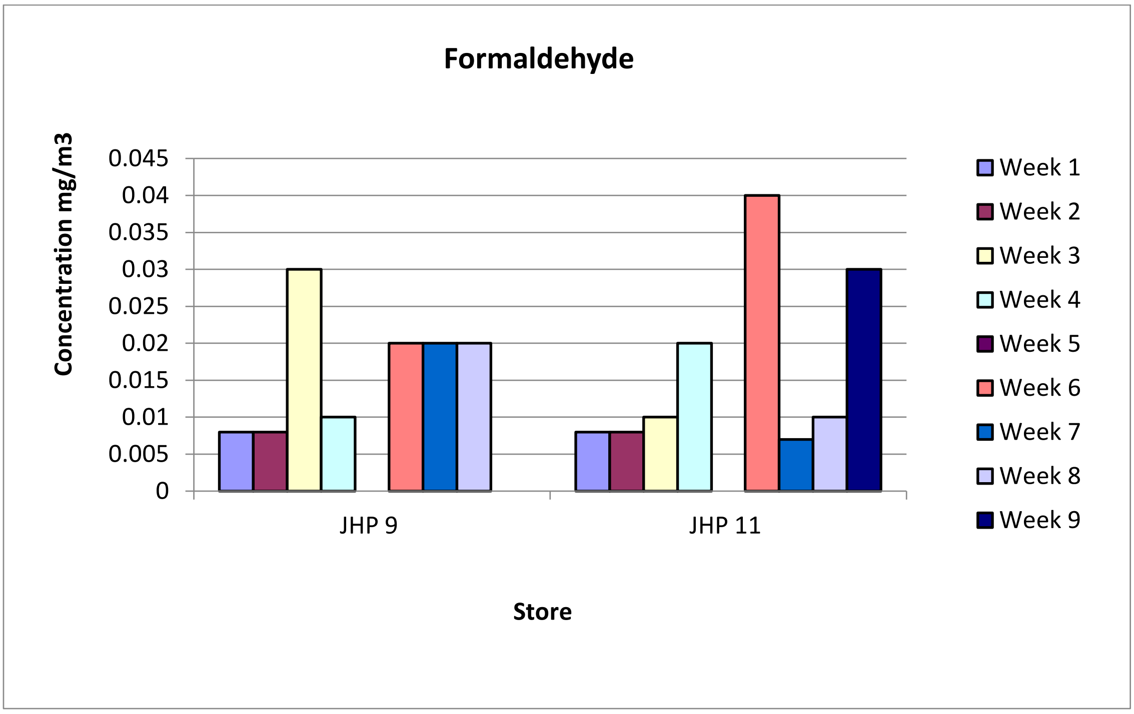


Figure 6.37. JHP9 and 11: total formaldehyde in-pile

A number of other terpenes were also measured and analysed with the results detailed in the appendix for 6-19 to 6-22. These have not been induced in this report because the focus was on the work place exposure limits as detailed in Table 6.2. These other terpenes followed the same pattern as the VOC's and this could be added to future work.

6.2.10. Results Of Effects Of Nitrogen Injection Within The Stored Biomass

On review of the data collected from the nitrogen injection, there appears to be a very positive temperature decrease of approximately 4°C on starting the gas flow from the thermocouples nearest to the injection point.

Figure 6.36 shows after approximately 2 hours, that the thermocouples above the injection point started to show temperature rise. This is assumed to be from the movement within the biomass pile of the warm air towards to the base of the pile being driven upwards from the nitrogen gas. Approximately 4 hours since gas starting, the temperature rise from the warm air moving up has reduced back to previous temperatures, and then continued to fall as the gas is still being injected.

Approximately 16 hours after the gas was started all thermocouples rapidly increased in temperature and stabilised and pre gas injection temperatures. This is now attributed to the gas bottles becoming empty. It is assume the flow control valve for the nitrogen was not suitable and the gas cylinders emptied too quickly.

The discharge rate was originally calculated to have allowed the gas injection to last for ~30 hours at a rate of ~4.7m^3 per hour. The gas appears to have run out after 16 hours therefore this gives and assumed injection rate (which might not have been constant) of 8.9m^3 per hour.

This work backs up the pilot work at 20L scale in chapter 5, that the nitrogen gas and or the air movement of gas, give a cooling effect. The other positive point of the nitrogen is it dew point of -67°C has shown on the 20L scale to give a drying effect to the pellets which will in turn give an increase in calorific value of the pellets due to reduced water. This calorific value effect could not be measured as part of the 40,000 tonne injection due to the small area of nitrogen injection. Additionally due to many factors, the nitrogen injection into the 40,000 tonne stores could not be repeated as part of this thesis work.

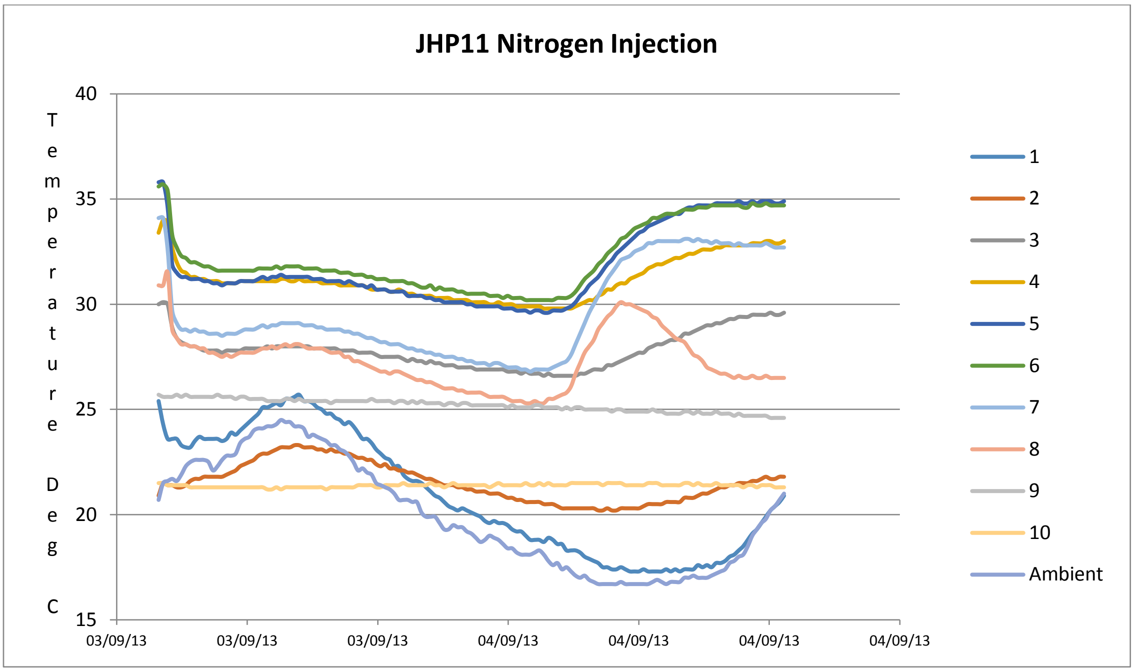


Figure 6.38. JHP11: nitrogen injection dome simulation

6.3. Conclusion Of Biomass Stored In Depths Of Up To 9m And 40,000 Tonnes

Biomass in the form of wood pellets may be stored for long periods without issue, however it is a known fact that biomass can be prone to self-heating, off gassing and can easily catch fire in certain circumstances. The conclusions here details guidance and instructions that are to be followed to ensure that Off Site Storage Facilities are managed effectively so that the risks associated with handling and storing biomass are reduced to as low as reasonably practicable. This work and conclusion has now formed a Drax Power Ltd. Management Instruction Document for the safe storage of biomass in temporary flat stores of the assessed design.

It should be noted that the off-site stores are owned and operated by 3rd parties who are contracted to store biomass. It essential that the operators of the storage facilities meet the requirements detailed in their contract with Drax Power Ltd. Managing the off-site storage facilities will require a robust biomass monitoring procedure and routine audits. From the results, store ventilation is looking to be the key factor in self-heating of biomass wood pellets. Although several other factors appear to be required either singularly or as multiples, the ability of the store to ventilate (moisture and gases) appears to be the initial activation for the whole process.

The scale of this project in terms of the test piles been monitored in excess of 30,000 tonnes, shows the limitations of published small basket test work and the extrapolation of predicted self-ignition temperatures , which simply have not been seen at this scale. Although now working from a starting point of approximately 30,000 tonnes, it is more realistic to scale up to a size of 80,000 tonnes, and the effect of the insulation of the biomass has been shown to give a potential temperature in excess of 150ºC from an additive temperature profile.

The moisture migration has been tracked on the small scale test-rig, and shown to have exited the pile. On the full scale dome, given the depth, this moisture might not exit the pile before it has condensed and this may result in higher concentrations of moisture in the upper levels of the biomass store. The gradient change of biomass pellet moisture therefore might lead to increased potential of self-heating, through both adsorption and microbial growths. The areas of very low moisture could become higher potential zone for ignition from either neighbouring self-heating or if exposed to external heating or ignition sources.

The other potential benefit seen on the small scale and off-site storage biomass piles, has been a cooling effect from the nitrogen flowing through the pile. This has shown to replicate the ventilation benefit seen in the temporary off-site storage facilities.

Measurements consisted of two types, oxidation / decomposition products and terpenes. The decomposition products are CO, formaldehyde, acetaldehyde ,total hydrocarbons which is mainly methane and acetone and water vapor. The terpenes are the volatile oils present in wood and are vaporized without a decomposition reaction being involved, except some may be formed by bacterial/fermentation processes.

A model can be set up where the initial oxidation releases CO, water (and the other decomposition products) and heat-and this reaction-produced water, together with vaporized terpenes and vaporized water from the biomass diffuse down the temperature gradient until the temperature is sufficiently lower so they condense; this releases heat due the latent heat of condensation thus promoting the outward expansion of the reaction zone. Here the CO acts as an indicator of the main reaction zone and the terpene emission acts as a marker of the advancing thermal front.

It seems to be possible to model, at least in general terms, the pile behavior based on research by Hughes et al (2017). Although for a different system but which has common reaction steps, biomass has an endothermic pyrolysis step/exothermic oxidation to CO coupled with a water evaporation step (and the condensation). In their work, the reaction scheme is set out in Figure 6.16 and the oscillatory behaviour in Figure 6.17. This oscillatory behavior has been in seen in the JHP storage monitoring. JHP9 has similar behaviour for the CO emission and VOC emission and it may be possible to make up such a model. This will be considered for future work.

CHAPTER 7. DRAX POWER LTD. POWER STATION DOME STORAGE AT SCALES UP TO 70,000 TONNES

7.1. Experimental Methods Drax Power Ltd. Biomass Storage Domes

Drax Power Ltd. Made a decision to construct a biomass storage facility based on plant requirements and with underpinning scientific data, some of which has been outlines earlier.

The dome storage constructed to house the biomass pellets is shown in Figure 7.1. Each storage dome has a volumetric capacity of 112,500 m^3 giving a total of 450,000m^3 of storage capacity which is approximately 292,000 tonnes at a design density of 650kg/m^3. At full load, each unit consumes 320 tonnes / h, so assuming no deliveries, the storage facility has a maximum capacity of 12 – 13 days reserve for 3 units at full load on a 24/7 basis.

Figure 7.1. Aerial view of Drax Power Ltd. Power Station, Drax Power Ltd. 2016

The domes are constructed from an inflated fibre re-inforced polymeric air-form with 50mm internally sprayed urethane foam. Shot-crete is then sprayed onto reinforcing bars in a number of layers to form the main structure, which is an average of 300mm thick. The inflated air form provides the outer protective layer.

Biomass is capable of forming explosive atmospheres due to the presence of combustible dust in cloud form. The domes were designed and constructed to minimise the risk of an explosion within the domes. This included a series of preventative measures, use of appropriate ATEX certified equipment and prevention of sparks or glowing embers entering storage by a series of sensors on the in-feed conveyors designed to detect sparks, heat and flames.

The domes are also equipped with frangible roof type explosion relief panels which will release in the event of an internal explosion. The panels are tethered to prevent panels being ejected. The domes have a reclaim system consisting of a ‘w’ formation base with Vibrafloor panels feeding onto underground reclaim conveyors. To reduce the risk of spark generation under filling conditions, the vibrating panels, motor covers and cable covers in the central drop zone are formed from 2304 Duplex stainless steel to eliminate the risk of a thermite spark. In addition to being potentially explosive, Biomass material also has the potential to self-heat in storage as described earlier and particularly in Chapter 6, and is therefore monitored for signs of biological activity or combustion. Thus in pile temperature measurement is an important parameter with respect to large volume storage management. Four multi-point temperature tethers are installed within each dome to monitor the temperature of the stored fuel (4 strings of thermocouples (9 per string – on 5 m intervals). See Figure 7.2 and Figure 7.3. Each cable has 9 individual thermocouples positioned at 5m intervals to give a spread of coverage from top to bottom as the fuel contents vary. The cables are suspended from the dome roof concrete via cast in penetrations and steel upstands to which the cables are secured via a clevis and sheer pin arrangement. (Designed to sheer at 50kN). The sheer pin and cable terminations are accessible externally via the head house peripheral platforms. There have not been any sheer pin failures.

Worldwide experience with respect to in-pile thermocouples is limited. Due to the internal mass flow forces, the environment within the fuel pile is arduous in terms of thermocouple life. Through commissioning, the design of the cables has revised and improved several times in terms of thermocouple attachment and sheathing. Thermocouple life is now improved but nevertheless the cables will require replacements at dome outages.

The domes are maintained with a low oxygen atmosphere by the addition of an inert gas, (nitrogen) through the base of the dome. Biomass fuel naturally 'off-gases' whilst in storage. The levels of carbon monoxide are monitored on a routine basis. In the event of any abnormal activity carbon monoxide levels will significantly increase, potentially by several orders of magnitude. Consequently two dual range carbon monoxide monitors are provided for each dome. To assist plant operators in monitoring of storage conditions within each dome, oxygen Depletion monitors are also installed. An analogue signal proportional to oxygen concentration within the dome is monitored and displayed at the operator interface for information purposes only.

Each storage dome is equipped with three independent fire suppression systems comprising facilities for injection of nitrogen at the dome base, injection of carbon dioxide at dome roof level (blanketing) and high level water deluge. They have a nitrogen injection distribution System (4 zones on the floor) as shown in Figure 7.6, carbon dioxide Injection System is via 6 snow horns on the roof and the manual water deluge systems is via 5 zones on the roof – central zone sprinklers and outer zone monitors. The nitrogen gas inerting system injects in the base of the dome via a matrix of stainless steel pipework and nozzles. This is fed from nitrogen liquid storage on the gas pad which is described in detail in section 4.4.5 gas storage and generation). The flow rate of this system can be progressively increased through various stages from normal operating mode (inerting) to Fire Suppressing Modes.

For these domes, background carbon monoxide (CO) levels are anticipated to be lower than 1000 ppm (assuming the pellets are inerted with nitrogen). The CO concentration will rise and fall with level and length of time in storage. Thus a number of alarms are in place:

- First Alarm Point = 1100 ppm.

- Hi-Hi Alarm Point is 1500 ppm. (This requires the attention of the Shift Supervisor)
- There is also high ‘Rate-of-Rise’ Alarm at 164 ppm/h for > 2 min.

If fuel abnormal activity is detected either by temperature or carbon monoxide it is possible to operate both the nitrogen generator and the liquid nitrogen systems simultaneously to increase the nitrogen flow to a nominal 12000m^3/h for a limited period. This can be admitted to one storage dome via four quadrants via pneumatic valves. Carbon dioxide blanketing can also be admitted via snow horns in the dome roof.

Water deluge to the dome can be manually initiated by plant operators via hand operated valves Admitting water to large volume storage would only be carried out if all other methods were either defective or in some way ineffective. Extreme caution is required when using the water deluge. It must be used sparingly for extinguishing surface fires or for cooling of roof support steel work in conjunction with other firefighting measures. If used excessively (many hours) the water could cause the pellets to swell with the potential to cause structural damage.

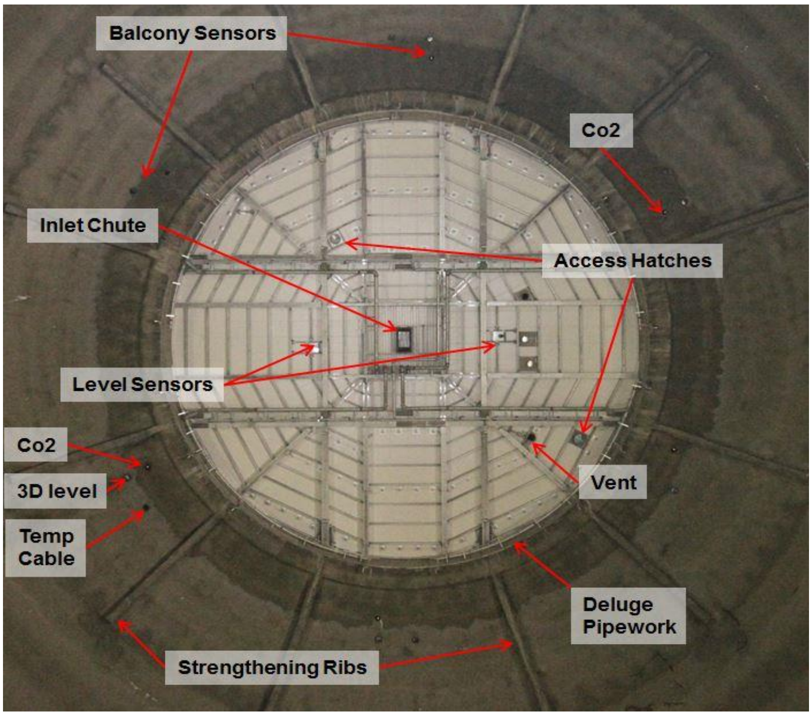


Figure 7.2. View inside dome looking up towards celling

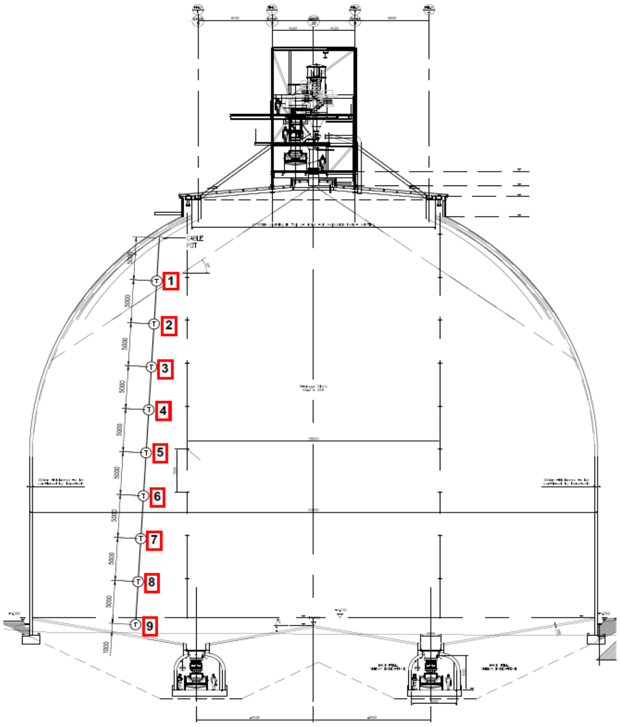


Figure 7.3. Cross section of a dome showing location of one of the vertical thermocouple strings

7.1.1. Gas Measurements From With The Biomass Stored In A Dome

To enable gaseous measurements from within the dome at quadrants 1 – 4 shown in Figure 7.6, an extraction tube was inserted horizontally into the base of the dome approximately 1 m from the outside surface of the dome at each quadrant. Extractive gases (condensable and non-condensable) were to be measured via 5mm internal diameter clear PVC tubing as described in the following section.

7.1.1.1. Volatile Organic Compounds Measured Within The Biomass Stored In A Dome

Volatile organic carbon from within the dome was analysed using a Rae systems ppbRae3000 gas detector. This unit has s built in extractive pump. The gas detector was connected to each of the sampling tubes within the pile in order to obtain a stable result and the reading recorded manually.

7.1.1.2. Non-condensable Gases Measured Within The Biomass Stored In A Dome

Concentration of CO, CO_2, O_2, SO_2 and flammable gases were analysed using a Drager XAM7000 with a built in extractive pump unit. The gas detector was connected to the sampling tube in order to obtain a stable result and the reading recorded manually. The unit was check for calibration prior to use against known gas standards.

7.1.1.2. Condensable Gas Measured Within The Biomass Stored In A Dome

Condensable gases were analysed from within the dome using sampling tubes for acetaldehyde, formaldehyde, hexanal, pentanal, furfural and glutaraldehyde (flow rate 0.3L/min for 45mins) and charcoal tubes for Turpentine, acetone, and butanoic and octanoic acids (flow rate 0.2L/min for 60mins)) These were attached to a pump unit and exposed for the specified period extracting via the tube. Analysis was performed ex-situ by a sub-contractor.

7.1.1.3. Temperature Measured Within The Biomass Stored In A Dome

A number of k-Type thermocouple bundles where constructed and installed on the base of the dome shown in Figure 7.4 enabling temperature measurements every 5m via a hand-held device. With reference to Figure 7.6, zone 1 and 4 thermocouples are located around the outside of base and zone 2 and 3 thermocouples progress towards the centre of the base. In both cases the numbering of the thermocouples is 1-9 , with 1 being the furthest i.e. 45m and 9 being the closest to the thermocouple reader sited on the outside of the dome.

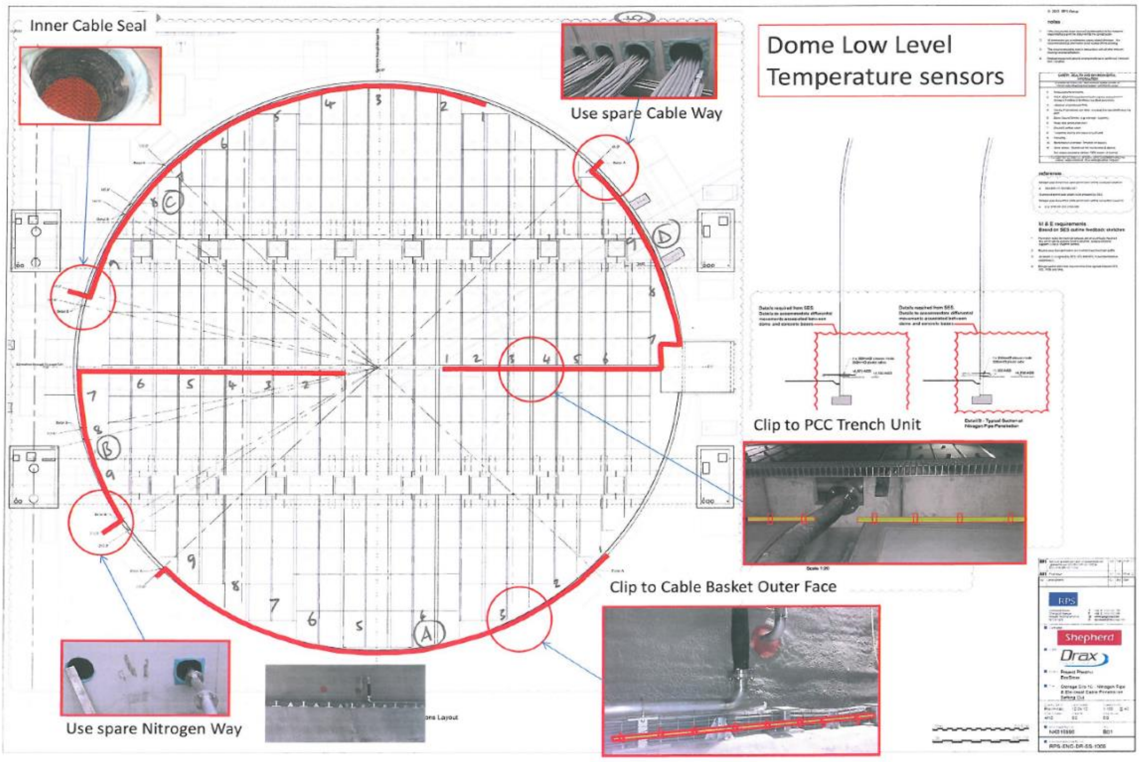


Figure 7.4. Installation and locations of thermocouples in base of dome

7.1.2. Measurement Of The Atmosphere Above Stored Biomass In A Dome

To enable gaseous measurements from within the headspace of the dome as shown in Figure 7.5, an extraction tube was inserted vertically from the top of the dome hatch to a depth of approximately 5 m. Extractive gases (condensable and non-condensable) were to be measured via 5mm internal diameter clear PVC tubing shown as the red line in Figure 7.5.

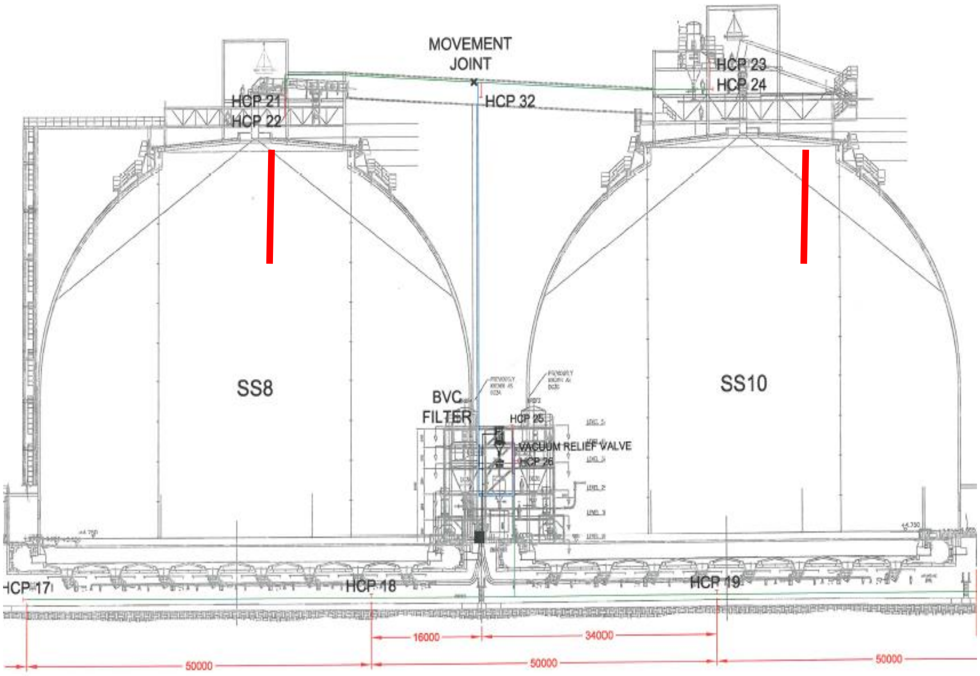


Figure 7.5. Dome head space extraction tubes shown in red, 5m long

7.1.2.1. Volatile Organic Compounds Measured Above The Biomass Stored In A Dome

Volatile organic carbon from within the dome headspace was analysed using a Rae systems ppbRae3000 gas detector with in-build extractive gas pump. The gas detector was connected to each of the sampling tubes shown in Figure 7.5 within the pile in order to obtain a stable result and the reading recorded manually.

7.1.2.2. Non-Condensable Gas Measured Above The Biomass Stored In A Dome

Concentration of CO, CO_2, O_2, SO_2 and flammable gases were analysed using a Drager XAM7000 with a pump unit with in-build extractive gas pump. The gas detector was connected to the sampling tube in order to obtain a stable result and the reading recorded manually. The unit was checked for calibration prior to use against known gas standards.

7.1.2.3. Condensable Gas Measured Above The Biomass Stored In A Dome

Condensable gases were analysed from within the dome using sampling tubes for acetaldehyde, formaldehyde, hexanal, pentanal, furfural and glutaraldehyde (flow rate 0.3L/min for 45min) and charcoal tubes for Turpentine, acetone, and butanoic and octanoic acids (flow rate 0.2L/min for 60min)) These tubes were attached to a pump unit and exposed for the specified period extracting via the tube. Analysis was performed ex-situe by a sub-contractor.

7.1.2.4. Measurement Of Dust Levels Above The Biomass Stored In A Dome

To enable dust measurements from within the headspace of the dome shown in Figure 7.5, an extraction tube was inserted vertically from the top of the dome hatch to a depth of approximately 10 m. Dust measurements were to be measured via 5mm internal diameter clear PVC tubing. Inhalable dust levels were determined using a Casella TUFF Plus pumped unit set at 2mL/min. Filter papers were dried and weighed prior to use. The sampling head with the filter paper was attached to the end of the extraction tube and then lowered into the dome. Measurements were taken whilst biomass product was free falling into the dome and therefore creating an assumed dust cloud. Measurements were also taken during periods of inactivity (no filling or reclaim). This was to provide background data. These filter papers were then dried and reweighed, and the level of dust was calculated.

7.1.2.5. Humidity Measured Results Above The Biomass Stored In A Dome

An OM-EL-USB USB data logger was utilised for temperature and temperature/relative humidity within the head space of the domes. The USB data logger is set-up at a sampling rate of once per 30 min and the stored data downloaded by plugging the module into a PC's USB port and running the included software. Software-selectable setup parameters include logging rate, start-time, high/low alarm settings, and temperature units (°C or °F). Data was then exported to Excel. These devices were located in each dome approximately 5m from the top as shown in Figure 7.5.

7.2. Dome Inertion Systems

7.2.1. Description Of Nitrogen Injection System

The nitrogen inerting system was design and installed by Air Products. A Pressure Swing Absorption (PSA) nitrogen generator is capable of producing ~ 2800 m^3/h at 95% purity. In addition to the on-site generator, provision for storage of pure liquid nitrogen was also included. The liquid nitrogen tanks are filled from road tankers, which must not be allowed to go empty (Stop using liquid if the level gets below 10% or they cannot be filled using the normal process due to temperature conditioning requirements.) It is very important to keep the tanks conditioned at their cryogenic temperature – if the tanks go empty, only an Engineer from BOC or Air Products is allowed to re-condition the tanks for filling, which is a very slow process.

The nitrogen tanks have a net usable combined volume of ~ 115m^3 of liquid (~ 70,000 kg). {One kg of liquid nitrogen at -160°C and 14 bar (g) will evaporate to ~ 0.85m^3 at ambient conditions}. At maximum evaporation rate, this system can vaporize ~ 7,000 kg of liquid nitrogen to ~ 6,000 m^3/h of Nitrogen gas (giving ~ 10 hours from 100% level. Drax Power Ltd. usually maintain the tank levels at ~ 50% – 75% giving about 5 hours supply at max rate).

The storage domes are provided with a floor matrix of distribution pipework and injection points (or “nozzles”) which are designed such that they do not block with fuel. Figure 7.6 shows the distribution matrix in the domes is segregated into four quadrants in order that individual areas of each store can be separately injected. These zones can be targeted where ‘hot spots’ may be indicated by the temperature monitoring instrumentation. The nitrogen distribution matrix is separated into four individually valved “quadrants” each designed for a flow rate of 3000 m^3/h. In the event that 3000 m^3/h is to be added to a dome as a whole, it can be achieved by cycling the four quadrants. If 6000 m^3 /h is to be added it will be added through two quadrants at a time, three quadrants used for 9000 m^3/h and four for 12,000m^3/h. These distribution nozzles are spring loaded 'poppets' designed to provide even distribution across the full dome cross-section using all the nozzles when the dome is empty or if it is unevenly filled.

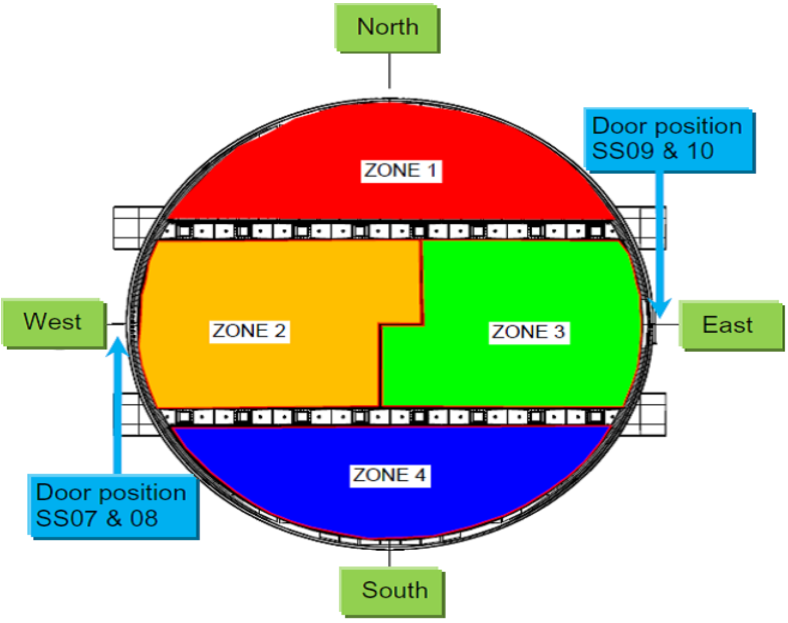


Figure 7.6. Plan view of base of dome showing nitrogen zones

7.2.2. Description Of The Carbon Dioxide Injection System

A CO_2 blanketing system is provided for fire suppression or firefighting. The CO_2 will be added through the roof of the dome, entering via 6 nozzles in the dome "crown". The CO_2 will be added to the dome in liquid phase at a rate, when gasified equivalent to 3000 m^3/h. (In reality – it turns solid as a snow which is delivered by 'snow horns' – the snow in turn sublimates directly to gas). The CO_2 is stored in liquid form and is delivered by road tankers. A suitable tanker offloading system has been provided. The liquid CO_2 storage tank is sized for 12 hours usage at a rate when gaseous of 3000 m^3/h. The storage domes have been provided with a 6 injection nozzles (snow horns) installed at roof level which are designed such that they do not block with fuel or dust and shall not be susceptible to freezing and hence blockage with CO_2. (Figure 7.2) The nozzles have been positioned to ensure even blanketing of the fuel profile and are designed to be removed from outside the dome. It is vital that the pressure on the CO_2 Tanks and piping be kept above 10 barg pressure. (If it drops below 5 barg, the liquid turns solid and cannot flow). This fuel profile will vary. The CO_2 is denser than air, so it will tend to collect in the low spots. Consideration has been given in the design to the avoidance of generating static electricity during the addition of CO_2

7.3. Computational Fluid Dynamics (CFD) Simulation Of Nitrogen Suppression In Drax Power Ltd. Dome

7.3.1. Aims

CFD modelling was performed by Air Products (using in-house software) using known theoretical data for nitrogen and biomass along with specific data provided by part of this thesis for fines and dust content and expected temperatures within the domes. The author and Air Products worked with the Swedish Technology Institute, to produce a report using everyone’s combined years of experience on current large scale biomass storage and small scale research. The research aim at Drax Power Ltd. was to quickly and thoroughly develop laboratory and pilot scale tests (see Laboratory, Chapter 5 and Temporary Storage Chapter 6 sections) and then scale-up to the current storage volumes in order to enable a more realistic extrapolation on potential events that may occur within the domes. A number of model scenarios have been run via CFD to evaluate and extrapolate findings from Laboratory and Temporary Storage, to storage within the domes.

7.3.2. Simulation Assumptions

Data was provided to Air Products to enable them to run their CFD model. The biomass pile diameter is 65m and the height is 38m resulting in a volume of 112,500 m^3 within a total dome volume is of 126,000 m^3. The dome is fully sealed but with a release valve at the top of the dome to be turned on when gauge pressure reaches 0.1 bar at the top. Relief is assumed to be central in the dome head and with a capacity of 15,000 m^3/h. The biomass is assumed to be at ambient temperature.

7.3.3. Model Description

- The biomass pile is treated as porous media with a porosity 0.5, and assuming 35% fines.
- nitrogen gas is injected from four zones at the bottom of the dome with T=15°C; one zone on at a time for one period of 6 hours and the nitrogen flow rate of each zone is at 2800 Nm^3/hour with a purity of 95%
- Devolatilization of CH_4 and oxidation of carbon are not considered
- A transient model is used with time step at 10 sec.
- Gravity force is included

7.3.4. Nitrogen System CFD Modelling:

Test 1 simulated the condition of 3000 m^3/h of nitrogen added to a dome "quadrant by quadrant". The time interval might be adjusted as a result of this work but a starting point of 6 h per quadrant was used to start this process. In this mode the outlet valves and inlet valves are closed, the nitrogen concentration in the dome will of course be gradually rising hopefully reducing the effect of O2 "re-entrainment" from the other 3 quadrants. The aim of this modelling is to validate the nozzle locations and demonstrate even distribution of the nitrogen in the dome without any significant "blind spots". Also determined was the time it will take to achieve an "inert" atmosphere in the dome. Based on laboratory TGA analysis and realistic nitrogen generation output a target figure of 10% O2 was be used.

Test 2 simulated 3000 m^3/h of nitrogen added to a dome "quadrant by quadrant" as test 1 but in this case the effect of variable permeability on the nitrogen distribution was model to ensure the gas does not "track" towards the (permeable) flow zones and therefore cause "blind spots" in the non-flowing zones.

Early work with Air Products indicated that oxygen can penetrate an otherwise fully inerted dome surprisingly quickly. Therefore test 3 simulated the effect of air leakage into the dome by modelling a leak of 150 m^3/h from an atmospheric source with no pressure differential. It was assumed the leak occurs when the dome is locked down and not being filled with nitrogen at the time and therefore not pressurized.

7.3.5. Carbon Dioxide System CFD Modelling:

The simulation in test 4 was to determine the cooling effect of the inert gas in order to determine the “inbreathing” capacity required for the dome vacuum relief valves. This was determined this for both CO_2 and nitrogen in isolation, and the effect was then be considered additively. The test assumed that the dome was full of Biomass at 27, 60 and 70°C. Test 4 also considered a case where the dome is empty and CO_2 is discharged accidentally.

7.4. Results And Discussion

7.4.1. Temperature Measurement

Figure 7.7 shows and example of temperature data collected from the base of the dome thermocouples. In all cases, the temperature remained quite stable and therefore only this example is shown in the main thesis, other data is included in the appendix 7-1 for reference. There are assumed three reasons for the stability of temperature monitoring at the base of the dome.

1. As shown in the temporary storage section, heat is shown to rise through the pile and the maximum temperature seen a few metres from the base of the pile.
2. The constant reclaim of ~300 t/h of fuel (split over 4 domes) will prevent a stagnant pile forming and therefore preventing heat accumulation
3. The larger concrete mass at the base will effectively act as a heat sink to earth maintaining a fairly steady temperature.

It is considered that, the number of temperature detection lines/positions are very limited considering the size of the dome and there is an obvious risk that self-heating could occur in some part of the dome without being detected. Temperature monitoring should not be considered as a primary “fire detection” system, but rather as indication of the general distribution inside the bulk material and provides a possibility to follow the temperature trend. However, with only four detection lines, each of these will represent a very large area and considering the low heat conduction properties of wood pellets, it is a considerable risk that self-heating could occur in some areas without being detected, at least in an “early stage”.

It is impossible to say how many detection lines would be optimum but as an example others are conducting temperature and gas measurements in a storage silo at a Swedish pellet manufacturer within the SafePellets project. The silo is 20 m in diameter and is equipped with 7 detection lines with sensors every 3 m (6 lines on about half radius with 5 sensors each and one in the centre with 6 sensors, in total 36 sensors). During the first week of measurements, the silo had been filled up to about 25 % and they have already seen that two single detectors at various lines have been up to about 40°C and 50°C while the remaining detectors inside the bulk have shown about 20-25 °C. This shows that there might be local heating and in this case each sensor line is covering about 45 m^2 in average. In Drax Power Ltd.’s case (63 m diameter, about 3120 m^2), a similar coverage area would correspond to about 70 lines. This is unrealistic and the drag forces from the lines would give a very high load to the dome construction but if there would be any possibilities to extend the number of lines, this would improve the possibilities to monitor the bulk storage.

It has been considered to measure the inert gas inlet temperature during “prevention” filling and the gas outlet temperature in order to calculate an average heat balance of the entire bulk material. It’s an interesting idea, but it is doubtful as there are so many factors making the calculation uncertain. As the bulk material has a heat capacity which is much higher than the gas, any generated heat will probably just be absorbed by the bulk material on its way to the surface and it will be a long delay before anything is recorded on the surface. There are also many other factors influencing the temperature, vaporization and condensation of water vapour, heat transfer through the walls (although well insulated), and the uncertainty in the temperature measurement themselves.

Accurate temperature measurements in an industrial environment is very difficult as there are many factors influencing the sensor temperature: size of sensor, radiation from hot or cold surfaces, heat transfer coefficient, velocity in measuring point, accuracy of data logging unit, etc. The use of fixed thermal imaging cameras was discussed and in certain situations, these could of course provide additional and valuable information. The camera will only record the surface temperature but it could be a good complement to the temperature detection lines and gas measurements to identify the location of any self-heating tendency by indication of areas with increased temperatures. It will probably not provide an early detection as it might take a long time for heated gases inside the dome to reach the surface and the gas will be cooled along the transport to the surface, but as IR-cameras are very sensitive and will cover a large area it could be a worthwhile investment. In a fire situation, it could provide important information about the conditions in the dome headspace although there is a risk that the sensitivity will be reduced by smoke and water vapour.

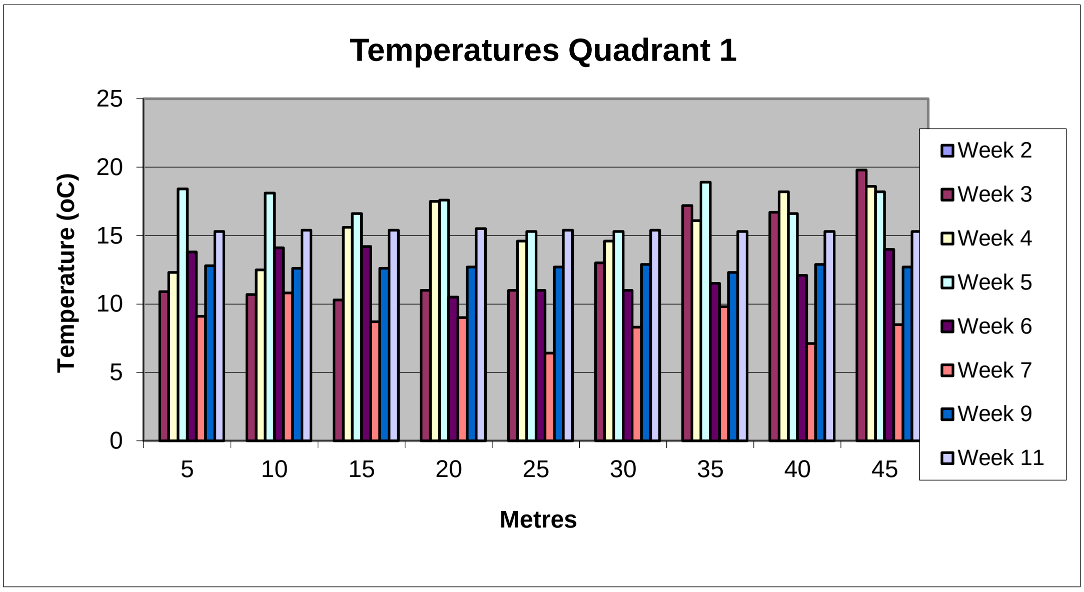


Figure 7.7. Temperatures quadrant 1 of dome

7.4.2. Dust in head space

Data supplied in Table 2.4 for minimum explosible concentration for the quoted samples of pine, bark, and southern yellow pine (SYP), shows the lowest value to be 25 g/m^3 for SYP (see Table 2.4). Values obtained for various mixed fuels including SYP from the Drax Power Ltd. domes are shown in Table 7.1 gives and average dust concentration of ~ 250 mg/m^3 with a single maximum of ~650 mg/m^3.The reason for the large difference between quoted data and actually did is simply due to previous limited experience at these volume and the assumption of treating dust in the same was as a gas i.e. an homogenous mix. The dust cloud is obviously very localised to the source ie dome entry point and by the time it reaches the sample location (or ignition source), it is considerably lower than minimum explosible concentration.

Table 7.1. Dome dust in head space measurements

Date	Description	Tonnage in dome	Fill rate	Duration of Monitoring	Filter Paper &	Filter Paper & Casing	Weight of Sample	Volume (l)	Ca TWA (mg/m^3)
11/03/2014	Dome 8 Background	68932	N/A	58	1287.22	1294.17	6.95	116	60
11/03/2014	Dome 8 train @ 11:07	70074	1655	125	1208.67	1209.93	1.26	250	5
12/03/2014	Dome 8 Background	68827	N/A	43	1412.94	1414.54	1.60	86	19
12/03/2014	Dome 8 train @ 11:07	69926	1582	88	1253.30	1286.43	33.12	176	188
12/03/2014	Dome 8 train @ 11:07	69926	1582	88	1505.33	1556.12	50.79	176	289
13/03/2014	Dome 8 Background	69213	N/A	52	1255.92	1257.16	1.24	104	12
14/03/2014	Dome 8 Background	69511	N/A	117	1278.79	1279.31	0.51	234	2
14/03/2014	Dome 8 Background	69511	N/A	117	1248.18	1248.74	0.56	234	2
17/03/2014	Dome 10 Background	16677	N/A	45	1246.15	1246.31	0.16	90	2
17/03/2014	Dome 10 @11:07	18009	1751	107	1225.79	1269.73	43.94	214	205
17/03/2014	Dome 10 @11:07	18009	1751	107	1432.94	1477.04	44.10	214	206
19/03/2014	Dome 8 Background	69104	N/A	58	1257.92	1268.36	10.44	116	90
19/03/2014	Dome 8 @11:07	72261	1866	112	1286.23	1431.15	144.92	224	647
19/03/2014	Dome 8 @11:07	72261	1866	112	1254.98	1356.50	101.52	224	453
21/03/2014	Dome 10 Background	4252	N/A	32	1515.58	1520.28	4.69	64	73
21/03/2014	Dome 10 @11:07	7214	1763	109	1270.61	1325.20	54.60	218	250
21/03/2014	Dome 10 @11:07	7214	1763	109	1274.84	1349.84	75.01	218	344

7.4.3. Gases In Head Space Of Dome

The constant gas monitoring system in the dome headspace is very good and might to a certain extent compensate for the limited temperature monitoring as the gas composition inside the dome headspace will provide a warning if a serious self-heating is on-going. Also here, it will be important to follow the trend and to learn what could be considered normal as there will always be a certain degree of CO in the dome due to normal “off-gassing”. It is also important to consider that the ventilation system in the dome will influence the readings and might result in too low readings. The use of two types of sensors, one for low concentrations (ppm) and one for high concentrations (%) is very good as the latter is important in a fire situation. In all monitoring, values of carbon monoxide, carbon dioxide, oxygen and sulphur dioxide remained low and therefore it shows that in a safe state, the domes rapidly exhaust all gases and therefore if any elevated gases are seen, this would indicate material that may be in an unsafe state. Original data is tabulated in appendix 7-3 and 7-8.

It has also been considered the value of measuring the relative humidity (RH) in the dome headspace. This might provide valuable information as a complement to the gas readings. In a fire situation, there will be an increased humidity due to the drying and combustion process. It might also be valuable to learn more about the possible drying effect caused by a constant inerting of the domes.

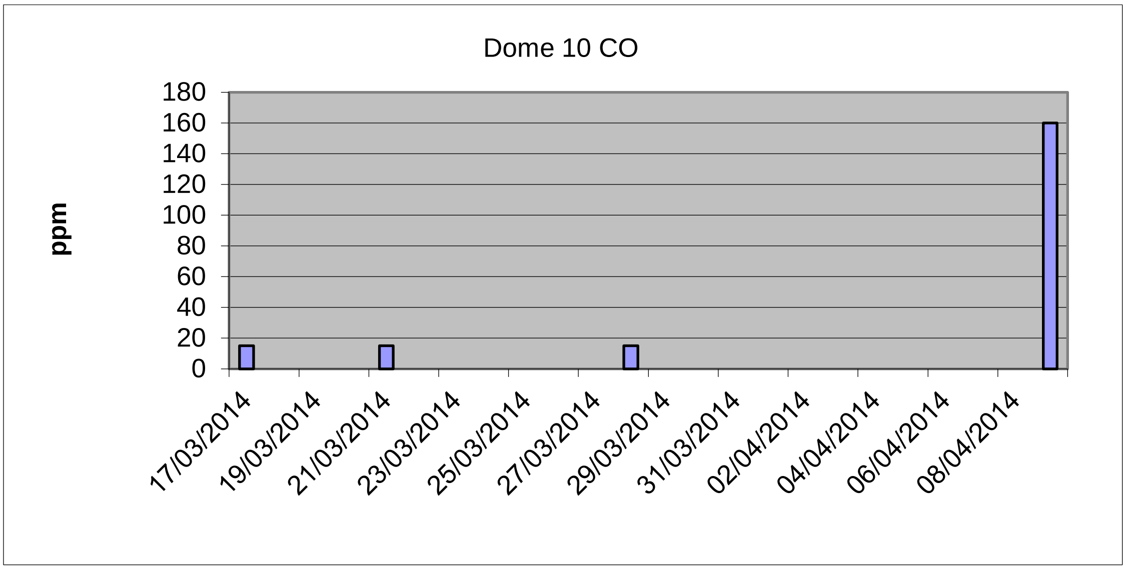


Figure 7.8. Dome 10: carbon monoxide measured in the biomass pile

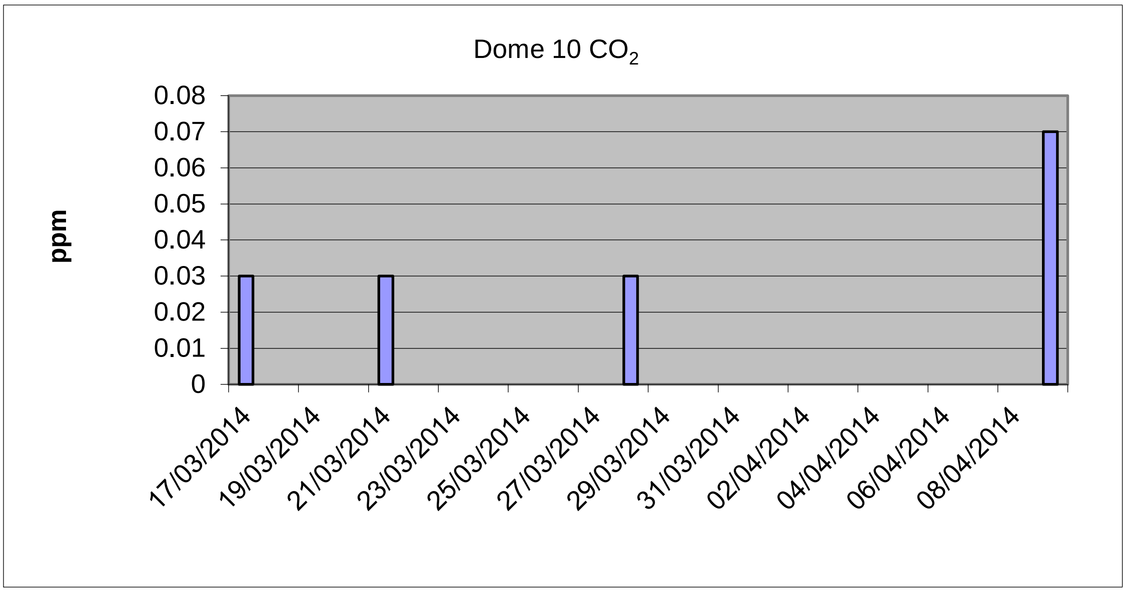


Figure 7.9. Dome 10: carbon dioxide measured in the biomass pile

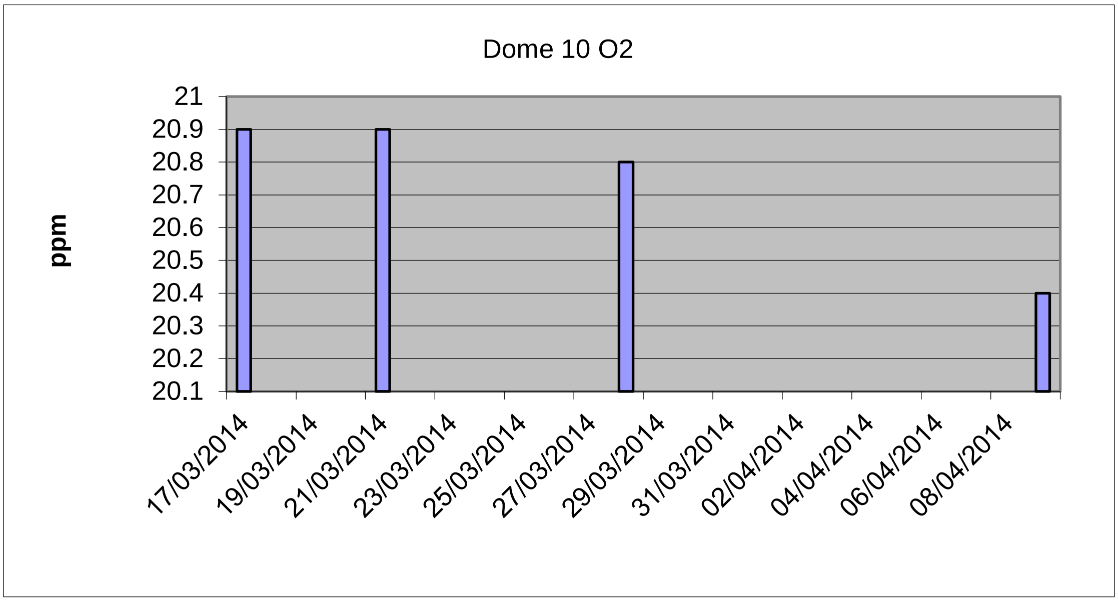


Figure 7.10. Dome 10: oxygen measured in the biomass pile

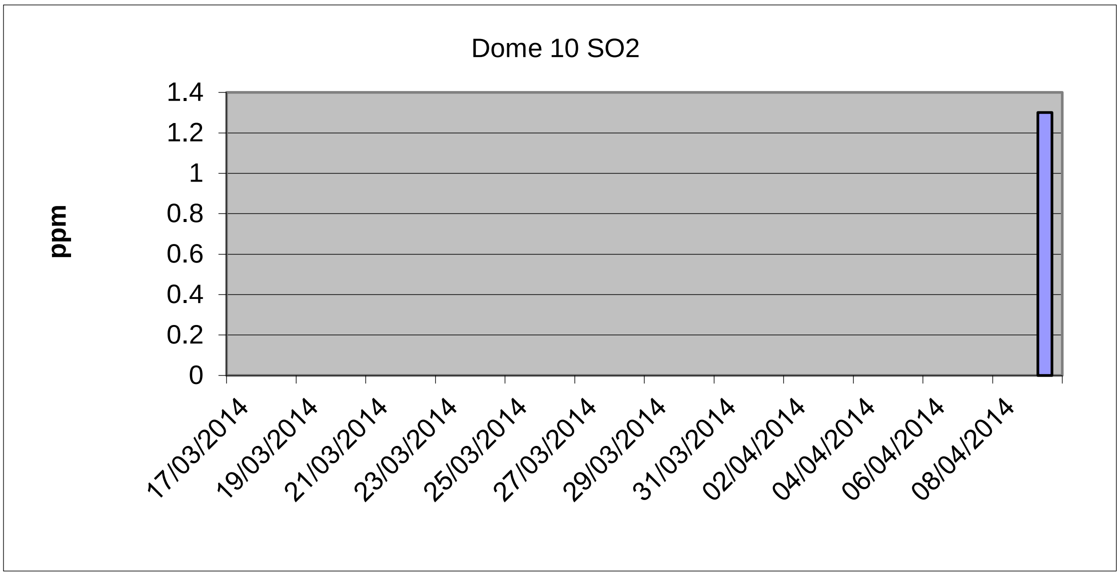


Figure 7.11. Dome 10: sulphur dioxide measured in the biomass pile

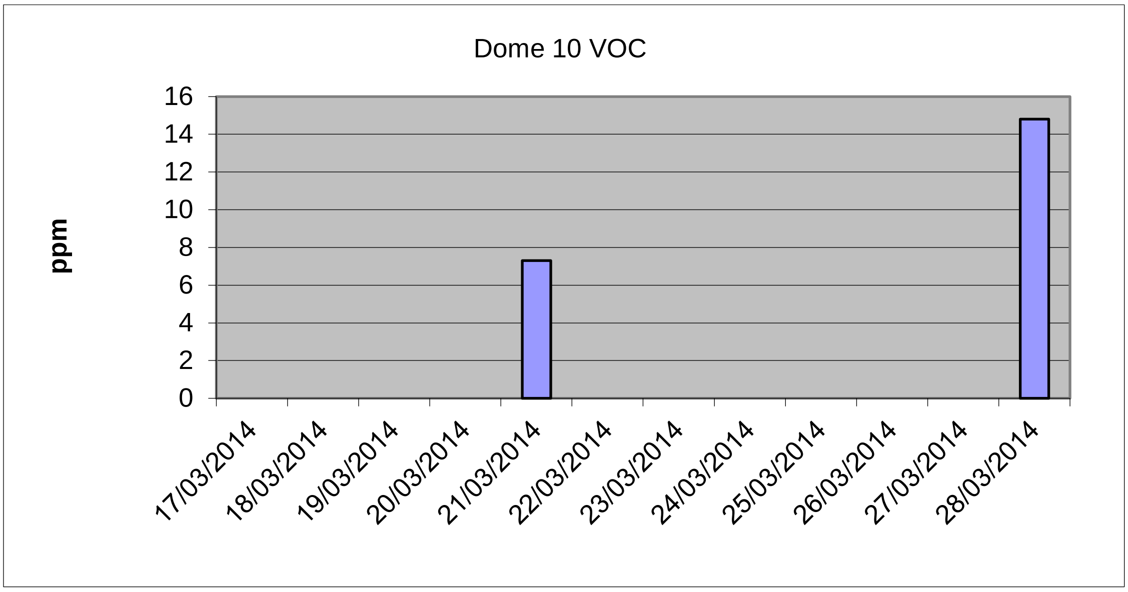


Figure 7.12. Dome 10: Volatile organic compound measured in the biomass pile

Figure 7.13 shows a period of approximately 2.5 months over which the head space of dome 10 was monitored for temperature and humidity. Temperature remained stable in the range 15 – 20^{o}C (approximately ambient) but humidity changed dramatically between the 26/02/2014 and the 14/03/2014, during which time the nitrogen gas was not being injected. During this period the humidity increased from ~40% relative humidity to ~60% relative humidity. This clearly shows the drying effect of the nitrogen on the biomass.

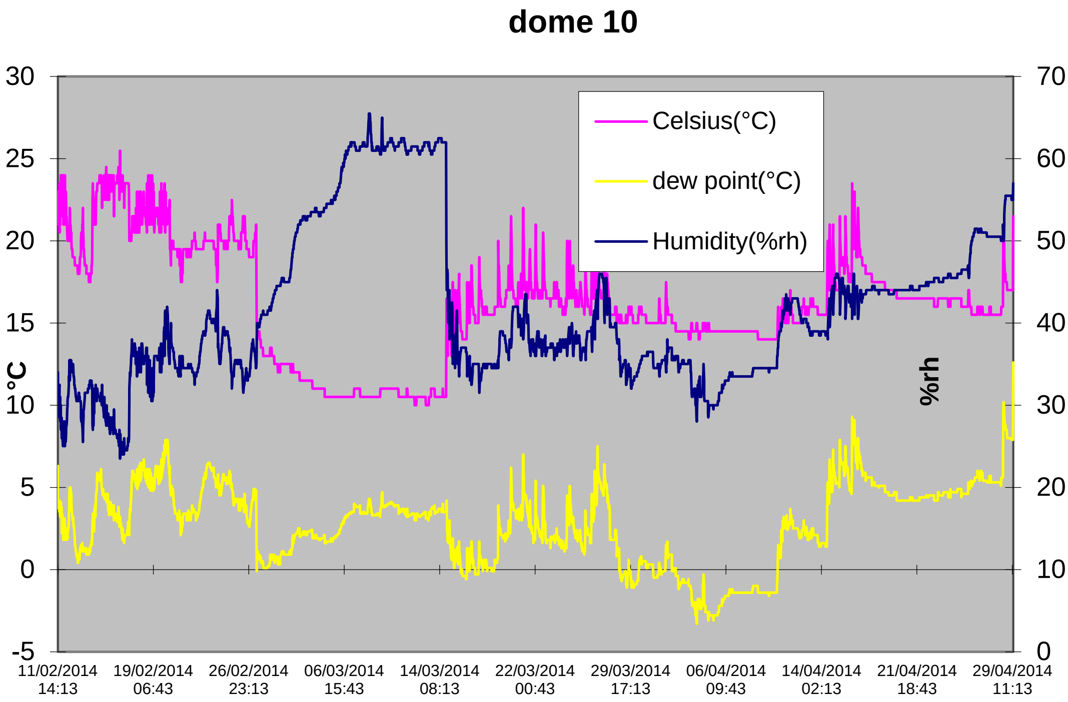


Figure 7.13. Dome 10: Humidity and temperature measured the in head space

7.4.4. Gases In Measured within the Biomass, In The Dome

Gas measurements were taken using a multigas detector (CO, CO_2, O_2, LEL and SO_2) and a volatile organic compounds (VOC) detector through pipes at the base of the domes. Original data is tabulated in appendix 7-7 to 7-7. Unlike the temporary storage section where these gases where relevant for personal safe access into the stores, no personal access is possible or allowed when biomass is in the domes. Therefore this data will be utilised for further assessment of changes of biomass material stored in the dome that might indicate a heating event that is not shown by any thermocouples or to compliment any values. All values shown in the graphs for volatile organic compound carbon monoxide and dioxide are stable and will be utilised for future research into dome self-heating. As stated in the domes temperature results, the number of thermocouples in the domes is very limited due to physical constraints, therefore it is considered that gas measurements (mainly carbon monoxide) will give the first and most accurate indications of a biomass in distress.

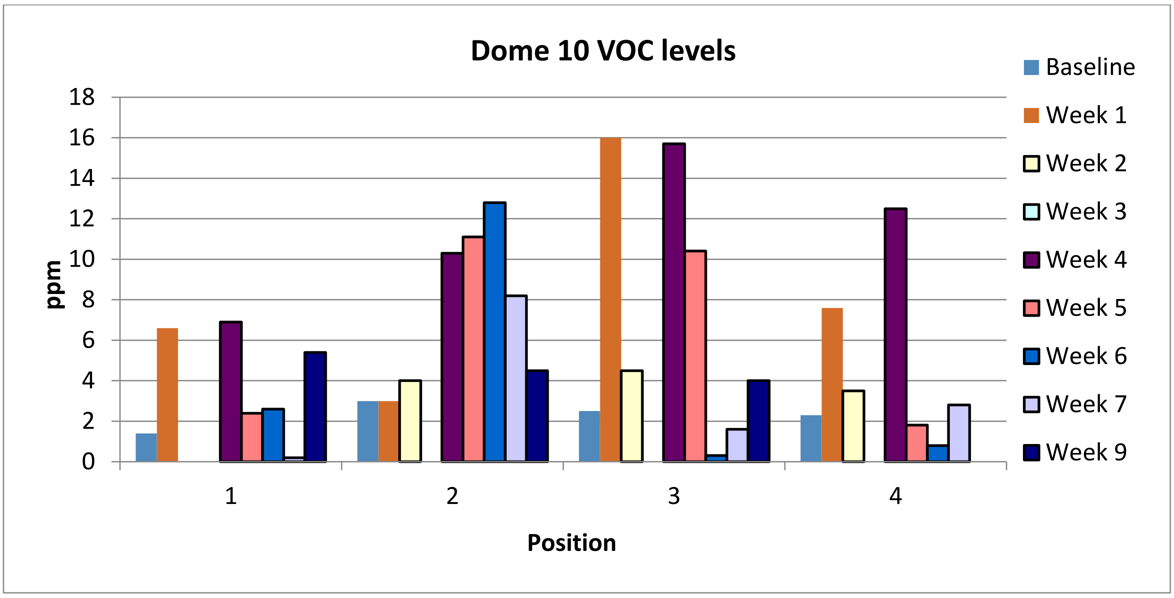


Figure 7.14. Dome 10: volatile organic compounds measured in the biomass pile

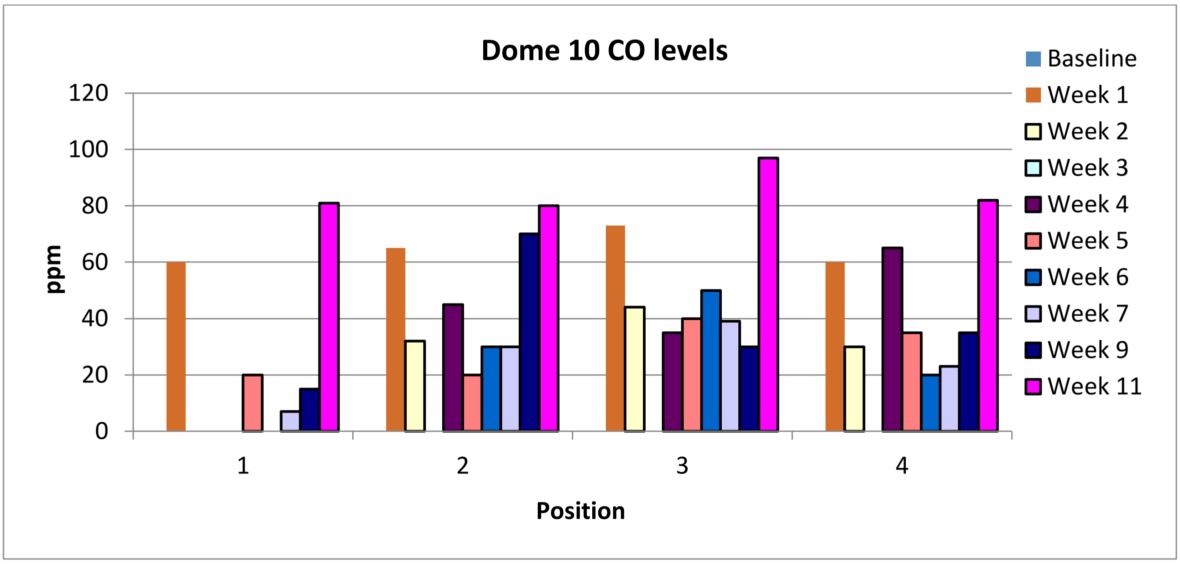


Figure 7.15. Dome 10: carbon monoxide measured in the biomass pile

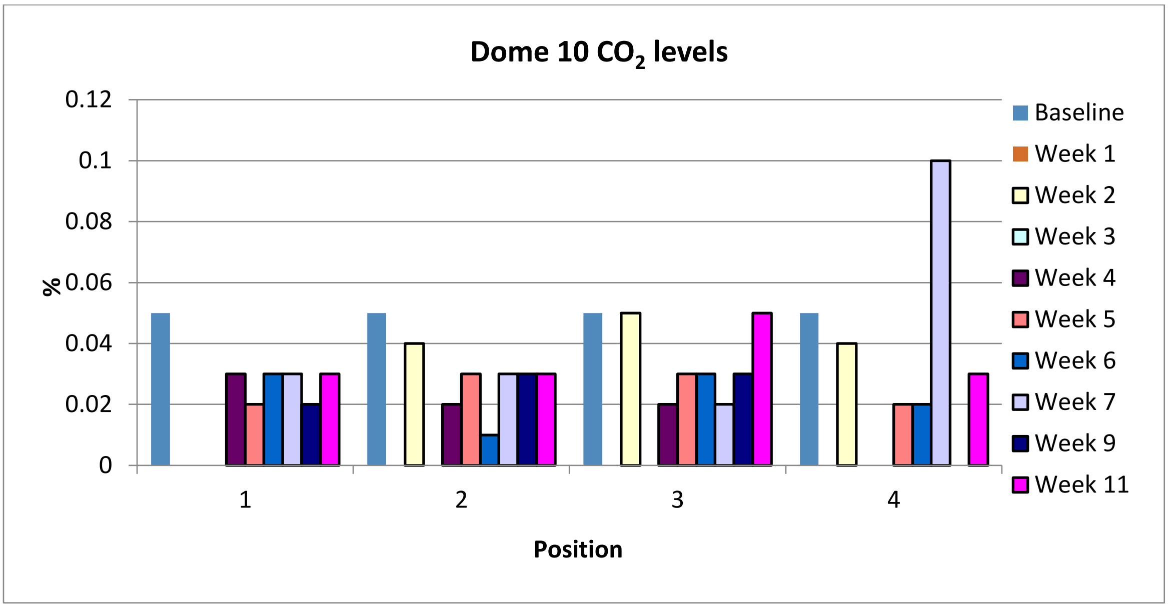


Figure 7.16. Dome 10: carbon dioxide measured in the biomass pile

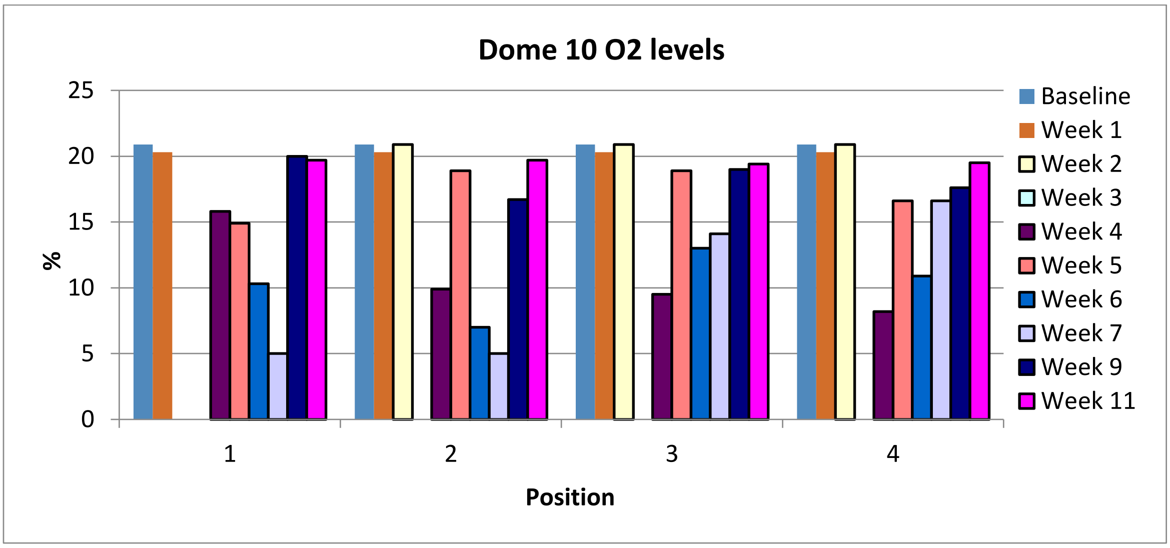


Figure 7.17. Dome 10: oxygen measured in the biomass pile

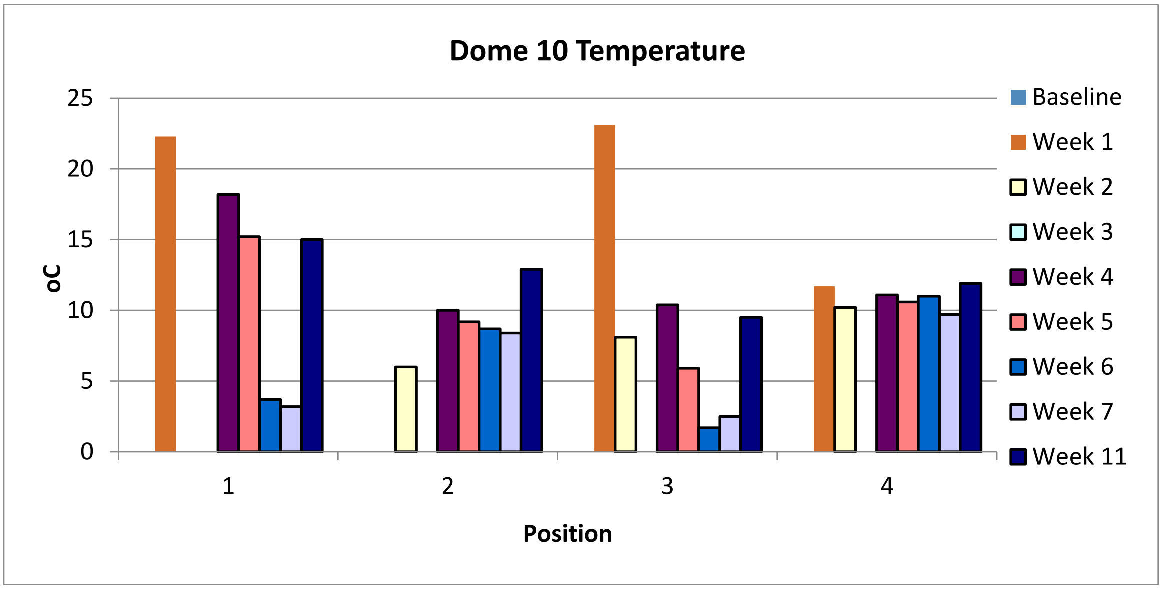


Figure 7.18. Dome 10: temperatures measured in the biomass pile

Although in both the laboratory and temporary storage sections, nitrogen injection was shown to give some cooling effect, this has not been possible to measure on the "domes" scale.

Case Study – SS9 from July 20, 2014 to August 19, 2014 (30 days during the summer):

- Average storage ~ 75,000 tonnes
- Average temperature gain of biomass ~ 3°C (~1°C every 10 days)
- Heat gained by biomass in 30 days = mcΔT = 75,000,000 kg x 2.5kJ/kg°C x 3°C = 562.5 gJ

This is equal to the combustion of 30 tonnes of biomass at ~ 18 gJ/tonne (1 tonne/day loss)

- Total volume of inerting nitrogen injected during the 30 days ~ 800,000 m^3 (~ 800,000 kg)   NOTE – this is ~ 6 volume changes
- Inlet temperature ~20°C; outlet temperature ~30°C
- Heat carried away by nitrogen in 30 days = mcΔT = 800,000 kg x 1.04 kJ/kg°C x 10°C = 8.3 gJ

This demonstrates that the cooling effect of the nitrogen is rather negligible. (~ 1.4%)

7.4.5. Volatile Organic Compound In Base Of Dome

Samples were taken using charcoal tubes with a pump at a flow rate of 12L/hour. Original data is tabulated in appendix 7-9 to 7-12. This draws the air through the tube and parameters of interest are adhered to them. These samples were then subcontracted for analysis for specific aldehydes and ketones.

Unlike the temporary storage Chapter 6 were these gases where relevant for personal safe access into the stores from Table 6.2, no personal access is possible or allowed when biomass is in the domes. The analysis was performed on the domes for completeness of this research as a direct comparison to the material stored in the offsite stores. Therefore in the same way as Chapter 6, a number of other terpenes were also measured and analysed with the results detailed in the appendix for 7-9 to 7-12. These have not been induced in this report because the focus was on the work place exposure limits as detailed in Table 6.2. These other terpenes followed the same pattern as the VOC’s and this could be added to in future work.

In all cases, the domes VOC values are lower than the offsite storage. This is attributed to the nitrogen gas in the dome diluting the dome atmosphere and preventing build-up of the gases.

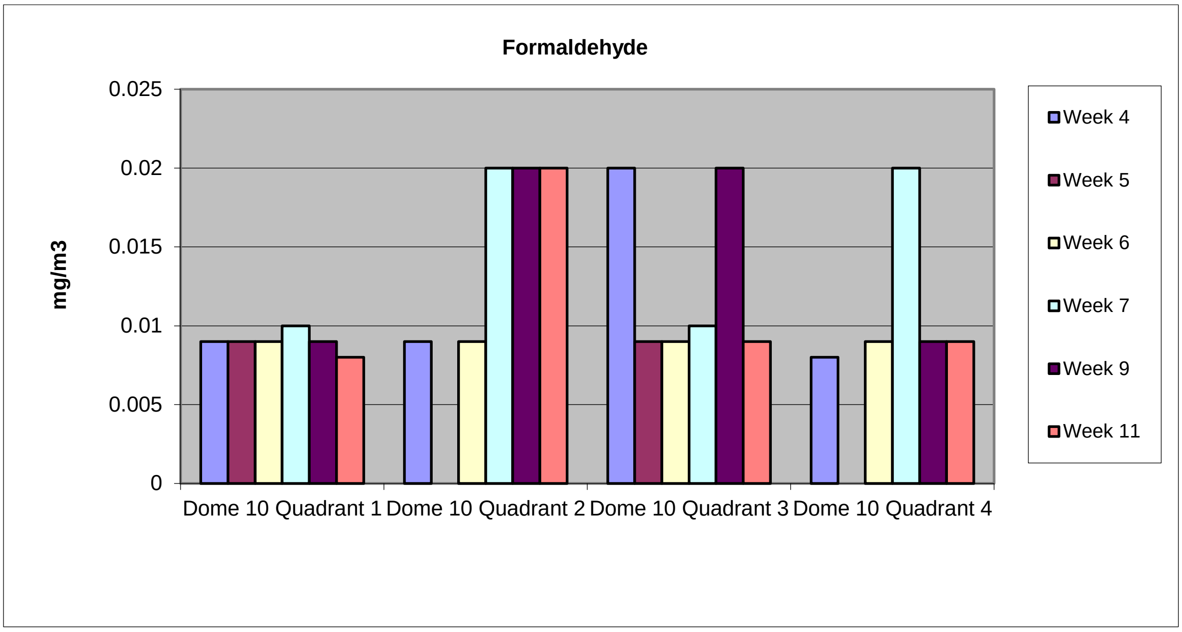


Figure 7.19. Dome 10: formaldehyde

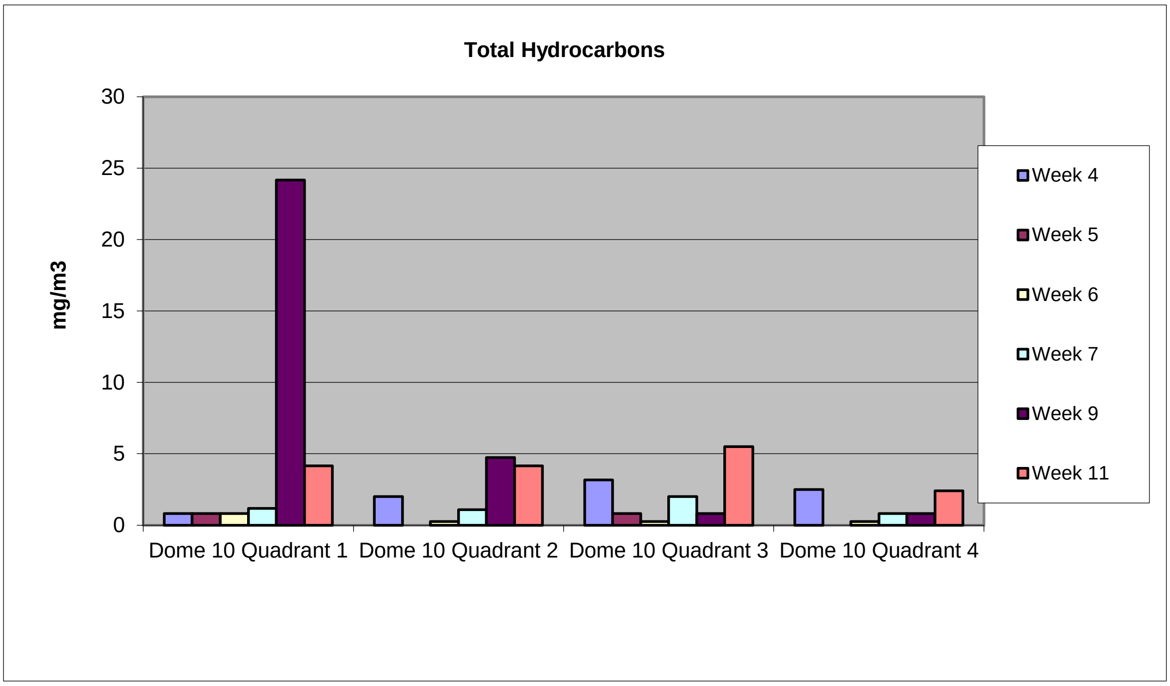


Figure 7.20. Dome 10: total hydrocarbons

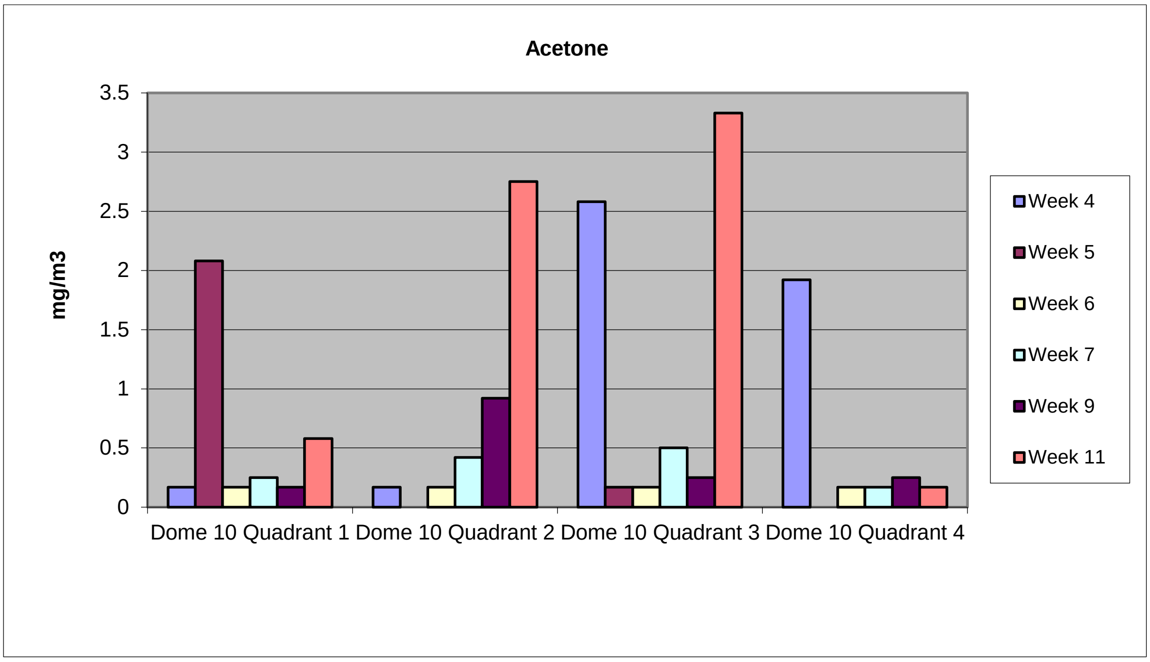


Figure 7.21. Dome 10: acetone

7.4.6. Management Modes For Drax Power Ltd. Domes

Experience storing biomass in large volumes at depths > 15m is quite limited. It is well known that a management strategy is required to control the self-heating that occurs above 15m. (Heat generated is a function of volume (m^3) whereas heat dissipation is a function of area (m^2); empirical studies have shown that storage of biomass in piles above 15m height, the heat generated exceeds the heat dissipated resulting in temperature rise.) It will take some time to gain operating experience to learn how the biomass reacts when stored in the dome shaped domes. Numerous models have been run and this research has extrapolated what could occur.

When the storage exceeds ~ 15,000m^3 (as shown on the APM level measurement system), it is good operating practice to inert the voidage between the pellets. Anything more than 20,000m^3, inerting is mandatory. Methodical injection of nitrogen from the onsite Pressure Swing Absorption (PSA) system to remove air should be established. This is available at rates of ~ 870 m^3/h (1 Compressor), 1,850 m^3/h (2 Compressors) or 2,800 m^3/h (3 Compressors); there are 4 zones of 22 nozzles each in the floor and layout of the piping is meant to give the best possible distribution evenly through the stockpile. An automated sequence of switching from 1 dome to the next every 6 hours is available.

The intent is to provide an inert gas in the voidage between pellets not to try to keep the headspace inert. The dome volume is ~ 127,500 m^3; with the extraction plant running and the air ingress via the kingspan roofing it is virtually impossible to keep the headspace oxygen concentration low. Nevertheless, the pellet voidage can be kept inert. The pellets will naturally release VOC's (Volatile Organic Compounds) such as alcohols, turpines, methane, etc. as well as carbon dioxide (CO_2) and carbon monoxide (CO); Drax Power Ltd. only monitors the CO. CO has been shown in Chapter 6 to be a good indicator of the pattern of behaviour of the other gases released such as aldehydes. This off-gassing process will tend to fill the voids. This accumulation of Volatile Organic Compound should be purged periodically, so a programme of methodical nitrogen injection should be part of the routine operation. This is shown in Table 7.2.

Table 7.2 at the time of writing this thesis is still in a preliminary stage and will be further fine-tuned and adapted as more data and experience is gained. It was compiled from a number of sources of data, including research from this thesis and information supplied by Air Products both from their experience and the CFD modelling. This table shows the expected amount of carbon monoxide to be off gassing at specific temperatures and tonnage of biomass in the dome. It also takes into account the amount of nitrogen injected into the dome.

Green cells are good operating practice, blue indicate safe but excessive use of works power and nitrogen. Yellow indicated a possible heating event/increasing carbon monoxide and therefore action should be taken i.e. increase nitrogen injection rate Red cells indicate very high values of carbon dioxide and again indicate the additional nitrogen /compressors should be unlisted. If no more nitrogen can be injected/compressors used on, other variable of dome tonnage can be adjusted i.e. lower/empty the dome.

Table 7.2. Domes nitrogen injection ratio table

DRAX BIOMASS ECOSTORE DOME STORAGE (SS7 - SS10) NITROGEN INJECTION RATIO :: CO RELEASED											
CO off-gassing rate	CO off-gassing rate	diluent rate	stock average	kilotonnes of product in the storage dome (NOTE - matrix shows the ratios)							
ml/t/hr	m3/kt/day	m3/day	temp.	10	20	30	40	50	60	70	80
10	0.24	5100	30°C	2125	1063	708	531	425	354	304	266
20	0.48	5100	40°C	1063	531	354	266	213	177	152	133
40	0.96	5100	50°C	531	266	177	133	106	89	76	66
80	1.92	5100	60°C	266	133	89	66	53	44	38	33
160	3.84	5100	70°C	133	66	44	33	27	22	19	17
320	7.68	5100	80°C	66	33	22	17	13	11	9	8
TIME TO INERT VOIDS IN STOCKPILE (HOURS)				6	13	19	25	32	38	44	51
ratio of cubic meters/day of Nitrogen injected to cubic meters/day of Carbon Monoxide released from the biomass (1 COMPRESSOR)											

CO off-gassing rate	CO off-gassing rate	diluent rate	stock average	kilotonnes of product in the storage dome (NOTE - matrix shows the ratios)							
ml/t/hr	m3/kt/day	m3/day	temp.	10	20	30	40	50	60	70	80
10	0.24	10400	30°C	4333	2167	1444	1083	867	722	619	542
20	0.48	10400	40°C	2167	1083	722	542	433	361	310	271
40	0.96	10400	50°C	1083	542	361	271	217	181	155	135
80	1.92	10400	60°C	542	271	181	135	108	90	77	68
160	3.84	10400	70°C	271	135	90	68	54	45	39	34
320	7.68	10400	80°C	135	68	45	34	27	23	19	17
TIME TO INERT VOIDS IN STOCKPILE (HOURS)				3	6	10	13	16	19	22	25
ratio of cubic meters/day of Nitrogen injected to cubic meters/day of Carbon Monoxide released from the biomass (2 COMPRESSORS)											

CO off-gassing rate	CO off-gassing rate	diluent rate	stock average	kilotonnes of product in the storage dome (NOTE - matrix shows the ratios)							
ml/t/hr	m3/kt/day	m3/day	temp.	10	20	30	40	50	60	70	80
10	0.24	15300	30°C	6375	3188	2125	1594	1275	1063	911	797
20	0.48	15300	40°C	3188	1594	1063	797	638	531	455	398
40	0.96	15300	50°C	1594	797	531	398	319	266	228	199
80	1.92	15300	60°C	797	398	266	199	159	133	114	100
160	3.84	15300	70°C	398	199	133	100	80	66	57	50
320	7.68	15300	80°C	199	100	66	50	40	33	28	25
TIME TO INERT VOIDS IN STOCKPILE (HOURS)				2	4	6	8	11	13	15	17
ratio of cubic meters/day of Nitrogen injected to cubic meters/day of Carbon Monoxide released from the biomass (3 COMPRESSORS)											

Key

⬜	EXCESSIVE BUT MINIMUM THE SYSTEM CAN DO
🟦	EXCESSIVE AND WASTING WORKS POWER
🟩	GOOD OPERATING PRACTICE
🟨	CO CONCENTRATION IN THE VOIDS > 10000 PPM BUT < 20000 PPM
🟧	CO CONCENTRATION IN THE VOIDS > 20000 PPM

There are four designed reasons for injecting nitrogen into the stored pellets:

1. Reduce the oxygen concentration from the voids. (akin to compacting coal in stockpiles)
2. Purge the Volatile Organic Compound as fast as they are released from the pellets into the voids.

3. Keep the sample probes ‘fresh’ with truly representative gas in the head space by displacing the Volatile organic compound upwards into the headspace.
4. In an event, prevent the spread of the smouldering mass.

Table 7.3 is a summary of management arrangements of the domes for six different scenarios. These scenarios are a combination of CFD modelling assumptions/results and Table 7.2. Table 7.3 again like Table 7.2 (at the time of writing this thesis it was still in draft format and will be further fine-tuned and adapted as more data and experience is gained).

It was compiled from a number of sourced of data, including research from this thesis and information supplied by Air Products both from their experience and the CFD modelling. The following subsections go into each scenario in more detail.

Table 7.3. nitrogen management of domes

Mode	Trigger point	Headspace extraction	Psa flow	Nitrogen liquid store	Mobile supply
1 – routine	No alarms	As required	1 compressor cycle all domes	N/a	N/a
2 – off-gassing	CO > 1500 ppm	Fan on	3 compressors cycle all domes	N/a	N/a
3 - heating up	Temp > 65°C rising	Fan on	3 compressors only to the dome in distress	~2,800 m^3/h	0
4 – self heating	Temp > 100°C rising	Fan on	3 compressors only to the dome in distress	~2,800 to 6,000 m^3/h	0
5 - smouldering	Temp > 140°C rising	Fan on	Shut down the psa. Use pure nitrogen only.	6,000 m^3/h	> 3,000 m^3/h
6 – fire	Open flames visible	Fan off	Inject CO_2 and judicious use of deluge water	6,000 m^3/h	> 3,000 m^3/h

7.4.6.1. Mode 1 – Routine Operation

During this mode nitrogen is being injected into all of the operating domes in a methodical manner from the PSA; normally using only one compressor, see Figure 7.22. Switching from one dome to the next is done automatically (if the dome is selected) and the sequencing around the zones is automatic if desired.

Filling and reclaim from a dome is permitted while being inerted. If all 4 domes are in auto mode, the sequence of purging would be:

- Zone 1, SS7 – SS8 – SS9 – SS10
- Zone 2 SS7 – SS8 – SS9 – SS10
- Zone 3 SS7 – SS8 – SS9 – SS10
- Zone 4 SS7 – SS8 – SS9 – SS10

Any dome not being exploited is deselected and the sequence skips over to the next automatically. Normally each dome would get 6 hours of purging each day at a rate of ~ 870 m^3/h (1 Compressor).

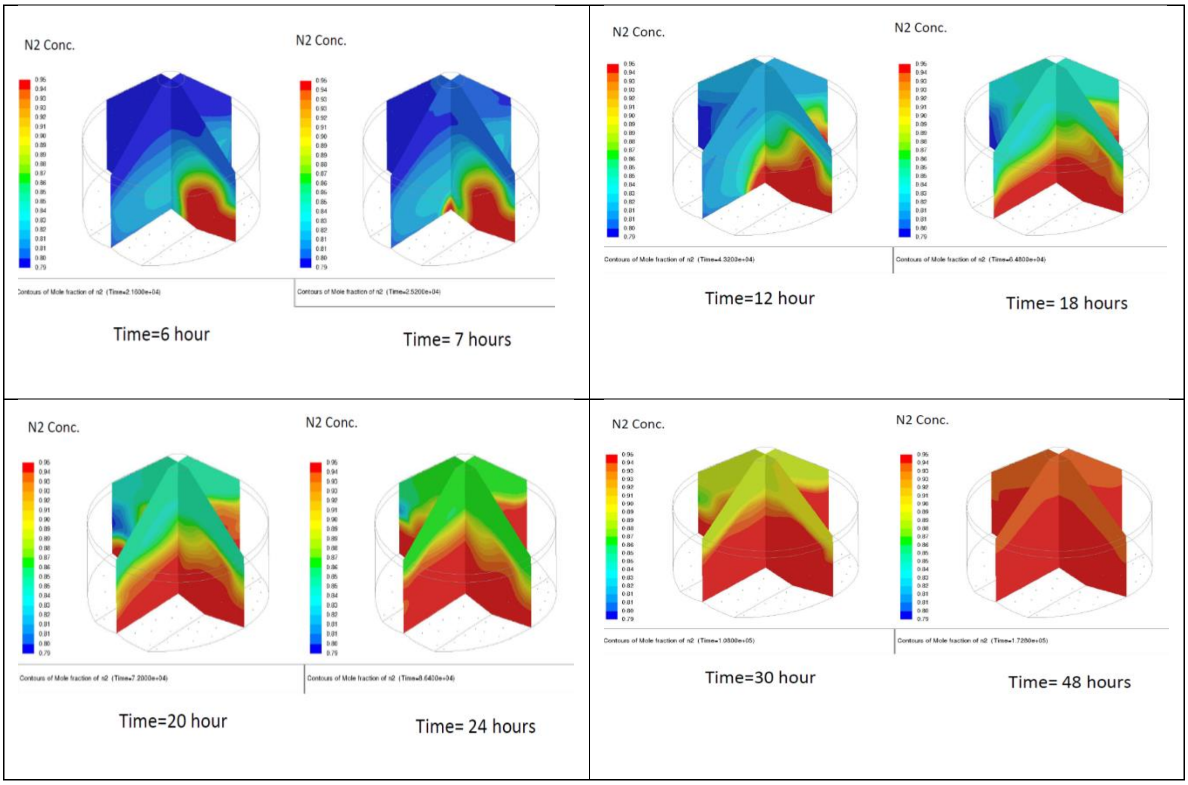


Figure 7.22. nitrogen distribution within the dome

7.4.6.2. Mode 2 - CO Off-Gassing Rate Has Exceeded The Alarm Point

Carbon monoxide off-gassing rate has exceeded the alarm point and can no longer be managed below alarm points with normal nitrogen injection and head space extraction

Carbon Monoxide (CO) alarms:

- High CO concentration Alarm Point = 1100 ppm
- High-high CO concentration Alarm Point is 1500.
- There is also 'Rate-of-Rise' Alarm at 164 ppm/hour (2.7 ppm/minute) for > 2 minutes (red).

The Materials Handling Supervisors should make an initial risk assessment of the situation. If the situation allows; filling should be stopped and the inlet valve closed. The dust extraction fan should be run continually with the intake only from the dome. Strategic reclaim should be managed to reduce the inventory. It is bad practice to allow personnel on a dome that is in distress or suspected to be in distress. The top of the dome and the explosion vent panel exclusion zones should be treated as higher risk access should be forbidden without a task risk assessment.

Nitrogen injection rate from the on-site PSA generator should be maximized (~2,800 m^3/h using 3 compressors) in the normal sequence with the other domes being exploited. Trends on the thermocouple strings in the temperature array and CO concentrations on the sample tubes may indicate the best zone(s) to use for the nitrogen injection. The decision may be taken to select specific zones rather than simple rotation through the sequence. As the nitrogen displaces the Volatile Organic Compound from the voids between the pellets, it is anticipated that there could be a rise in headspace CO (especially if the material has sat for a long time with no inerting). This is normal; it is far better to displace the Volatile Organic Compound with nitrogen than with air.

The dome volume is 127,500 m^3, so at ~2,800 m^3/h, it will take ~ 48 hours to completely displace an empty dome. Assuming the dome is at maximum level, the voidage between pellets takes up about 35% of the volume, so it would take

~ 18 hours to purge completely. When the dome is completely inerted, the CO should drop below alarm point.

7.4.6.3. Mode 3 – Dome In Distress

The dome is heating Up (temperature rise has exceeded the alarm point and can no longer be managed below alarm points with strategic reclaim etc.)

Temperature Alarms:

- High Temperature Alarm Point (amber) from one or more of the thermocouple strings in the temperature array = 60°C
- High-high Temperature Alarm Point (red) from one or more of the thermocouple strings in the temperature array = 65°C
- High rate of rise from the Temperature Sensor (red) on the Dust Extraction Filter outlet = 60°C/hour (1°C/ minute) for > 2 min.

This step is considered to be a continuation of mode 2 and the same process limitations apply.

Nitrogen Injection rate from the on-site PSA generator should continue to be maximized (2,800m^3/h using 3 compressors) but directed only to the dome in distress. The extraction fan for the dust filter unit should be left running to aid dilution of the off-gassing products from the headspace. Monitor the situation carefully for indications of escalation of the problem. If the tunnels are still showing normal fresh air conditions and the ventilation plant is still working normally, a Risk Assessment may allow inspection of the outlets with a temperature sensing gun and/or thermal imaging camera. (If necessary, this could be done by fire-fighters equipped with breathing apparatus following the guidelines of the Confined Space documentation).

The nominated person and his team can evaluate the situation to determine if things are improving or degrading. Once the assessment is complete, every effort should be made to strategically reclaim to reduce the inventory of material. (Note – the best way to reduce temperature of the pile is to reclaim from it; this exposes the material to the head space and increases the surface area exposed for cooling.) The reclaim conveyor belt normal operating limit is 65°C (whereupon the Heat Detector will trip the belt). Hook up data loggers to the floor mounted thermocouples to track floor level temperatures. This can be helpful in determining which quadrant to reclaim from (coolest product first out). Watch the Heat detector trends on the reclaim belt(s) to help select the coolest quadrant for reclaim

7.4.6.4. Mode 4 – Self-Heating

This is considered to be a further escalation of mode 2 and 3 and the same process limitations apply. If analysis of trends shows that heating-up is moving towards 'self-heating' (temp. > 100°C); the flow rate and purity of the nitrogen gas should be enhanced by using 3000m^3/h (gaseous) vaporised from liquid nitrogen in addition to the 2800m^3/h being generated from the PSA, to give a total flow of 5800m^3/h. The nitrogen gas from the liquid store is high purity (nominally 100%). It gives the added benefit of more completely inerting the voidage between pellets reducing the Oxygen even further. The Supervisor must authorise the opening of the manual valves on the outlet of the vaporizers from the liquid nitrogen storage tanks. Once the extra nitrogen is well established, every effort should be made to strategically reclaim to reduce the inventory of material. If further analysis of trends such as off gas temperature and/or in-dome temperature are causing the operator to believe that self-heating is escalating towards smouldering; the flow rate and purity of the nitrogen gas will be enhanced by using 6,000m^3/h (gaseous) vaporised from liquid nitrogen in addition to the 2800m^3/h being generated to give a total flow of 8,800m^3/h.

The evaporators will stop auto-cycling to allow a total gas flow of 6,000 m^3/h. They will need attention to keep them functioning without completely icing up (the use of mobile steam cleaning equipment can help). It is very likely at this point in time that the supplier of liquid nitrogen will be involved and they may be able to advice on how to keep the evaporators at optimum throughput. This should stabilize the temperature and bring the headspace gases back into control under the alarm point. If not, it may be necessary to go to mode 5.

7.4.6.5. Mode 5 - Smouldering

This is considered to be a further escalation of mode 4 and the same process limitations apply. Trends such as off-gas temperature and/or in-dome temperature and data-loggers are causing the operator to believe that the product is smouldering (temp. > 140°C); the flow rate and purity of the nitrogen gas will be enhanced by using 9,000m^3/h (when gaseous) of liquid nitrogen. The PSA should be shut down so that only pure nitrogen is admitted. BOC has equipment that is capable of generating 12,000 m^3/h from a lorry. The piping to any one dome is capable of handling 12,000 m^3/h and it should be maxed out.

Nitrogen tanker delivery with mobile evaporation equipment will further enhance on-site production. As before, the on-site evaporators will need attention to keep from icing up completely.

- Zero m^3/h @ 95% purity from on-site generation (PSA).
- 6,000 m^3/h @ 100% purity from on-site liquid storage evaporated to vapour.
- 3,000 m^3/h @ 100% purity from Delivery Tanker Fleet and mobile evaporator plant.

Any one dome is designed to take a maximum of 12,000 m^3/h; ideally it is best to use pure nitrogen if that rate is available. There are nitrogen lorries designed to generate more than 12,000 m^3/h from a single unit. If such a unit is brought to Drax Power Ltd, it would be best to exploit the pure liquid supply and the PSA should be shut down so that the nitrogen going to the dome in distress is 100% pure at the maximum rate. Once this extra nitrogen is well established, again every effort should be made to strategically reclaim to reduce the inventory of material.

Usage of nitrogen gas should be treated as situation management – not extinguishment. It is virtually impossible to extinguish a nodule of smouldering biomass with nitrogen. The biomass material has oxygen within the cellulose matrix. It does not need air. (the entire nitrogen resource flowing for 1 hour has less cooling effect than water in 1 zone for 1 min) the objective is to manage the smouldering to allow strategic extraction of material and keep the dome walls/internal equipment from overheating. With care, you can get to the point where it is safe to remove the door and ultimately quench the biomass. CO_2 will ‘knock down’ open flames and quench a surface fire; this can be used any time if the situation analysis indicates it could be beneficial.

7.4.6.6. Mode 6 – Fire (Evidenced By Visible Flames And Smoke)

Shut the Dust Filter Extraction fan off to stop the mechanical assisted draft. Manually open the actuated damper for the filter to allow off-gassing to occur through the filter. The dome will go slightly positive pressure to the differential across the bags. It is most likely that the bags will burn off. Judicious use of the deluge system can bring the flames under control. Then switch back to the gas if possible. The deluge can be applied to any of the 4 zones as required. A booster pump is available to maximise dispersion as required.

7.4.6.7. CO_2 Mode - Fire Suppression/Fire Fighting

At any time during management of a “dome in distress” a decision to operate the CO_2 system can be made to form a “blanket” to smother a deep seated fire or to fight directly a surface fire. The CO_2 system can be used independently of the nitrogen system or simultaneously with it.

7.5. Conclusions

The concept of using the large scale dome storage for long term storage of biomass is not an ideal solution as the risks with self-heating problems normally increases with storage volume and storage time. In this case, the storage volume probably exceeds all previous experience and thereby there are many questions related to the “scale factor” where there is really no knowledge or experience. The only silo known of with a similar size is a silo at DONG Energy in Denmark at their Avedore Station with a capacity of 100,000m^3 . However, the turn-over time in the DONG silo is according to knowledge relatively short, maximum in the order of some weeks to some months.

As the quality and the properties of the pellets stored in the domes will vary, it will be very important to continuously collect knowledge and gain experience and by a long-term supervision try to detect and eliminate any tendencies to self-heating as soon as possible. The knowledge gained from the temporary stores has shown the following verification in the domes: Although the domes are well insulated and sealed, the nitrogen system has shown several benefits. Initially installed as an intention system for fire, which laboratory TGA testing has shown will have an effect, the main benefit from the nitrogen injection is through dilution and movement of the natural biomass off-gassing.

At full load on the three biomass units each of 645 MW, approximately 21,000 tonne of material is being burnt/ extracted from each dome, therefore the time for retention within the domes is minimal, accounting for three domes in service and one out for service/ stand-by. Although, the temporary stores have shown given good quality starting material and a store suitably ventilated and insulated to eliminate or reduce condensation and humidity within the store will enable safe storage of material in excess over 12 months.

As shown in both the Chapter 6 and this chapter temperature profiles, heating develop ~5m from the base of the pile. The domes operate on a top fill, bottom discharge which equally drawn down over the whole base or selected areas can be extracted as heating shows. This ever changing movement of the pile has shown to greatly reduce the heating area by exposing the pellets that are heating in the centre to either a location closer to the surface or disposed of completely. Like historic coal handling techniques, material up to 60°C is safely transported along conveyor systems and directly into the boiler is a proven way of clearing the warm area.

Self-heating is a serious problem during wood pellet storage. This research focused on investigating parameters (conditions) affecting the self-heating process and predicting the critical conditions for spontaneous combustion in stored wood pellets along with safety of personal. Experiments were carried out to determine preferred design of storage fatalities, industrial scale reasons for self-heating, off-gas in relation to both self-heating and personal safety and scale-up to domes. An in-house Drax Power Ltd. domes specific risk chart was created for self-heating potential within the domes.

The main concern of fire in the domes it that it is introduced from an outside source. If the Drax Power Ltd. biomass management procedures are followed, it is very unlikely to have a serious self-heating issue that could lead to fire. If the control systems are maintained for the upstream unloading and conveyance plant and maintenance procedures are followed, it is very unlikely that fire could be introduced to a storage Dome from an outside source. If it does happen, the situation will very rapidly go to Mode 5 – Smouldering and Mode 6 – Fire (evidenced by visible flames and smoke). The firefighting strategy, based on an installed fixed system for inert gas injection, both at the dome bottom and to the headspace, is very good. The system is also designed both for fire prevention and firefighting which provides additional safety which is important considering the size of the storage. The gas distribution system at the dome bottom is divided into four sections, each covering one quadrant of the dome. There is also a number of operation modes for the system to handle various scenarios from normal conditions to severe fire situations.

Detection/extinguishing systems along conveyor systems Is a very important part of the overall fire protection of the plant as “external” fire sources according to some fire statistics are a more common cause of fires than self-heating. The conveyor systems are protected with sprinkler systems combined with heat sensors at strategic positions. The conveyor system below the domes, which must also be operated to discharge a dome in a fire situation, is very strategic for the entire plant and it is extremely important that these are not damaged in case of smouldering material is discharged. It is also important to consider the possibilities for manual supervision and fire fighting in case of such “emergency discharge” as a complement to the sprinkler system.

The inerting of the dome using the on-site nitrogen generator (mode 3) provides an additional possibility to reduce the likelihood for self-heating and spontaneous ignition. By the use of this system, it is expected to “flood” a dome with nitrogen in about 36 hours. The gas injection will then be following a sequence where the gas is injected into one quadrant at the time in order to keep the oxygen level inside the bulk at a low level which seems very positive. However, it has still to be determined whether such a continuous inerting procedure could cause any problems due to the drying effect on the pellets over long-term storage. The gas will be very dry and absorb water from the pellets close the gas inlet and cause an increased humidity in the pellets at some distance from the inlet due to condensation. This process might cause a “wave” of increased humidity slowly moving upward in the pellets as the pellets at the lower regions of the dome is slowly becoming dryer.

When the gas with increased humidity reaches the dome headspace, this might cause water condensation on the pellet surface and the dome construction if not ventilated. However, as there are four domes that will be kept inerted using the nitrogen generator, there will not be a constant gas flow and the drying effect might not be considerable. However, the movement of water inside bulk material, e.g. when mixing dry and humid material inside a storage, is known to be one possible reason for self-heating and it is therefore important to study this effect when the domes are in operation. The O_2 measurements in combination with RH-measurements in the dome headspace could be used to study such effect.

Depending on the situation, the various modes of firefighting allow an increased gas flow into the dome by use of liquid nitrogen stored in cryogenic tanks. The maximum flow rate is 12 000 m^3/h which is corresponding to an injection rate of about 3, 9 kg/m^2 h. This does not reach 5 kg/m^2 h, as recommended in the book “Dome Fires”, but it is believed this will be enough considering that the dome will normally be kept at a low oxygen level by the “prevention mode”. Further, it will be possible to increase the injection rate in certain areas of the dome by directing the flow into one or several of the four quadrants. The dome construction could also be considered to be very tight which will reduce the loss of gas in normal conditions. However, it is important that the valves at the discharge openings at the dome bottom are as gas tight as possible, as gas leakage might both contribute to loss of nitrogen but might also result in an increased level of oxygen close to the opening.

In the recommendations, the total amount of gas is estimated to 5-15 kg/m^3 (gross dome volume). This is a figure based on real fire incidents in domes, but also here, the dome volumes have been very small compared to domes. Based on the fire incident in the DONG silo during 2012, where the silo was kept inerted for more than 20 days, there are indications that the amount of inert gas exceeded 30 kg/m^3. (No official figures reported yet). This indicates that there is a need to plan for delivery of very large quantities of gas in case of a fire.

In order to handle a possible explosion event inside the dome, there will be a large opening (27 m in diameter) in the dome construction to enable pressure relief through explosion panels. One concern expressed is that in case of a fire situation where there is an explosion, the panels will open and generate a large total opening area which will not be possible to close again. This will affect the possibilities to keep the dome inerted, especially during windy conditions. This means that the total consumption of gas might increase considerably (see above). If possible, any measures to facilitate the panel openings to be closed again would improve the possibilities for a successful firefighting operation. Another factor that should be checked is that the strength of the connection between the dome and the “new roof” construction covering the opening in the dome is designed for the opening pressure of the panels. There are several examples were the explosion panels have not opened, instead the entire roof have lifted from the dome wall due to the explosion.

The gas nozzles at the dome bottom are spring loaded to ensure a pressure drop of about 0.5 bar over the nozzle to ensure a balanced gas distribution. The pressure drop is also expected to significantly exceed the pressure drop over the bulk material based on permeability measurements. The gas nozzles are of course very critical for the inerting procedure and it is extremely important that they are not blocked and that the spring load construction is working properly. It will therefore be important to supervise the flow rates and pressure during “prevention filling” to ensure that there are no blockages.

CHAPTER 8. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

8.1. Summary Of Conclusions

The common element in all three investigations (laboratory scale, temporary storage and domes scale) is moisture and its effects on both the material an interaction with its storage. The laboratory scale focused on more controllable factors of biomass, its potential to self-heat, through the laboratory research into the pH effects of moisture on the biomass and the link to the lignocellulosic components. Additionally the potential link of the heavy metals concentrations in the Agricultural Residues and the toxicity effects on enzyme growth, thus restricting temperature rise. Thermogravimetric analysis has shown that due to the inherent chemical oxygen of the biomass pellets, even 100% nitrogen will only slow/reduce the combustion of biomass (once heating has started). The moisture migration has been tracked on the small scale test-rig, and shown to have exited the pile. On the full scale dome, given the depth, this moisture might not exit the pile before it has condensed and this may result in higher concentrations of moisture in the upper levels of the biomass store.

Scaling up to the size of the temporary stores, the repeating element of moisture indicated that store ventilation is likely to be the key factor in self-heating of biomass wood pellets. Although several other factors appear to be required either singularly or as multiples, the ability of the store to ventilate (moisture and gases) appears to be the initial activation for the whole process. Although now working from a starting point of approximately 30,000 tonnes, it is more realistic to scale up to a size of 80,000 tonnes, and the effect of the insulation of the biomass has been shown to give a potential temperature in excess of 150^{o}C from an additive temperature profile. The other potential benefit seen on the small scale and off-site storage biomass piles, has been a cooling effect from the nitrogen flowing through the pile. This has shown to replicate the ventilation benefit seen in the temporary off-site storage facilities.

The knowledge gained from the temporary stores has shown although the domes are well insulated and sealed, the nitrogen system has shown several benefits. Initially installed as an intention system for fire, which laboratory TGA testing has shown will have an effect, the main benefit from the nitrogen injection is through dilution and movement of the natural biomass off-gassing. The temporary stores have shown given good quality starting material and a store suitably ventilated and insulated to eliminate or reduce condensation and humidity within the store will enable safe storage of material in excess over 12 months.

As shown in both the temporary stores and the domes temperature profiles, heating develop ~5m from the base of the pile. The domes operate on a top fill, bottom discharge which equally drawn down over the whole base or selected areas can be extracted as heating shows. This ever changing movement of the pile has shown to greatly reduce the heating area by exposing the pellets that are heating in the centre to either a location closer to the surface or disposed of completely. Like historic coal handling techniques, material up to 60°C is safely transported along conveyor systems and directly into the boiler is a proven way of clearing the warm area.

The main concern of fire in the domes it that introduced from an outside source. If the Drax Power Ltd. biomass management procedures are followed, it is very unlikely to have a serious self-heating issue that could lead to fire. If the control systems are maintained for the upstream unloading and conveyance plant and maintenance procedures are followed, it is very unlikely that fire could be introduced to a storage dome from an outside source. Detection/extinguishing systems along conveyor systems is a very important part of the overall fire protection of the plant as “external” fire sources according to some fire statistics are a more common cause of fires than self-heating.

It has still to be determined whether such a continuous inerting procedure could cause any problems due to the drying effect on the pellets over long-term storage. The gas will be very dry and remove water from the pellets close the gas inlet and cause an increased humidity in the pellets at some distance from the inlet due to condensation. This process might cause a “wave” of increased humidity slowly moving upward in the pellets as the pellets at the lower regions of the dome is slowly becoming dryer.

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8.2. Recommendations For Industrial Application

Based on the results of this study, the following recommendations are made for the industrial practitioners.

- Ventilation inside of the dome is essential when designing a wood pellets storage system. This can either come from atmospheric air or an inert gas i.e. nitrogen. This is not as others have suggested for cooling the pellets, (although some effects has been noted,) but more for displacement and control of condensable and non-condensable gases which can either propagate a fire or add to if a fire is initiated. Ventilation also transports away moisture which has also shown to imitate self-heating both through adsorption and microbiological growth.
- Full control of the logistical chain from sourcing fibre to pellet manufacture through to the final storage are critical to ensure high quality pellets are produced at all times, thus preventing problems starting initially from off-gassing, temperature rise and high dust levels.
- Temperature monitoring has limited use on large scale due to the physical constraints of installing thermocouples and therefore other monitoring parameters are deemed to be more effective and rapid to changes in the biomass. The main parameter being carbon monoxide via off-gassing for which a management strategy has been produced for the Drax Power Ltd. domes as part of this research.

8.3. Recommendations For Future Work

The primary aim for this work was for Drax Power Ltd. power station to quickly identify risks of storage of biomass at large scales never reached anywhere else in the world of ~6 million tonnes per annum stored/burnt in storage facilities of 120,000 m^3 (~70,000 tonnes). The objectives have clearly been met to achieve Drax Power Ltd.'s goals of 100% biomass burn on three, 645 MW but in this rapid development, some aspects of a traditional PhD thesis have and could not be covered. This have been overcome in some ways with close ties with Leeds University and the Biomass and Fossil Fuel Research Association (BF2RA), acting as a steering group member and mentor of PhD students. Although there are confidentiality clauses linked to this thesis, much knowledge and data has been shared anonymously with these organisations feeding into others research.

During this study, effect of moisture content, bulk density, pellet age, pellet size are investigated. Self-heating of wood pellets is a complex process and affected by multiple factors. Further research needs to be done to quantify all factors affecting wood pellets safe storage and self-heating potential. The following is a set of recommendations for future study.

- Risk factors have been allocated to the safe storage at Drax Power Ltd. and its unique storage and handling systems. This research could be expanded
- Much work has been done by others at small scale (Less the 1m) on self-heating potential of new biomass types but their data, if scaled up to Drax Power Ltd. scale would give unrealistic self- heating ignition temperatures and in some cases negative values. By utilising the data gained from this research, points can be added to these small scale test by others at the 40,000 and 75,000 tonne levels (10 /50m depth) and re-evaluate the ignition potentials.

8.4. Reference

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Appendices

Appendix 6-1: JHP9 Volatile Organic Compounds

JHP 9 VOC									
	41569.0	41577.0	41584.0	41592.0	41599.0	41606.0	41613.0	41618.0	41625.0
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
1.0	2.5	10.4	2.9	3.8	4.7	13.5	1.7	6.2	
2.0	4.6	8.7	5.8	5.8	8.0	11.3	2.2	6.5	
3.0	4.5	6.5	4.7	5.0	5.5	10.8	3.1	3.7	
4.0	3.8	6.0	5.0	4.4	6.5	11.7	4.8	5.2	
5.0	3.5	5.0	5.0	5.0	6.2	10.2	4.6	4.5	
6.0	5.0	6.0	6.0	6.5	7.0	12.7	2.1	5.6	
7.0	4.7	6.4	4.8	4.3	7.3	13.3	1.6	3.7	
8.0	3.8	6.0	4.0	3.5	6.0	11.8	1.2	3.7	
9.0	5.0	12.0	7.5	2.4	6.7	12.6	1.4	5.1	
10.0	2.7	6.7	2.6	2.2	4.7	4.8	1.0	2.5	
11.0	5.0	8.0	5.4	3.7	8.7	13.6	2.1	5.8	5.7
12.0	1.9		1.7	1.5	1.2	0.5	1.5	2.5	
13.0	0.6		0.3	0.2	0.2	0.1	0.1	0.3	

Appendix 6-2: JHP9 Carbon Dioxide In Pile

JHP 9 CO									
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
1.0	17.0	20.0	12.0	8.0	13.0	27.0	0.0	11.0	
2.0	20.0	21.0	13.0	16.0	15.0	26.0	0.0	8.0	
3.0	0.0	14.0	11.0	10.0	10.0	21.0	0.0	7.0	
4.0	7.0	15.0	10.0	15.0	11.0	21.0	7.0	5.0	
5.0	7.0	11.0	10.0	10.0	10.0	20.0	5.0	6.0	
6.0	14.0	15.0	13.0	11.0	11.0	21.0	0.0	6.0	
7.0	14.0	19.0	15.0	9.0	13.0	26.0	0.0	7.0	
8.0	14.0	15.0	13.0	8.0	14.0	27.0	0.0	7.0	
9.0	16.0	23.0	17.0	10.0	11.0	29.0	0.0	6.0	
10.0	7.0	18.0	12.0	6.0	8.0	13.0	0.0	7.0	
11.0	30.0	31.0	16.0	8.0	20.0	25.0	0.0	4.0	12.3

Appendix 6-3: JHP11 Volatile Organic Compounds

JHP 11 VOC									
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
1.0	0.3	0.8	0.0	2.0	1.2	0.0	2.1	1.5	0.1
2.0	1.0	0.3	1.8	2.6	1.4	0.8	2.0	2.9	0.9
3.0	1.5	0.6	1.5	2.5	1.2	2.1	1.7	4.5	2.2
4.0	2.5	0.8	3.4	3.0	2.0	4.6	3.2	6.6	6.6
5.0	1.3	0.7	1.9	4.6	1.1	5.4	1.6	6.6	2.9
6.0	1.0	0.4	1.3	2.5	1.5	3.0	2.7	7.5	1.5
7.0	1.6	0.5	2.0	2.0	1.9	7.3	1.6	8.6	2.0
8.0	1.5	1.5	3.4	0.8	3.3	7.8	1.6	3.1	6.0
9.0	1.0	0.9	2.2	1.2	2.3	2.8	2.0	2.3	2.3
10.0	1.2	0.9	2.3	1.5	2.1	2.6	1.9	2.2	2.2
11.0	2.0	0.3	1.9	1.5	5.2	3.0	1.8	2.1	1.1
12.0	3.0	0.6	1.0	1.4	5.5	6.4	1.9	3.4	1.7
13.0	0.8	0.3	0.5	2.2	3.5	6.0	2.6	0.8	0.8
14.0	0.6	0.3	0.7	2.5	3.1	1.6	2.6	1.3	0.6

Appendix 6-4: JHP11 Carbon Dioxide

JHP 11 CO									
Position	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
1.0	0.0	0.0	0.0	0.0	6.0	2.0	0.0		0.0
2.0	3.0	2.0	6.0	6.0	5.0	4.0	0.0		0.0
3.0	5.0	4.0	8.0	7.0	5.0	5.0	0.0		3.0
4.0	15.0	15.0	22.0	13.0	6.0	18.0	7.0		7.0
5.0	6.0	10.0	16.0	13.0	4.0	21.0	0.0		7.0
6.0	4.0	7.0	12.0	8.0	7.0	10.0	0.0		3.0
7.0	5.0	8.0	11.0	5.0	5.0	19.0	0.0		6.0
8.0	5.0	10.0	16.0	5.0	10.0	19.0	0.0		7.0
9.0	3.0	7.0	10.0	5.0	7.0	12.0	0.0		3.0
10.0	3.0	6.0	10.0	4.0	8.0	10.0	0.0		4.0
11.0	4.0	5.0	8.0	4.0	9.0	14.0	0.0		2.0
12.0	9.0	7.0	8.0	6.0	9.0	15.0	0.0		0.0
13.0	0.0	3.0	5.0	9.0	10.0	17.0	0.0		3.0
14.0	0.0	3.0	4.0	9.0	7.0	10.0	0.0		0.0

Appendix 6-5: JHP9 Temperature In Pile

JHP 9 temperature										
		22/10/2013	30/10/2013	06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013	17/12/2013
	Depth from bottom of pile	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	5	22.4	16.5	16.1	17.5	16.8	17.7	15.7	15.3	
	4	31.5	30.2	30.7	32.5	31.6	30.6	28.8	28	
	3	35.5	35.7	36.6	37.6	36.9	35.2	33.6	32.4	
	2	36.4	36.9	37.9	38.8	37.9	36.5	34.7	33.7	
	1	35.2	35.8	36.6	37.3	36.4	35.5	34.3	33.4	
	0	32	31.2	31.2	31.4	30.8	30.5	29.8	29.7	
	Ambient in store	18.2	13.2	10.9	9.9	8.8	10.3	9.2	8.8	
	Ambient outside store	16.7	12.2	8.3	8.8	7.7	8.9	8.1	9.9	

Appendix 6-6: JHP11 Temperature In Pile

JHP 11 temperature										
	Depth from bottom of pile	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	8	17.3	11.5	8.4	6.9	5.9	11.3	8	4	6.4
	7	20.4	10.6	14.9	11.7	14.5	8.9	8.6	5.4	8.5
	6	31.1	24	26.2	25.6	23.6	19.7	17.5	17.2	18.2
	5	34	28.2	33.6	34.9	32.9	29.2	30.1	28.1	27.2
	4	33.9	34.1	36.4	39.8	41.4	40.6	39.1	36.1	33.7
	3	35.7	37.5	40.9	38.1	45.8	43.6	41.4	40.1	38.7
	2	38.7	42.6	42.7	38.8	45.3	43.4	42.1	44.1	39.9
	1	42	40.2	39.4	37.9	40.2	37.6	41.2	40.5	35.3
	0	30.4	28.8	27.7	27.1	30.5	27.4	30.2	30.6	26.1
	Ambient in store	15.9	13.3	11.3	10.7	8.8	11.5	9.5	9.3	8.9
	Ambient outside store	16.7	12.2	8.3	8.8	7.7	8.9	8.1	9.9	8

Appendix 6-7: JHP9 Gases In Pile – 2m From Bottom

JHP 9 2m from bottom of pile										
		22/10/2013	30/10/2013	06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013	17/12/2013
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	CO (ppm)	260	176	149	103	75	53	24	21	
	SO2 (ppm)	0.8	0.5	0.3	0.3	0.3	0	0	0	
	CO2 (%)	0.1	0.08	0.07	0.05	0.05	0.05	0.15	0.03	
	O2 (%)	20.4	20.4	20.5	20.6	20.6	20.9	20.9	20.9	
	VOC (ppm	0	20	18.3	18.4	17.7	13.5	9.2	12	

Appendix 6-8: JHP9 Gases In Pile – 4m From Bottom

JHP 9 4m from bottom of pile									
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
	CO	153	96	77	54	41	39	14	15
	SO2	0.7	0.4	0.2	0	0.2	0	0	0
	CO2	0.1	0.07	0.05	0.05	0.04	0.05	0.14	0.03
	O2	20.6	20.5	20.6	20.9	20.9	20.9	20.9	20.9
	VOC	0	20.4	17.3	17	15	13	9.9	7.5

Appendix 6-9: JHP9 Gases In Pile – 6m From Bottom

JHP 9 6m from bottom of pile									
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
	CO	38			18	16	26	1	8
	SO2	0.4			0	0	0	0	0
	CO2	0.05			0.04	0.03	0.05	0.14	0.03
	O2	20.9			20.9	20.9	20.9	20.9	20.9
	VOC				12.3	10.1	13.6	11.4	10.6

Appendix 6-10: JHP9 Gases In Pile – 2m From Bottom

JHP 11 2m from bottom of pile										
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	CO	500	452	370	267	190	131	19		45
	SO2	3.1	0.8	0.6	0.6	0.4	0	0		0
	CO2	0.17	0.16	0.14	0.12	0.1	0.1	0.15		0.04
	O2	19.8	19.9	20.1	20.9	20.5	20.9	20.9		20.9
	VOC		68	111.3	113.4	119.7	80.8	63	45.6	33

Appendix 6-11: JHP1 Gases In Pile – 2m From Bottom

JHP 11 4m from bottom of pile										
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	CO	197	140	106	83	64	48	27		22
	SO2	1.9	0.4	0.4	0.2	0	0	0		0
	CO2	0.08	0.06	0.06	0.06	0.05	0.05	0.15		0.03
	O2	20.5	20.5	20.6	20.9	20.9	20.9	20.9		20.9
	VOC		19	28.4	37	44.7	25.8	17.8	16.9	16

Appendix 6-12: JHP1 Gases In Pile – 4m From Bottom

JHP 11 6m from bottom of pile										
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	CO	24	14	13	14	12	8	6		3
	SO2	1.3	0.2	0	0	0	0	0		0
	CO2	0.03	0.03	0.03	0.03	0.03	0.05	0.15		0.03
	O2	20.9	20.9	20.9	20.9	20.9	20.9	20.9		20.9
	VOC		9	7.1	6	5.7	3.9	5.5	4.5	4.2

Appendix 6-13: JHP1 Gases In Pile – 8m From Bottom

JHP 11 8m from bottom of pile										
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	CO	5	3	4	14	7	2	0		0
	SO2	0.4	0	0	0	0	0	0		0
	CO2	0.03	0.03	0.03	0.05	0.03	0.05	0.15		0.03
	O2	20.9	20.9	20.9	20.9	20.9	20.9	20.9		20.9
	VOC		2.1	2.2	3.3	3	2.3	3.6	2.2	1.2

Appendix 6-14: JHP9 Microbiological

JHP 9 Microbiological									
		22/10/2013	30/10/2013	06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013
		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
	TVC	189	22	81		10	10		
	Total Fungi	77	101	55					

Appendix 6-15: JHP11 Microbiological

JHP 11 Microbiological									
		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
	TVC	420	70	77		24	4		
	Total Fungi	80	62	66			64		

Appendix 6-16: JHP9 Dust In Atmosphere

JHP 9 Dust										
		22/10/2013	30/10/2013	06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013	17/12/2013
		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Inhalable Dust	0.45	0.31	0.3		0.2	0.3	3.89		
	Respirable Dust	0.02	0.03	0.03		0.04	0.03	0.14		
	Max Inhalable Dust	10.05	3.16	6		1.75	10.07	20.45		
	Max Respirable Dust	0.11	0.07	0.13		0.25	0.19	0.32		

Appendix 6-17: JHP11 Dust In Atmosphere

JHP 11 Dust										
		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Inhalable Dust	0.62	0.91	0.38	0.72	0.25	0.29	2.57		1.69
	Respirable Dust	0.02	0.04	0.03	0.03	0.03	0.03	0.07		0.06
	Max Inhalable Dust	13.33	21.05	12.31	5.27	10.66	5.22	23.35		20.64
	Max Respirable Dust	0.24	0.41	0.35	0.06	0.17	0.16	0.46		0.55

Appendix 6-18: Personal Dust Monitoring

Personal dust										
		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Personal Dust JMA	5.77	5.41	5.27	5.49	3	5.32	0.72	2.08	3.93
	Personal Dust LB	5.53	5.64	4.72	5.47	4.2	6.34	2.26		5.73

Appendix 6-19: JHP9 Volatile Organic Compound In Atmosphere

JHP 9										
		22/10/2013	30/10/2013	06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013	17/12/2013
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Total hydrocarbons	0.83	0.83	0.83	0.83	3.67	0.84	0.83	0.84	
	Acetone	0.17	2.2	0.92	2.6	3.25	8.83	0.75	1.42	
	A-Pinene	1	1	1	0.92	1.08	0.84	0.25	0.42	
	Limonene	0.17	0.17	0.25	0.17	0.25	0.25	0.08	0.17	
	3-Carene	0.58	0.75	0.92	0.75	1.33	1.92	0.58	1.42	
	Terpinolene	0.25	0.25	0.25	0.25	0.25	0.26	0.25	0.26	
	Mycrene	0.25	0.25	0.25	0.25	0.67	0.75	0.25	0.26	
	Octanoic	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	
	Butanoic	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	
	Acetylaldehyde	0.89	1.56	1.56	1.41		4	1.93	3.04	
	Formaldehyde	0.008	0.008	0.03	0.01		0.02	0.02	0.02	
	Hexanal	1.56	2.22	2.3	1.78		3.93	1.78	2.22	
	Valeraldehyde	0.41	0.74	0.81	0.69		1.56	0.71	0.89	
	Furfural	0.04	0.04	0.04	0.04		0.04	0.04	0.04	
	Glutaraldehyde	0.008	0.008	0.008	0.008		0.008	0.008	0.01	

Appendix 6-20: JHP11 Volatile Organic Compound In Atmosphere

JHP 11										
	Gas	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Total hydrocarbons	0.83	0.83	0.83	0.83	0.83	0.84	0.83	0.84	0.83
	Acetone	0.17	0.17	0.17	0.17	0.17	1.17	0.42	0.17	0.17
	A-Pinene	0.25	0.25	0.25	0.25	0.25	0.17	0.25	0.26	0.25
	Limonene	0.08	0.08	0.08	0.08	0.08	0.09	0.08	0.09	0.08
	3-Carene	0.25	0.25	0.25	0.25	0.25	0.42	0.25	0.26	0.25
	Terpinolene	0.25	0.25	0.25	0.25	0.25	0.26	0.25	0.26	0.25
	Mycrene	0.25	0.25	0.25	0.25	0.58	0.84	0.25	0.26	0.25
	Octanoic	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
	Butanoic	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84
	Acetylaldehyde	0.04	0.03	0.29	0.73		0.6	0.89	0.65	0.26
	Formaldehyde	0.008	0.008	0.01	0.02		0.04	0.007	0.01	0.03
	Hexanal	0.05	0.07	0.36	0.74		0.5	0.65	0.45	0.21
	Valeraldehyde	0.02	0.02	0.13	0.29		0.19	0.27	0.19	0.11
	Furfural	0.04	0.04	0.04	0.04		0.04	0.04	0.04	0.04
	Glutaraldehyde	0.008	0.008	0.008	0.008		0.008	0.008	0.01	0.01

Appendix 6-21: JHP9 Volatile Organic Compound In Pile

JHP 9 2m								
		06/11/2013	14/11/2013	21/11/2013	28/11/2013	05/12/2013	10/12/2013	17/12/2013
	Gas	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Total hydrocarbons	17	23	21.2	0.84	0.83	4.33	
	Acetone	37	71	27.3	14.58	3.17	0.67	
	A-Pinene	1	1.9	1	0.75	0.5	0.42	
	Limonene	0.75	1.6	0.67	0.67	0.5	0.42	
	3-Carene	0.25	0.25	0.25	0.26	0.25	0.26	
	Terpinolene	0.25	0.25	0.25	0.26	0.25	0.26	
	Mycrene	0.25	0.25	0.92	1.08	0.42	0.33	
	Octanoic	0.09	0.09	0.09	0.09	0.09	0.09	
	Butanoic	0.84	0.84	0.84	0.84	0.84	0.84	
	Acetylaldehyde	7.85	6.07		5.48	3.56	2.67	
	Formaldehyde	0.04	0.06		0.04	0.04	0.05	
	Hexanal	0.05	2.07		2.44	2.59	2.44	
	Valeraldehyde	0.89	3.41		2.59	2.15	1.85	
	Furfural	0.07	0.05		0.09	0.06	0.04	
	Glutaraldehyde	0.008	0.008		0.008	0.008	0.01	

Appendix 6-22: JHP11 Volatile Organic Compound In Pile

JHP 11 2m								
	Gas	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9
	Total hydrocarbons	8.8	7.6	21	2.67	2	0.84	0.83
	Acetone	67	95	46	62.67	35	12.5	1.8
	A-Pinene	2.8	1.8	0.5	0.42	0.25	0.26	0.25
	Limonene	0.08	0.08	0.08	0.09	0.08	0.09	0.08
	3-Carene	0.25	0.25	0.25	0.26	0.25	0.26	0.25
	Terpinolene	0.25	0.25	0.25	0.26	0.25	0.26	0.25
	Mycrene	0.67	0.33	1	1	0.42	0.34	0.25
	Octanoic	0.09	0.09	0.09	0.09	0.09	0.09	0.09
	Butanoic	0.84	0.84	0.84	0.84	0.84	0.84	0.84
	Acetylaldehyde	9.85	4.74		5.85	6	9.26	3.56
	Formaldehyde	0.04	0.04		0.04	0.04	0.04	0.05
	Hexanal	0.5	3.11		1.78	1.93	1.7	0.41
	Valeraldehyde	1.63	2.96		2	1.85	1.56	0.47
	Furfural	0.04	0.04		0.04	0.1	0.04	0.04
	Glutaraldehyde	0.008	0.008		0.008	0.008	0.01	0.01

Appendix 7-1: Temperature In Base Of Dome By Quadrant

		20/11/2013	03/12/2013	12/12/2013	20/12/2013	07/01/2014	14/01/2014	22/01/2014	29/01/2014	11/02/2014	24/02/2014
	metres	Baseline	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
1	5				10.9	12.3	18.4	13.8	9.1	12.8	15.3
	10				10.7	12.5	18.1	14.1	10.8	12.6	15.4
	15				10.3	15.6	16.6	14.2	8.7	12.6	15.4
	20				11	17.5	17.6	10.5	9	12.7	15.5
	25				11	14.6	15.3	11	6.4	12.7	15.4
	30				13	14.6	15.3	11	8.3	12.9	15.4
	35				17.2	16.1	18.9	11.5	9.8	12.3	15.3
	40				16.7	18.2	16.6	12.1	7.1	12.9	15.3
	45				19.8	18.6	18.2	14	8.5	12.7	15.3
2	5			8.6	10.8	11.7	19	11.3	8.2	11.4	11.3
	10			11.8	12.7	12	14.3	11.5	8.3	11.3	11.3
	15			10.9	11.3	11.7	14.8	7.8	8.1	11.3	11.3
	20			9.7	11.8	11.8	17.1	15.7	7.2	11.4	11.4
	25			10.9	12.2	12.6	17.6	16.4	6.7	11.4	11.3
	30			9.8	12.5	11.8	17.7	9.2	7	11.3	11.3
	35			10.7	13.1	11.4	17.7	9.2	6.1	11.2	11.2
	40			9.3	12.7	13.3	17.6	13.5	6.7	11.1	11.3
	45			7.7	10.8	11.1	17.7	9.6	8.1	11.1	11.3
3	5			6.3	11.5	20.1	21.7	18.6	9.2	11.4	15.3
	10			8	10.2	13.6	16	18.1	9.3	11.5	15.3
	15			8.6	10.3	13.7	17	18.1	8.2	11.4	15.3
	20			7.6	10.8	18.5	24.1	15.2	10.3	11.5	15.3
	25			8.2	10.4	14.1	15.7	19.2	10.9	11.4	15.2
	30			14	12.5	17.3	9.8	18.4	8.6	11.4	15.3
	35			10.5	15.7	19.6	10.9	15	7.8	11.3	15.1
	40			8.6	16.6	19.2	20.6	15.3	8.5	11.4	15.2
	45			14	18.8	18.1	16.2	10.6	6.1	11.4	15
4	5			6.6	13.4	13.2	19.2	9.6	11.3	11	12.2
	10			9.5	13	12.4	11.9	13.7	10.7	11	12.3
	15			7.9	11.8	14.8	15.5	16.7	10.7	11	12.2
	20			6.6	12.1	14.1	17.4	17.4	10.2	11	12.2
	25			12.2	11.8	12.8	20.9	8.7	12.2	10.7	12.2
	30			9	12.5	14.1	14	19.2	11	11	12
	35			7.5	14.1	12.9	9.3	13.7	10.8	11	12.1
	40			8	13.5	13.2	10.1	15.6	11	11	12.1
	45			9.2	12.4	12.7	21.5	8.6	11.9	11	12.1

Appendix 7-2: Dust In Head Space Of Dome

Date	Description	Tonnage in dome	Fill rate	Duration of Monitoring	Filter Paper &	Filter Paper & Casing	Weight of Sample	Volume (l)	Ca TWA (mg/m^3)
11/03/2014	Dome 8 Background	68932	N/A	58	1287.22	1294.17	6.95	116	60
11/03/2014	Dome 8 train @ 11:07	70074	1655	125	1208.67	1209.93	1.26	250	5
12/03/2014	Dome 8 Background	68827	N/A	43	1412.94	1414.54	1.60	86	19
12/03/2014	Dome 8 train @ 11:07	69926	1582	88	1253.30	1286.43	33.12	176	188
12/03/2014	Dome 8 train @ 11:07	69926	1582	88	1505.33	1556.12	50.79	176	289
13/03/2014	Dome 8 Background	69213	N/A	52	1255.92	1257.16	1.24	104	12
14/03/2014	Dome 8 Background	69511	N/A	117	1278.79	1279.31	0.51	234	2
14/03/2014	Dome 8 Background	69511	N/A	117	1248.18	1248.74	0.56	234	2
17/03/2014	Dome 10 Background	16677	N/A	45	1246.15	1246.31	0.16	90	2
17/03/2014	Dome 10 @11:07	18009	1751	107	1225.79	1269.73	43.94	214	205
17/03/2014	Dome 10 @11:07	18009	1751	107	1432.94	1477.04	44.10	214	206
19/03/2014	Dome 8 Background	69104	N/A	58	1257.92	1268.36	10.44	116	90
19/03/2014	Dome 8 @11:07	72261	1866	112	1286.23	1431.15	144.92	224	647
19/03/2014	Dome 8 @11:07	72261	1866	112	1254.98	1356.50	101.52	224	453
21/03/2014	Dome 10 Background	4252	N/A	32	1515.58	1520.28	4.69	64	73
21/03/2014	Dome 10 @11:07	7214	1763	109	1270.61	1325.20	54.60	218	250
21/03/2014	Dome 10 @11:07	7214	1763	109	1274.84	1349.84	75.01	218	344

Appendix 7-3: Dome Gases In Head Space

Dome 10				
	17/03/2014	21/03/2014	28/03/2014	09/04/2014
VOC		7.3	14.8	5.8
CO	15	15	15	160
CO2	0.03	0.03	0.03	0.07
O2	20.9	20.9	20.8	20.4
SO2	0	0	0	1.3

Appendix 7-4: Dome In Pile Volatile Organic Compound

	20/11/2013	03/12/2013	12/12/2013	20/12/2013	07/01/2014	14/01/2014	21/01/2014	29/01/2014	11/02/2014	24/02/2014
	Baseline	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
1	1.4	6.6			6.9	2.4	2.6	0.2	5.4	
2	3	3	4		10.3	11.1	12.8	8.2	4.5	
3	2.5	16	4.5		15.7	10.4	0.3	1.6	4	
4	2.3	7.6	3.5		12.5	1.8	0.8	2.8		

Appendix 7-5: Dome In Pile CO

	Baseline	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
1	0	60			0	20	0	7	15	81
2	0	65	32		45	20	30	30	70	80
3	0	73	44		35	40	50	39	30	97
4	0	60	30		65	35	20	23	35	82

Appendix 7-6: Dome In Pile CO_2

	Baseline	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
1	0.05				0.03	0.02	0.03	0.03	0.02	0.03
2	0.05		0.04		0.02	0.03	0.01	0.03	0.03	0.03
3	0.05		0.05		0.02	0.03	0.03	0.02	0.03	0.05
4	0.05		0.04		0.03	0.02	0.02	0.1	0	0.03

Appendix 7-7: Dome In Pile O_2

	Baseline	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
1	20.9	20.3			15.8	14.9	10.3	5	20	19.7
2	20.9	20.3	20.9		9.9	18.9	7	5	16.7	19.7
3	20.9	20.3	20.9		9.5	18.9	13	14.1	19	19.4
4	20.9	20.3	20.9		8.2	16.6	10.9	16.6	17.6	19.5

Appendix 7-8: VOV's In Head Space Of Dome

Gas	11/03/2014	19/03/2014	09/04/2014
Tonnage	68932	72261	75065
Total hydrocarbons	2.42	3.92	3.7
Acetone	1.17	3.83	18
A-Pinene	0.25	0.25	0.33
Limonene	0.08	0.08	0.08
3-Carene	0.25	0.25	0.25
Terpinolene	0.25	0.25	0.25
Mycrene	0.25	0.42	0.25
Acetylaldehyde	0.78	1.25	2.17
Formaldehyde	0.02	0.01	0.01
Hexanal	0.02	0.92	0.33
Valeraldehyde	0.1	0.56	0.49
Furfural	0.04	0.04	0.05
Glutaraldehyde	0.04	0.13	0.33

Appendix 7-9: Volatile Organic Compound In Base Of Dome Quadrant 1

	07/01/2014	14/01/2014	21/01/2014	29/01/2014	11/02/2014	24/02/2014
Gas	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
Total hydrocarbons	0.83	0.83	0.83	1.17	24.17	4.17
Acetone	0.17	2.08	0.17	0.25	0.17	0.58
A-Pinene	0.28	3.58	0.25	0.25	0.25	0.25
Limonene	0.08	0.17	0.08	0.08	0.08	0.17
3-Carene	0.25	0.25	0.25	0.25	0.25	0.25
Terpinolene	0.25	0.25	0.25	0.25	0.25	0.25
Mycrene	0.25	0.25	0.25	0.25	0.25	0.25
Acetylaldehyde	0.04	0.12	0.04	0.08	0.08	0.16
Formaldehyde	0.009	0.009	0.009	0.01	0.009	0.008
Hexanal	0.05	0.06	0.02	0.03	0.04	0.07
Valeraldehyde	0.02	0.03	0.1	0.02	0.02	0.04
Furfural	0.05	0.05	0.05	0.05	0.05	0.05
Glutaraldehyde	0.009	0.009	0.009	0.01	0.009	0.009

Appendix 7-10: Volatile Organic Compound In Base Of Dome Quadrant 2

Gas	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
Total hydrocarbons	2		0.25	1.08	4.75	4.17
Acetone	0.17		0.17	0.42	0.92	2.75
A-Pinene	1.92		0.25	0.25	0.25	0.25
Limonene	0.08		0.25	0.08	0.42	0.25
3-Carene	0.25		0.08	0.25	0.25	0.25
Terpinolene	0.25		0.25	0.25	0.25	0.25
Mycrene	0.58		0.25	0.25	0.58	0.42
Acetylaldehyde	0.18		0.2	0.16	0.42	0.73
Formaldehyde	0.009		0.009	0.02	0.02	0.02
Hexanal	0.13		0.02	0.1	0.32	0.28
Valeraldehyde	0.05		0.03	0.05	0.1	0.18
Furfural	0.05		0.05	0.05	0.05	0.05
Glutaraldehyde	0.009		0.009	0.01	0.009	0.009

Appendix 7-11: Volatile Organic Compound In Base Of Dome Quadrant 3

Gas	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
Total hydrocarbons	3.17	0.83	0.25	2	0.83	5.5
Acetone	2.58	0.17	0.17	0.5	0.25	3.33
A-Pinene	4.17	0.25	0.25	0.25	0.25	0.25
Limonene	0.17	0.08	0.08	0.08	0.17	0.17
3-Carene	0.25	0.25	0.25	0.25	0.25	0.25
Terpinolene	0.25	0.25	0.25	0.25	0.25	0.25
Mycrene	0.25	0.25	0.25	0.25	0.25	0.58
Acetylaldehyde	0.27	0.22	0.15	0.31	0.21	0.78
Formaldehyde	0.02	0.009	0.009	0.01	0.02	0.009
Hexanal	0.16	0.12	0.02	0.16	0.21	0.67
Valeraldehyde	0.08	0.06	0.02	0.07	0.06	0.39
Furfural	0.05	0.05	0.05	0.05	0.05	0.05
Glutaraldehyde	0.009	0.009	0.009	0.01	0.009	0.009

Appendix 7-12: Volatile Organic Compound In Base Of Dome Quadrant 4

Gas	Week 4	Week 5	Week 6	Week 7	Week 9	Week 11
Total hydrocarbons	2.5		0.25	0.83	0.83	2.42
Acetone	1.92		0.17	0.17	0.25	0.17
A-Pinene	1.92		0.25	0.25	0.25	0.25
Limonene	0.08		0.08	0.08	0.08	0.08
3-Carene	0.25		0.25	0.25	0.25	0.25
Terpinolene	0.25		0.25	0.25	0.25	0.25
Mycrene	0.67		0.25	0.25	0.25	0.25
Acetylaldehyde	0.42		0.13	0.62	0.13	0.02
Formaldehyde	0.008		0.009	0.02	0.009	0.009
Hexanal	0.34		0.02	0.4	0.04	0.02
Valeraldehyde	0.13		0.03	0.17	0.03	0.02
Furfural	0.05		0.05	0.05	0.05	0.05
Glutaraldehyde	0.009		0.009	0.01	0.009	0.009