

Chapter 1:

Introduction

1.1 Scope of the project

The work contained within this thesis was part of a larger project, which aimed to develop sustainable materials utilising indigenous UK renewable materials at all stages of production. A biorefinery approach was envisioned to produce general purpose boards utilising waste biomass derived substituents as both the substrate and the binder (Figure 1.1).

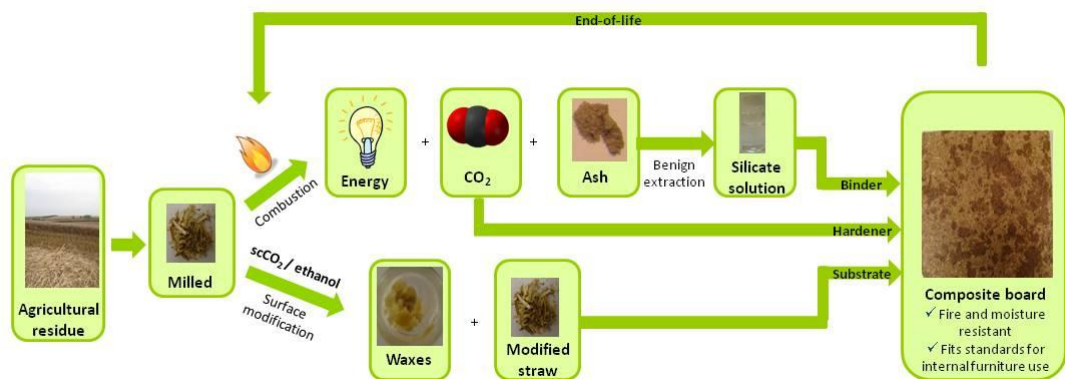


Figure 1.1: Concept for the formation of inorganic composite boards utilising waste materials throughout (Originally in colour)

The work within this thesis focused on one aspect of this project; understanding the formation of combustion residues from agricultural wastes and the production of alkali silicate solutions from those wastes as a binder for composite boards. To this end several avenues of research were explored.

The impacts of the combustion process on the inorganic species within the combustion material. One variety of wheat straw was investigated in detail to understand the impact of combustion conditions on the mineralogical, physical and chemical characteristics of the ashes and chars formed. Work focused on the extraction and aqueous solubility of all elements and their interdependency, with a particular emphasis on silicon and potassium. Previous work has concentrated on the impact of inorganic species, mostly alkali metals and halogens, on combustion properties.¹ However, understanding of the formation of combustion residues and specifically how this impacts on their utilisation as a valuable material has received limited attention in the scientific literature.

Variation between wheat straw varieties and different biomass materials. Several varieties of wheat straw collected over three years, along with wood chips and miscanthus straw, were compared to understand the impact of the initial elemental composition on the physico-chemical characteristics of the ashes formed and the extraction of elements. This is vital for understanding how the wheat straw variety, growing conditions and biomass species affect the use of the combustion residues formed.

Pretreatment of wheat straw. The negative impacts of alkali metals and halogens on combustion in large scale boilers has led to research studies into the extraction of these elements prior to combustion.² Other researchers have looked at the valorisation of wheat straw by the extraction of high value epicuticular waxes.³ However, the impact of these pretreatment processes on the mineralogical composition and extraction of combustion residues was previously unstudied.

Alkali silicate from biomass-fired combustion boiler residues as a binder in composite boards. The formation of an alkali silicate solution from biomass-fired boiler combustion residues was investigated and utilised as a binder to form particleboards. The use of alkali silicates hasn't previously been demonstrated as a binder at low concentrations for lignocellulosic substrates.

1.2 The Challenge: Climate Change, Peak Oil and Green Chemistry

The concept of sustainability has developed as a key idea for how all human needs can be met within the boundaries of the finite resources available on earth, such that in the future these needs could be met indefinitely. The key definition of sustainable development was coined by the Brundtland Commission in 1987 as development that “meets the needs of the present without compromising the ability of future generations to meet their own needs”.⁴ It links environmental, social and economic sustainability.

The need to incorporate sustainability into all aspects of our lives has never been greater at a time when we face two great challenges: the end of cheap and abundant petroleum sources and the impact of climate change from the unsustainable use of fossil fuels.

Over the past 50 years the economies of the most industrialised and more-economically developed countries have rapidly expanded, based on cheap and abundant fossil fuels as the lifeblood for everything from agriculture to consumer products, energy and transport. Demand for oil is continuing to grow as many of the least-economically developed countries, particularly China, the Middle East and Brazil, follow the same developmental route.⁵ As the available, and easily extractable, oil reserves are depleted and as demand continues to grow we will reach a global point of 'peak oil', where demand will overtake the ability to increase total production.⁶ This could result in extremely high oil prices, with detrimental impacts for everyone in society, unless alternative solutions are found in anticipation of these problems. The chemical industries are particularly dependent on petrochemicals as the building block for almost all products developed over the past century, with 98% of organic chemicals produced in the United States coming from petroleum feedstocks in 1998.⁷ This makes these industries highly susceptible to changes in the economics of oil supply and demand and therefore they must be at the forefront of finding sustainable alternatives.

In addition, our use of fossil fuels has had a major impact on the wider environment, increasing the amount of atmospheric carbon dioxide from 280 ppm at pre-industrial levels to 379 ppm in 2005, and exceeding the measured natural range over the past 650,000 years.⁸ The mean global temperature has increased by $0.74\text{ °C} \pm 0.18\text{ °C}$ over the past 100 years, with scientific evidence indicating that it is extremely likely that there has been a substantial contribution from anthropogenic induced warming.⁹ The probable result will be large changes to the global climate system over the coming centuries, resulting in challenges for ecosystems, including human, across the world.⁸

This combination of peak oil and climate change, relating to our unsustainable use of fossil fuels, along with the political, economic and social pressure to 'do something about it' has created a driving force which demands that the current 'business as usual' model for energy production and the chemical industries must change.

An additional important, but frequently neglected, issue is the increasing scarcity and cost of a wide range of elements.¹⁰ The price of indium, used for LCD screens and solar cells, stayed relatively stable from the 1980s up to the year 2000, at between $\$85\text{-}200\text{ kg}^{-1}$, but has since dramatically increased to a maximum of $\$918\text{ kg}^{-1}$ in 2006, reducing to $\$500\text{ kg}^{-1}$

in 2009 due to the global recession.¹¹ It is predicted that indium could be depleted within 5-10 years.¹⁰ Even the price of potash, the soluble source of the vital plant nutrient potassium, has been steadily increasing from \$280 t⁻¹ in 2005 to \$820 t⁻¹ in 2009.¹² With 93% of the worldwide production being used as a fertiliser, this is a vital concern for the agricultural industry. This underscores the necessity to ensure complete recovery, recycling and reuse of all elements; 'elemental sustainability', not just carbon in a biorefinery approach.

A green chemistry approach aims to tackle these challenges by utilising renewable resources and developing new techniques and tools that will enable innovative and novel sustainable chemicals for human needs to be manufactured. In 1996, the International Union of Pure and Applied Chemistry (IUPAC) defined Green Chemistry as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances".¹³ Anastas and Warner described 12 fundamental principles setting out how this can be achieved:⁷

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.

8. Unnecessary derivatisation (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents.

The overall concept that integrates all of these principles is 'benign by design'; incorporating these principles at the beginning of the design and research process. The wider project that this work is part of exemplifies these principles by aiming to utilise waste and renewable feedstocks (principles 1 and 7), incorporate all parts of the initial material into the final product (principle 2), reduce energy use during manufacturing (principle 6) and design for utilisation at end-of-life (principle 10), whilst also taking into account the broader aspects of sustainability.

1.3 Energy from biomass

In order to tackle these sustainability challenges, several pieces of legislation have been implemented globally and nationally. The Climate Change Act commits the UK to cutting levels of greenhouse gas emissions by 80% by 2050 on the 1990 baseline.¹⁴ In the shorter term, the UK is also legally bound to produce 15% of all energy and 10% of road energy from renewable resources by 2020 under the EU Renewable Energy Directive (RED).¹⁵

In 2008, the UK produced 533 million tonnes of CO₂, 10% below the 1990 baseline.¹⁶ The majority of these emissions were produced during energy generation and transportation and attributed to transportation, electricity and heating, particularly by businesses and domestic dwellings (Figure 1.2). Of these emissions, 43% came from the use of gas, 30% from oil, 22% from coal, 2% from other solid fuels and 3% from non-solid fuel sources.¹⁶

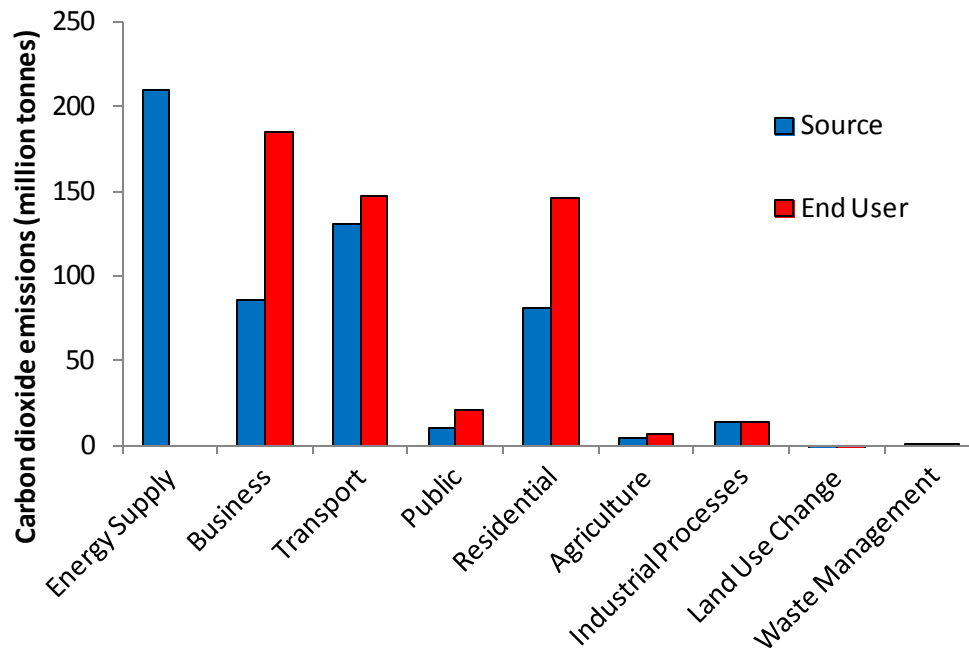


Figure 1.2: UK 2008 CO₂ emissions by sector attributed either to the source of the emissions or the end user¹⁶ (Originally in colour)

This highlights the huge challenge faced in switching the UK away from its current dependence on fossil fuels and reducing greenhouse gas emissions by the level required. The necessity for this is noticeably acute in energy production.

Biomass is a carbon source that is renewable over a short timescale, by fixing CO₂ during growth via photosynthesis and releasing it during decomposition. Biomass is potentially the only globally distributed indigenous material capable of replacing all aspects of fossil fuel usage to produce electricity, heat, solid, liquid and gaseous fuels and materials (Figure 1.3).

Both Defra's 2007 'UK Biomass Strategy' and the Department for Energy and Climate Change's 'Renewable Energy Strategy 2009' demonstrate varied opportunities for the utilisation of biomass to help meet the UK's legislative demands.^{17, 18} The UK Government predicts that 5% of the nation's heat and power (70 TWh) could be cost-effectively generated from indigenous biomass by 2020.¹⁷ Currently, combustion remains the default technology for energy production from biomass and wastes due to the lower technological hurdles.¹⁹ However, other technologies such as anaerobic digestion, gasification and pyrolysis are being extensively explored.

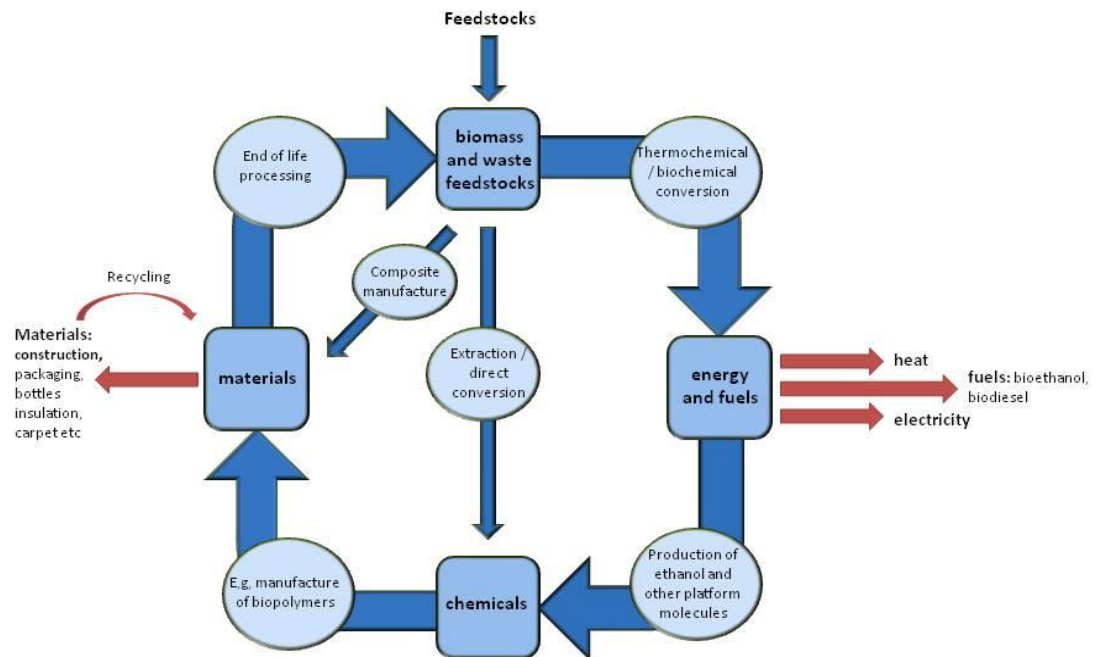


Figure 1.3: The potential of biomass for creating energy, fuels, materials and chemicals (developed from Ref 20) (Originally in colour)

1.3.1 Potential biomass sources

The potential of different indigenous biomass feedstocks to contribute to energy production in the UK are listed in Table 1.1 from modelling taking into account competing resource demands and technical, environmental and supply constraints.²¹ This data indicates that agricultural crop residues and wood wastes currently offer the largest potential source of biomass for energy via thermochemical conversion, particularly when unsuitable wet organic materials are excluded. Miscanthus and short rotation coppice (SRC) have the potential to provide a large energy resource in the future on environmentally sustainable land.²¹ UK and EU Governments are incentivising the planting of these perennial biomass crops due to their high yields, low fertiliser requirements and predicted high greenhouse gas emissions savings.²²

Worldwide an estimated 95-115 EJ γ^{-1} of energy could be extracted sustainably from forestry and crop residues by 2050, with 53-61% of this coming from crop residues.²³ An additional 232-1349 EJ γ^{-1} could be available from dedicated energy crops on surplus agricultural land.²³ This compares to a total global primary energy demand of 517 EJ in 2010.²⁴ The variation in potential energy production from biomass particularly depends

on land-use requirements for animal products (using more than 70% of global agricultural land in 2002), and technological advancements in food production.²³

This investigation focuses on crop residues as one of the largest, most widely available and least studied sources of biomass for energy production. In addition, comparisons are made to waste wood and energy crops as alternative current and future sources of biomass for energy.

Table 1.1: Energy potential of UK biomass feedstocks²¹

Feedstock	Sources	Energy potential 2009 (PJ y ⁻¹)	Energy potential 2020 (PJ y ⁻¹)
Energy crops	Short rotation coppice (SRC) willow or poplar, and miscanthus	0-20	150-180
Crop residues	Straw from crops including wheat and oil seed rape	69 (not all collected)	69 (100% collected)
Stemwood	Hardwood and softwood tree trunks	4.5	17.5
Forestry residues	Wood chips from branches, tips and poor quality stemwood	0	19.3
Sawmill co-product	Wood chips, sawdust and bark made when sawing stemwood	2.4	19.5
Arboricultural arisings	Stemwood, wood chips, branches, foliage from municipal tree surgery operations	1.5 (+4.6 currently landfilled)	3.2
Waste wood	Clean and contaminated waste wood	19	149 (in 2030)
Organic waste	Paper/card; food/kitchen; garden/plant and textiles wastes	40 (13; 10; 16; 1 respectively)	40
Sewage sludge	From Waste Water Treatment Works	15.2	24.6
Animal manures	Manures and slurries from cattle, pigs, sheep and poultry	0.27	5.8
Total maximum energy potential (PJ)		171.9	527.9

1.3.2 Agricultural residue availability in the UK

In 2008 James Copeland and David Turley studied the national and regional supply/demand balance of agricultural straws in the UK.²⁵ They found a potential total annual straw yield of 11.9 million tonnes from wheat (54%), oilseed rape (21%), barley (20%), oats (4%), other cereals (1%) and linseed (0.1%).²⁵ After calculating the current straw use in the livestock and mushroom industries they estimated that there is a 3 million tonne annual cereal straw surplus (mainly wheat), concentrated in the East of England. In

addition, 2.5 million tonnes of oilseed rape straw could be available that isn't presently recovered. However, the report also stressed the nutrient value, particularly of potassium, of the straw that is removed.²⁵ The study by Copeland and Turley clearly identified wheat straw as the most abundant agricultural residue available in the UK. The decision to focus on an understanding of the utilisation of indigenous agricultural residues therefore led to the choice of wheat straw as the main focus of this investigation, with some comparisons to other crop residues. As one of the main staple crops grown across the world, the results and lessons learnt from this study may also be applicable more widely.

1.3.3 Biomass composition

The composition of biomass varies depending both on the species and the geographic location in which it has been grown. Nevertheless, in general, crop residues, such as cereal straws, consist of five main components: cellulose, hemicellulose, lignin, extractives and ash. Typical values for herbaceous plants range from 40-50% cellulose, 20-40% hemicellulose, 15-20% lignin and 5-10% extractives.²⁶ Woody biomass generally has a higher lignin but lower hemicellulose content.

In terms of energy production, the polysaccharide content of biomass makes the material much more oxygen rich than coal, with materials with a higher lignin content having a lower O/C ratio and a corresponding higher calorific value.²⁷ Additionally, in comparison to coal, biomass contains more moisture, has a lower density, contains less sulfur, less nitrogen, more silica, potassium and chlorine, less aluminium and iron and has a lower heating value.²⁸ Some of these differences are beneficial, whilst others create technological challenges. High moisture contents reduce the thermal efficiency of combustion, can cause problems during ignition and lower the maximum flame temperature.²⁹ The optimal moisture content is around 15%, although furnaces can usually cope with a maximum of 65% moisture.³⁰ Chopped straw has a bulk density of 50-120 kg m⁻³ compared to 800-900 kg m⁻³ for bituminous coals.³¹ This increases both the carbon and monetary costs of transportation, reduces the heating value per unit volume, and makes it difficult to continuously feed the straw and control the rate of burning.^{29, 31} Densification of biomass to 500-1000 kg m⁻³ is possible using several different technologies, such as pelletisation, however it increases the production cost.³⁰ A more

decentralised system of smaller energy facilities is therefore attractive to reduce transportation distances, despite the increased capital costs and labour requirements.³¹ Increasing job creation in rural areas is, however, beneficial and is an argument in the UK Government's desire to create a 'greener' economy.

A wide variation in the ash content and distribution of inorganic species can be observed both within agricultural residue types and between them (Table 1.2). Irrigation and fertiliser usage in the growth of herbaceous plants leads to higher contents for almost every inorganic species in comparison to wood.² The alkali content is, in particular, much higher in the herbaceous materials in comparison to the woody and coal sources. Silica and potassium are the two major ash forming species for all of the agricultural residues, excluding rape straw. The mix of inorganic species within each material affects both the combustion properties of the fuel and the design and operation of combustion systems. These issues are discussed in more detail in section 1.4.2.

Table 1.2: Ash content, elemental composition and calorific value data for a variety of biomass materials and coal

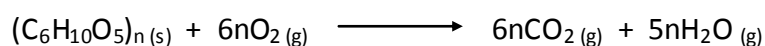
Residue type	Ash (wt% dry basis)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl	HHV (MJ / kg dry basis)	Alkali index (kg M ₂ O / GJ)	Ref	
Wheat straw	Imperial Valley (USA)	12.8	35.8	2.5	1.0	4.7	2.5	10.5	18.4	5.5	1.5	14.7	17.2	2.15	2
	(China)	10.0	36.9	8.0	6.3	8.1	3.0	9.2	17.4	4.5	2.0	5.2	16.2	1.64	32
	2000 (Denmark)	4.8	35.3	1.1	0.1	10.2	2.4	0.5	30.1	6.2	2.6	3.4	16.8	0.88	33
	Soisson (Spain)	5.7	64.0	0.3	0.2	5.4	1.8	0.1	17.0	1.8	1.6	2.8	16.3	0.60	33
	2001 (Denmark)	4.8	67.0	0.2	0.2	8.7	2.2	0.1	14.0	2.2	2.4	2.1	17.4	0.39	33
	Marius (Spain)	4.9	65.0	0.8	0.6	11.0	1.7	0.1	9.1	2.5	2.3	1.2	17.1	0.26	33
Other agricultural straws available in UK	Winter barley	6.9	25.2	0.2	0.1	6.9	2.2	5.1	40.2	5.1	1.9	6.9	16.5	1.89	33
	Spring barley	5.7	37.2	nd	nd	12.5	1.0	0.9	17.8	2.7	1.4	1.4	nd		33
	Oat straw	3.8	15.2	0.3	0.1	26.5	3.3	4.5	17.4	6.4	6.7	0.8	17.4	0.48	33
	Rape straw	2.7	2.4	4.2	1.6	48.7	3.1	0.2	15.2	3.8	1.4	0.5	17.0	0.24	33
Agricultural residues around the world	Rice straw	20.9	72.3	0.1	0.3	2.1	2.1	2.7	11.8	1.1	1.8	4.1	14.7	2.05	2
	Cotton straw	7.4	17.7	10.8	2.4	9.0	7.3	6.8	30.2	5.8	4.3	4.9	15.9	1.73	32
	Maize	7.1	33.0	3.7	1.6	17.0	4.4	0.4	22.0	1.7	1.9	5.4	16.4	0.97	33
	Sugarcane bagasse	8.5	42.6	23.2	16.2	3.0	2.0	0.6	3.0	0.5	1.3	0.1	17.7	0.17	2
	Switchgrass	3.8	62.8	0.3	0.9	6.2	1.7	0.4	11.7	1.5	4.2	0.1	18.7	0.24	2
Wood	Wood fuel	4.5	37.5	14.1	0.6	7.6	17.0	3.6	1.4	2.2	6.0	2.2	18.7	0.12	2
	Red Oak	1.2	38.3	8.1	7.6	12.8	1.0	0.4	8.6	1.8	1.0	<0.01	19.0	0.06	34
Macroalgae	<i>Laminara digitata</i>	25.8	0.4	0.1	1.0	5.0	5.2	19.6	14.8	-	6.7	-	17.6	3.23	35
Coal	Eastern Kentucky	7.6	51.6	32.5	4.5	1.1	0.4	0.2	1.3	1.3	0.3	2.3	31.0	0.04	34

1.4 Combustion of biomass and the impact of inorganic species

The process of burning biomass is one of the oldest and simplest chemical conversions carried out by mankind. Globally, biomass still provides around 14% of the world's energy requirement, and 35% of the energy in developing countries.²⁸ But as described by Petterson *et al.*:³⁶

“It is easy to start a fire, but to burn a fuel at optimal conditions regarding complete combustion, clean exhaust gases with respect to NO_x, SO_x, HCl, HF and trace element emissions as well as to achieve reliable operation conditions is altogether a challenge.”

The stoichiometric equation for the combustion of biomass using the basic empirical formula for cellulose can be represented as:



Thermogravimetric analysis has been used to identify the stages of biomass combustion.²⁶ An initial mass loss up to 120 °C is caused by evaporation of the contained moisture along with high-energy volatiles. The main mass loss occurs between 180 – 375 °C as the solid lignocellulosic material begins to decompose and devolatilise releasing organic compounds that burn in the gas phase.³⁰ This step is similar to the processes occurring during pyrolysis. Research within the latter area has given rise to a 3-component model: hemicellulose and cellulose decompose in parallel and are mainly responsible for the mass loss, whilst lignin decomposes over a broader temperature range and is responsible for the majority of the char formed.²⁶ At higher temperatures (375 – 525 °C), in an oxygen-rich atmosphere, the residual chars combust at a slower rate.³⁰

1.4.1 Combustion technologies

The main aims in combustion systems are to maximise boiler efficiency for the production of steam and to minimise undesirable gas emissions.³⁰ The two main biomass combustion technologies in use are grate-fired and fluidised bed combustion (FBC) boilers.³⁷

1.4.1.1 Grate fired combustion

Grate-fired boilers vary in capacity from around 4-200 MW and consist of (Figure 1.4):

1. A fuel feeding system
2. Grate assembly
3. Secondary air supply
4. Ash discharge system
5. Heat exchange system

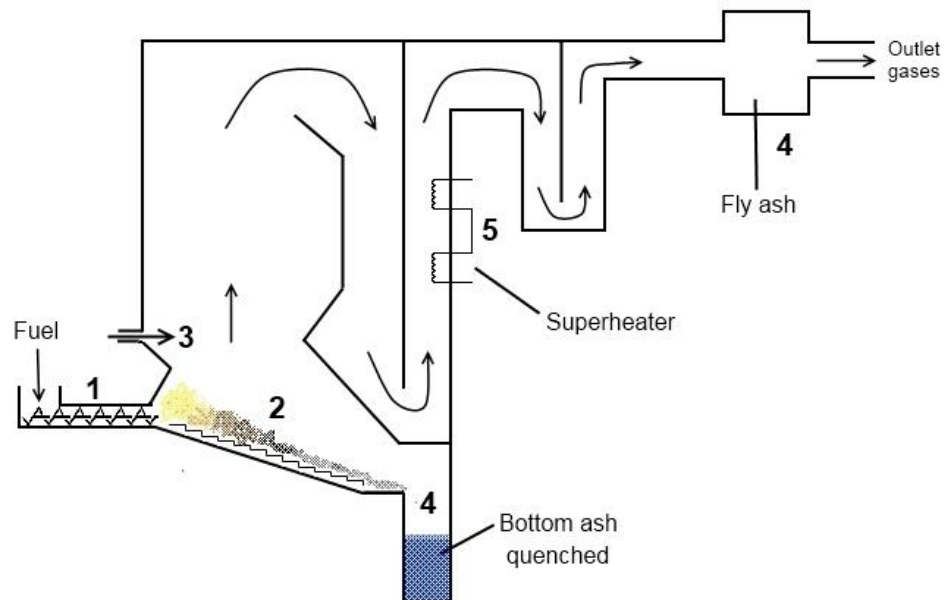


Figure 1.4: Basic grate-fired biomass combustion plant design (Originally in colour)

The grate assembly is responsible for ensuring good mixing of the fuel and that there is a sufficient air flow and residence time for the complete combustion of slower burning chars.²⁹ Generally a residence time of 20-40 minutes is required.³⁸ The top layer of the fuel ignites due to radiant heat from the furnace and flames above the bed.³⁹ The flame front moves down through the bed against the primary air supply. After reaching the grate a char burnout front moves in the opposite direction. Primary air is injected up through the grate. In modern systems a substoichiometric amount of air is likely to be added, with a secondary air supply added higher up in the furnace box.^{30, 40} This helps to ensure complete combustion to prevent emissions of pollutants such as hydrocarbons (C_xH_y), CO, particulates and polyaromatic hydrocarbons.⁴¹ It can also prevent NO_x emissions and volatilisation of inorganic species by enabling a lower temperature and less air to be used at the fuel bed.⁴²

The hot flue gases transfer heat to water cooled tubes in the superheaters. Additional economisers capture the waste heat by heating the boiler feedwater. The bottom ash that falls through the grate is discharged to an ash receptacle and is often quenched in water.⁴³ Fine particulate fly ash, which has followed the flue gases, is collected in bag filters.⁴³

Few studies indicate the actual grate temperature in industrial combustion units, however, furnace gas exit temperatures and furnace temperatures are typically between 800 – 900 °C; flame temperatures above the grate may be higher.⁴⁴ In Denmark, the Government's requirement to burn large volumes of straw since 2004, has led to the development of dedicated straw-fired co-generation plants which can operate at lower furnace exit gas temperatures of 640 - 760 °C.⁴⁵ An additional superheater, utilising gases from straw pyrolysis, can be used to superheat the steam for power generation.

1.4.1.2 Fluidised bed combustion

In fluidised bed combustion (FBC) an inert refractory material, usually silica sand,³⁶ is used as the bed material, with the fuel suspended within it. Air is added through a hole under the bed, which increases the volume of the bed, causing it to become 'fluidised'.³⁰ The constant movement of the bed material improves the temperature distribution, ensures intimate mixing of the fuel and oxidant and enables the addition of additives, such as limestone, to minimise pollutants.³⁰

Both of these technologies are flexible to a wide variety of fuels and are used at dedicated biomass facilities around the world, with FBC a more recent technological development. However, despite some advantages, the latter is prone to bed agglomeration when using high alkali fuels, such as straw, and the initial capital and maintenance costs are higher.³⁷ The research contained within this thesis did not study fluidised bed combustion as the travelling grate boiler is the most common design for biomass combustion and produces an ash material based only on the initial elemental composition of the fuel is formed.⁴⁶

1.4.2 Impact of inorganics during grate-firing of herbaceous biomass

Within the past decade, extensive investigations have been undertaken into the combustion of wheat straw.^{1, 32, 40, 45, 47-52} This has been due to both an explosion of

interest in the production of energy from renewable fuels and the realisation of the difficulties in utilising straw in traditional combustion boilers.^{1, 42} The combustion of wheat straw has been found to differ greatly to coal and woody biomass sources. This is primarily due to its distinct ash chemistry, including higher total ash content, alkalinity, chlorine and silica content (Table 1.2), resulting in lower ash melting points.⁵³ The impact of this can be severe slagging, fouling and corrosion.

Fouling is the deposition of solid materials on heat transfer zones, such as superheaters, beyond the furnace cavity.⁵⁴ Slagging is the formation of fused or sintered materials on radiant heat transfer surfaces within the furnace cavity, or of agglomeration of fluidised-bed materials.³⁷ These problems have been found to occur extensively during the combustion of wheat straw, in particular, decreasing the thermal efficiency of the system and at its worse causing the shutdown of boilers.^{33, 44-46, 55, 56} In California, none of the biomass power plants built have been able to burn straw due to these problems.¹

The main causes of fouling, slagging and corrosion from herbaceous materials are:

1. The reaction of potassium with silica, with chlorine as a facilitator causing the formation of low temperature eutectics.⁴⁴
2. The reaction of potassium with sulfur to form potassium sulfates on superheater surfaces.¹
3. High gas phase concentrations of KCl deposited by condensation on heat-transfer surfaces.³³
4. Corrosion induced by chlorine on superheater surfaces.

The impacts of the three main ash forming components in wheat straw are discussed in more detail below.

1.4.2.1 Potassium

Studies indicate that potassium is present in biomass as cations associated with oxygen-containing functional groups or precipitated as chloride, carbonate, oxalate or sulfate salts.⁵² Chemical fractionation suggests that 70-80% of the potassium present is either water soluble or ion exchangeable.⁴⁶ In comparison, in coal the alkali metal is usually bound within stable minerals.⁵⁷

In laboratory studies, potassium losses during wheat straw combustion positively correlate with temperature.⁵⁶ Evolution has been observed to occur over two stages: a small amount at lower temperatures (180-500 °C), suggested to be due to release of potassium associated with organic species;⁵² and 50-90% at higher temperatures (> 700 °C).³⁸ Correlation with chlorine losses intimates that the majority of this is due to the vaporisation of sylvite, with KCl amongst the most stable gas-phase alkali containing species,¹ however, some of the potassium is still retained in the ashes.⁵⁶ STA studies imply that this is a result of the reaction of K_2CO_3 with SiO_2 ,³³ with more potassium captured in the bottom ashes in higher silica content straws.^{38,50}

Potassium can also influence the combustion and pyrolysis processes, with the onset of devolatilisation and the char burnout phase observed to occur at lower temperatures when even a small amount of potassium is present.⁵²

1.4.2.2 Chlorine

The high chlorine content of wheat straw can cause corrosion on the surface of superheater tubes.²⁸ Lab-scale studies differ in their observations of the temperature of chlorine loss. Some have noted 25-70% of chlorine to be released at < 500 °C with the remainder above 700 °C.³⁸ Others have only detected chlorine losses to occur above 770 °C due to the vaporisation of sylvite.⁵⁶ Many researchers have highlighted that chlorine, rather than alkali concentration in fuels, can be the limiting factor in controlling the total amount of alkali volatilised by supporting the transfer of alkali to the surface of the fuel.⁴⁶

1.4.2.3 Silicates

Potassium silicate eutectics formed in the combustion bed can melt or soften at temperatures as low as 700 °C.¹ Ternary silicates, containing a small quantity of sodium, can have liquidus temperatures as low as 540 °C.⁴⁰ Equilibrium calculations of the combustion of wheat straw indicate the presence of liquid silicates from 500 - 1200 °C.⁴⁰ By studying the solubility of potassium from wheat straw chars at 700 – 900 °C, significant amounts of potassium silicate were hypothesised to be formed above 700 °C.⁵⁸ As mentioned previously, these low melting silicates can cause bed agglomeration in FBC or, if present on refractory surfaces, can capture flyash through inertial impaction and sticking, leading to the build-up of deposits.⁴⁴

All of these issues depend on the melting point and evaporation of inorganic species within the solid fuel. Ash fusion tests are therefore frequently used to try and predict the behaviour of biomass ash during combustion.⁵³ The slagging index, which measures the mass of alkali within the material as a ratio of the calorific value, was developed for coal to predict the risk of problems during combustion of different coals. Levels of $< 0.17 \text{ kg GJ}^{-1}$ indicate a low slagging risk and levels $> 0.34 \text{ kg GJ}^{-1}$ indicate that the fuel is virtually certain to cause melting, vaporisation and condensation of deposits on surfaces.³⁰ High slagging indices are observed in wheat straw samples from around the world (Table 1.2).

1.4.3 Reducing fouling and slagging

There are two main methods to resolve the issues caused by the inorganic composition of the fuel. The first is to control the combustion conditions, reducing the furnace exit temperature to below the initial deformation temperature of the ash, this may need to be as low as $680 \text{ }^\circ\text{C}$ for herbaceous biomass fuels.⁵⁴ The alternative is to remove the offending inorganic species, specifically potassium and chlorine, prior to combustion.

Several researchers have studied the leaching of wheat straw with water, by rain washing before harvesting, manual washing after harvesting, or with acid.^{2, 44, 59} Typically $> 80\%$ of the alkali metal and $> 90\%$ of the chlorine concentration in the initial fuel can be removed with water washing, particularly via complete immersion,² with a substantial reduction within 2 minutes.⁴⁴ This was found to enormously reduce the release of HCl and KCl during combustion and increase the fusion temperature from $800 \text{ }^\circ\text{C}$ to a maximum of $1300 \text{ }^\circ\text{C}$.^{2, 44} Acid washing was found to remove even greater amounts of alkali material.⁵⁹ However, some organic material, and its calorific value, was also removed during both water and acid washing.⁵⁹ Analysis of the cost effectiveness of reducing the inorganic content of rice straw indicated additional costs were $\$13 \text{ t}^{-1}$ for rain leached straw collected in the spring or $\$18 \text{ t}^{-1}$ for industrially leached straw.⁶⁰ This compares to the price of wheat straw collected and stored following harvesting which has varied between $\text{£}37\text{-}73 \text{ t}^{-1}$ in the UK during the past decade.⁶¹

Jensen *et al* suggested an alternative pretreatment option by studying the pyrolysis of straw at $550 \text{ }^\circ\text{C}$ followed by char washing.^{62, 63} 80-95% of the potassium was released within 120 min, slower than for straw washing, whilst 90% of the chlorine was released

within 20 minutes. However, variations of pyrolysis temperature and time, leaching of other inorganic species or the impacts of leaching on the combustion of the char were not studied.

Despite the research described above, the challenges of the influence of inorganic species on the combustion of herbaceous biomass have yet to be completely solved, and whilst many studies have focused on the combustion processes and gas-phase release of inorganics, few have studied the mineralogical changes occurring within the ashes, and importantly how this impacts on the reutilisation of the inorganic species.

1.5 Current uses of residues from thermochemical conversion of biomass

The large-scale utilisation of wheat straw, and similar biomass materials, in combustion systems will result in the formation of a significant quantity of new waste: biomass fly ash and bottom ash. The valorisation of these waste materials is vital to ensure recovery and reuse of the inorganic species, in line with an elemental sustainability and biorefinery vision, and to add economic value.

The issue of the disposal and utilisation of the ash from biomass combustion has been highlighted as a major issue.³⁰ In large-scale combustion tests on wheat straw the total ash produced has been found to be as much as 12% by weight of the initial straw, with fly ash making up 28% of the ash.⁴³ In countries where the utilisation of biomass residues is more developed, particularly in Scandinavia where wood is widely used, the increasing amount of ash residue is leading to the search for utilisation methods other than landfilling.⁶⁴

The most frequently cited alternative applications for biomass ashes are in: 1) agriculture, as a fertiliser or soil amendment; and 2) construction, by partly replacing cement or as an aggregate in road building.⁶⁵

1.5.1 Agriculture

The return of biomass ashes to soils is considered invaluable to reduce fertiliser usage and recycle the nutrients removed with the plant. Nutrients of particular importance are

phosphorus, potassium, magnesium and calcium. Nitrogen is almost totally lost during combustion. However, landfilling is currently the primary disposal method for combustion residues.⁶⁶ In the US, currently 90% of ash from the combustion of paper production residues goes to landfill.⁶⁷ The overwhelming majority of research on the reutilisation of ash has been carried out on wood ash, particularly in the US, Sweden, Finland and Denmark, specifically to return it to forest soils. This has led to the development of standards for threshold values of components in ash for recycling on forest floors (Table 1.3).⁶⁴ Combustion ashes are also considered as potential liming agents to reduce acidity in soils.⁶⁸

The specific mineral and organic content of the ashes formed affects its use, with these varying even between wood species.⁶⁷ The mineral content of herbaceous biomass is higher than wood and therefore produces a proportionally larger amount of ash following combustion, and also has a significantly different elemental distribution. However, very little work has studied the changes in nutrient content and availability with combustion conditions from these types of ash, particularly within the UK. Lab-scale studies in Germany have recently shown that rye straw ash can have a beneficial impact on yields of ryegrass and maize.⁶⁹ Rape straw ash contains more calcium and has been observed to have a higher liming effect than wheat straw ash.⁴³ However, the heavy metal concentrations of ashes can cause concern. In Denmark, the limiting concentration for Cd in ashes is 5.0 mg kg^{-1} , which has been found to be exceeded in some straw ashes.

1.5.2 Construction

The vast quantities of coal fly ash produced have led to the development of its use as a standard additive in concrete as a pozzolan;⁷⁰ approximately 6.7 million tonnes of coal fly ash were used in this way in the US in 1994.⁷¹ A pozzolan is a siliceous material that by itself has little or no cementitious property, but will react with calcium hydroxide in the presence of water to form a material with cementing properties.⁷² However, fly ash from biomass doesn't meet the current standards,⁷⁰ due to the high alkali and chloride concentrations and lower alumina levels in the ashes.⁶⁵ Therefore, further research is required to study the use of biomass ashes for this application and others. Researchers have found that several agricultural waste ashes are suitable for use as a component of

Table 1.3: Recommendations of the Swedish Forest Agency on threshold values for constituents in ash aimed for recycling on forest soils (Data from Ref 64)

	Minimum	Maximum
Macronutrients		
(% ash db)		
Ca	12.5	
Mg	1.5	
K	3.0	
P	0.7	
Micronutrients		
(mgkg⁻¹ db)		
B		800
Cu		400
Zn	500	7000
As		30
Pb		300
Cd		30
Cr		100
Hg		3
Ni		70
V		70

concrete including rice husk ash,⁷³ sugarcane ash,⁷⁴ palm oil fuel ash,⁷⁵ and wheat ash.⁷⁶ However, most of these studies were carried out on ashes produced at the lab-scale, combusted at lower temperature than normally used in power plants and did not study the effects of a range of parameters.

Olive and bone meal ash have also been used to make fire-resistant lightweight construction boards and clay bricks in combinations with other materials,^{65, 77} and several biomass ashes have been shown to be effective adsorbents for the removal of dyes from waste streams on a lab scale.^{71, 78, 79}

This highlights several potential opportunities for the utilisation of wheat straw and other agricultural ashes. However, no studies have investigated the full impacts of combustion conditions on the physical, chemical and textural changes occurring during the combustion of wheat straw and how these affect, influence and direct the applications of

the unique waste ashes formed. In addition, most studies have focused on the utilisation of fly ashes and not approached utilisation from a holistic viewpoint. The inorganic composition of the waste ashes should be the starting point for directing the potential applications, with silicon and potassium the most abundant elements in wheat straw ash (Table 1.2).

1.6 Silica from biomass

1.6.1 Silicon's presence in biomass

Silicon is one of the most abundant minerals present in plant tissues.⁸⁰ Within soil, silicon is mostly found in the form of insoluble crystalline silica and silicates with soluble silicic acid present at around 0.1 - 2.0 mM.⁸¹ The conversion of silicon in the soil to deposited silica within plant tissues is an incredibly efficient, though little understood, process and there is currently very little utilisation of this vast resource. As Currie and Perry eloquently express:⁸²

“Plants, diatoms and sponges are capable of accumulating, storing and processing Si to create ornate hierarchical patterned biosilicas. The production of silica by organisms is carried out in an aqueous environment from under-saturated solutions of silicic acid, at atmospheric pressure and with temperatures ranging between 4 and 40 °C, and this production, amounting to gigatons per annum, vastly outweighs that produced industrially.”

The ability of plants to accumulate silica to a higher concentration than that of the soluble silica in the soil is not uniform throughout the plant kingdom and neither are the silica structures formed and the location of them within the plant.⁸¹ Silica accumulation ability appears to be highly dependent on the high-level phylogenetic position of the plant, with this ability mainly present in primitive land plants and monocot angiosperms, particularly the family *Poaceae*, also known as grasses.⁸⁰ This family includes the major agricultural species such as rice, wheat and other important plants such as bamboo. Studies have shown that of various different grass species, uptake of silicon from a solution of silicic acid is in the order rice >> wheat > triticale > sorghum > rye > maize > barley.⁸³ In these plants, silicon is actively taken up by the roots in the form of silicic acid, although efflux

and influx transporter genes have so far only been identified for rice.^{84, 85} Once in the root, the silicic acid is transported to the xylem and then to the shoot, stem and leaves by the transpiration stream, where it becomes concentrated due to evaporation and polymerisation and is deposited as a thin layer of amorphous silica in the cell walls below the cuticle layer.^{86, 87} The effect of the strong pull of the transpiration stream is that the silicon concentration is higher in older tissues, leaves and the shoot than in the stem (Table 1.4).⁸⁸

Table 1.4: Percentage of silica found in different parts of the wheat plant.⁸⁸

Wheat organ	SiO ₂ (%)
Culm/stem	1.5 ± 0.2
Leaf sheath	5.8 ± 0.9
Leaf blade	5.7 ± 1.4
Rachis	1.1
Influorescence	3.8 ± 0.9
Bulk	2.3 ± 0.3

Although silicon is not classified as an essential mineral for plants, except for certain algae and *Equisetaceae*,⁸⁹ benefits due to the presence of Si include: increased resistance to chemical (high levels of salt or toxic metals) and physical stresses (drought and high temperature);⁸⁹ added strength and stiffness of the stems and leaf blades thereby increasing light interception;⁹⁰ and increased pest and fungal resistance.⁸⁵ This has led to the utilisation of silicon fertilisers for sugarcane and rice, which show decreased yields when silicon accumulation is low.^{86, 90}

The relative Si shoot concentrations vary across different agricultural and energy crops (Table 1.5).⁸⁰ Of the species cultivated in the UK, miscanthus and wheat display the highest uptake of silica.

Table 1.5: Relative silica concentration in the shoots of several agricultural and energy crops.⁸⁰

Species	Common name	Mean relative shoot Si concentration
<i>Oryza sativa</i>	Rice	4.12
<i>Equisetum arvense</i>	Horsetail	3.99
<i>Miscanthus sinensis</i>	Miscanthus / Elephant grass	2.86
<i>Triticum aestivum</i>	Wheat	2.46
<i>Panicum virgatum</i>	Switchgrass	2.01
<i>Hordeum vulgare</i>	Barley	1.82
<i>Quercus robur</i>	English oak	1.54
<i>Saccharum officinarum</i>	Sugarcane	1.51
<i>Avena sativa</i>	Oat	1.51
<i>Secale cereal</i>	Rye	1.26
<i>Brassica napus</i>	Oilseed rape	-0.12

1.6.2 Composition and inorganic distribution

The levels of silica in shoot concentrations are matched by the concentration of silica in the biomass following harvest (Table 1.2): *Poaceae* species contain the highest concentrations; oilseed rape, of the *Brassicaceae* family, has a particularly low level.

Potassium is generally also present at high levels, and at a much higher level than sodium. This results in a varying $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio for each different biomass source, both between different species and from different studies of the same species (Table 1.6). The results for wheat straw show a ratio generally in the range of commercially produced alkali silicates. Where they are not, this is probably due to the loss of potassium by rain leaching prior to harvesting.⁹¹ This data indicates the potential for the production of alkali silicates from the ashes of these biomass materials using only the inherent inorganic species. The variability in the elemental composition within the same species in different studies highlights the dependence of the mineral content of the plant on many other factors. This underpins the need for any technology that is developed to utilise biomass sources to be extremely robust to variations in the source materials. However, the wide variation of the ratio of silica and alkali minerals in different biomass ashes could

potentially allow a degree of controllability to the molar ratio of the final silicate solution formed.

Table 1.6: Main element concentrations of initial dry biomass and silica:alkali ratios.

	SiO ₂ (%)	K ₂ O (%)	SiO ₂ :K ₂ O (wt)	Cl (%)	CaO (%)	Ref
Wheat straw	4.6	2.4	1.9	1.9	0.6	2
Wheat straw	3.7	1.7	2.1	0.5	0.8	32
Wheat (Marius)	3.6	1.0	3.8	0.2	0.3	33
Wheat Denmark 2001	3.2	0.7	4.8	0.1	0.4	33
Wheat (Soisson) Spain	3.2	0.4	7.1	0.1	0.5	33
Wheat Denmark 2000	1.7	1.4	1.2	0.2	0.5	33
Winter barley	1.7	2.8	0.6	0.5	0.5	33
Spring barley	2.1	1.0	2.1	0.1	0.7	33
Oat straw	0.6	0.7	0.9	0.03	1.0	33
Rape straw	0.1	0.4	0.2	0.01	1.3	33
Rice straw	15.1	2.5	6.1	0.8	0.4	2
Sugarcane bagasse	3.6	0.3	14.4	0.009	0.2	2
Switchgrass	2.4	0.4	5.4	0.004	0.2	2
Wood fuel	1.7	0.1	26.4	0.1	0.3	2
Macroalgae (<i>Laminara digitata</i>)	0.1	3.8	0.03	-	1.3	34
Eastern Kentucky Coal	3.9	0.1	39.7	0.2	0.1	35

1.7 Alkali silicates – chemistry and uses

Alkali silicates have been known since the seventeenth century and by 1855 were being manufactured commercially.⁹² However, many aspects of alkali silicates are still not well understood, in particular regarding their structure and reactivity in solution. Nevertheless, alkali silicates do have several known chemical and physical properties that make them useful to study as a potential binder for lignocellulosic systems, with silicate solutions having been utilised as adhesives in many applications.

1.7.1 Alkali silicates

Alkali silicates are solutions or solids of silicate anions and alkali metal cations. These systems can be expressed as M₂SiO₃ but are more usually defined by the molar ratio or

$x\text{SiO}_2:\text{M}_2\text{O}$, where $\text{M} = \text{Li}, \text{Na}$ or K . It is this molar ratio together with the solids concentration in solution and the alkali metal used that defines the physical and chemical properties of the alkali silicate system. Since the molar ratio and solids concentration is highly variable and can be controlled, this produces a system with a wide variety of applications.

1.7.2 Structure of alkali silicates

A wide variety of different silicate structures are formed in solution. Evidence indicates that the species are all compact and tetrahedrally co-ordinated with many similar species in dynamic equilibrium.⁹³ The condensation processes that occur to form polymeric species are still not fully understood and are of particular interest for researchers understanding sol-gel chemistry and zeolite synthesis.⁹⁴ Condensation is generally believed to be catalysed by hydroxyl ions from both theoretical and experimental studies.^{92, 95, 96} The mechanism suggested involves deprotonation by a hydroxyl ion followed by a two-step condensation reaction with silicic acid via a five-coordinate reaction intermediate stabilised by three strong hydrogen bonds, followed by loss of water (Figure 1.5).⁹⁵ The anionic species formed may be charge stabilised by an alkali cation. Computer modelling is increasingly being used to try and understand the reactions that may be occurring due to the complexity of the different species present and the difficulty of accurately gathering thermodynamic information for individual species using experimental methods.

1.7.2.1 Analysis by ^{29}Si NMR

The specific species that are formed in solution and during polymerisation under different conditions are also still not well understood. A Q^i description was developed by Engelhardt *et al* to describe the connectivity of silicon atoms and help identification by ^{29}Si NMR.⁹⁷ Q^0 represents silicate structures in which the silicon atom is not connected to any other silicon atoms through an oxygen bridge (monomeric species), whilst Q^4 denotes a silicon atom that is connected to four other silicon atoms at each tetrahedral linkage (Figure 1.6). ^{29}Si NMR peaks have been assigned to the different Q^i species in solution (Table 1.7).⁹⁸

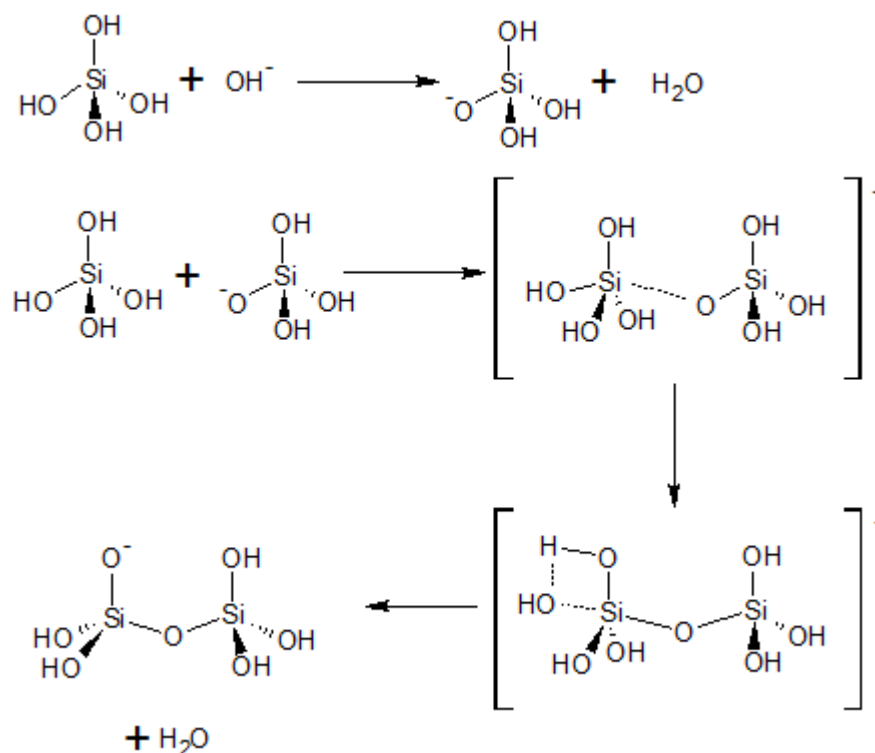


Figure 1.5: Proposed mechanism for the condensation of silicic acid⁹⁵

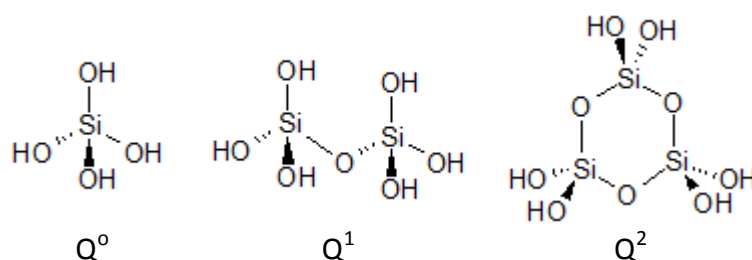


Figure 1.6: The structure of a few species identified in silicate solutions by ²⁹Si NMR

Table 1.7: Assigned ²⁹Si NMR shifts for silicate species with different connectivities in solution (with respect to tetramethylsilane)⁹⁸

Q ⁱ connectivity	-δ(ppm)
Q ⁰	~ 72
Q ¹	~ 79
Q ² _(3R) (cyclic trimer)	~ 82
Q ² _(4R) and Q ³ _(3R) (three ring)	~ 87 – 92
Q ³ _(4R) (four ring)	~ 96 – 98
Q ⁴	~ 108 (broad)

Identifying specific species in solution using ^{29}Si NMR is made difficult due to the presence of many similar species in dynamic equilibrium and due to the low abundance of ^{29}Si which prevents the visibility of ^{29}Si - ^{29}Si coupling.⁹³ Greater success has been achieved by studying the changes in the integrated band intensities of the different Q^i peaks with changing silicon concentration,⁹⁹ cation type,⁹⁸ pH,¹⁰⁰ and molar ratio (Figure 1.7).^{99, 101, 102} These indicate that at a pH above ~ 10.7 and as solutions become more siliceous, more complex polymeric species, Q^3 and Q^4 , are formed at the expense of the monomer and dimer.¹⁰² It is also noticeable that cyclic species are favourably formed during condensation processes. In addition, it has been found that decreasing the concentration of the solution decreases the degree of polymerisation and vice versa.⁹⁸

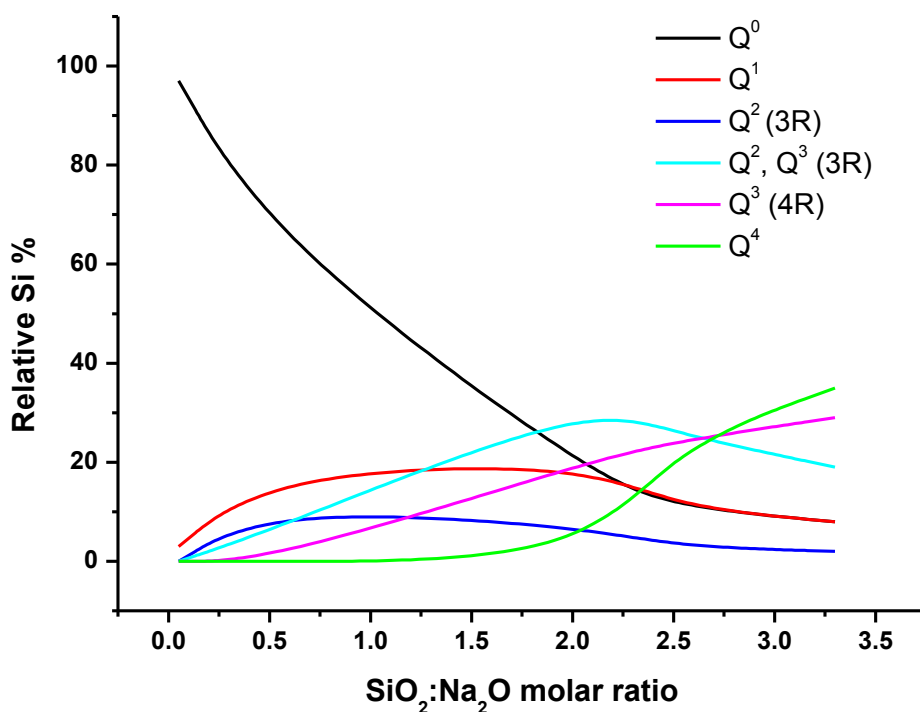


Figure 1.7: Changes in silicate species distribution with changing $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratio at a SiO_2 concentration of 0.4 M. (Data from Ref 99)

1.7.2.2 Analysis by infrared

Although ^{29}Si NMR can provide extremely useful, detailed and quantitative information about silicate solutions, other researchers have used cheaper and less time intensive techniques, such as infrared (IR) spectroscopy, to gain an understanding of silicate solutions. IR can enable the characterisation of silicate solutions, albeit at a much lower resolution and with some controversy remaining around assignments of bands to specific vibrational modes.^{103, 104}

The main infrared absorption bands of alkali silicates are observed between 1250 and 700 cm^{-1} with a strong broad band due to asymmetric Si-O-Si stretching vibrations, usually centred around 1000 cm^{-1} . Bass and Turner have correlated the changes in silicate speciation observed by ^{29}Si NMR with the changing peak structure observed in the IR spectra by deconvolution (Table 1.8).⁹⁹ They suggest that higher wavenumber sections of the band correspond to more complex anionic species. They then observe that as the molar ratio decreases the high frequency edge of the band shifts to lower frequency, suggesting a reduction in the complexity of the anionic species present. Bands in the range 950-1020 cm^{-1} appear to more sensitive to the local silicate environment.¹⁰⁵ However, band assignment was undertaken by comparing low concentration solutions due to better resolution of the ^{29}Si NMR peaks at 0.4 M concentrations.

Table 1.8: Bass and Turner's assignments of components of main sodium silicate infrared band to different silicate anion types.⁹⁹

Assignment	Wavenumber (cm^{-1})
SiO- small anions	850-900
Monomer + dimer	910-950
Linear Q^1	965-985, 995-1005
SiO^- cyclic anions	1010-1020
$\text{Q}^2_{(3\text{R})}$ rings	1020-1050
$\text{Q}^3_{(3\text{R})}$, $\text{Q}^2_{(4\text{R})}$ rings, linear Q^2	1030-1070
$\text{Q}^3_{(4\text{R})}$ rings	1050-1120
Polymer	1100-1300

Osswald and Fehr attempted to assign IR bands of concentrated potassium silicate solutions based on a comparison with IR studies of silica gels.¹⁰⁶ They correlated the shift of the frequency of the main band to the presence of surface Si-O-K groups, weakening neighbouring Si-O-Si bonds, and the high frequency shoulder of the main band to the situation where neighbouring oxygen atoms asymmetrically vibrate 180° out of phase with each other, rather than to the presence of more highly polymerised species.¹⁰⁷ Halasz *et al* tried to distinguish between bands related to monomeric and polymeric silicate species by using aqueous solutions of Na_2SiO_3 , which almost exclusively contain monosilicate ions at pH's > 10.¹⁰⁴ Their aqueous ATR FTIR spectra showed broad bands, without a high frequency shoulder, that shifted to lower wavenumbers with increasing

concentration or increasing alkali content, which they related to the degree of dissociation in the solution.

1.7.3 Setting processes

The chemical and physical properties of alkali silicates vary depending on their molar ratio and solids concentration. Of particular interest with respect to this project are the properties relating to the use of alkali silicates as a binder. There are three setting reactions that alkali silicates can undergo, which each impart different characteristics on the final material. In addition, compatibility with the substrate material must be considered, with the solutions performing most effectively on hydrophilic, non-oily surfaces, where they can achieve proper wetting and, hence, maximum adhesion.

1.7.3.1 Dehydration

Viscosity increases rapidly as moisture is removed and more rapidly for higher ratio silicate solutions.¹⁰⁸ The glassy nature of the bond formed imparts strength and rigidity, however, the insolubility of the bond is dependent on the ambient temperature and humidity.¹⁰⁹ Heating to around 250 °C is required to cross-link the silicate species and impart a high moisture resistance.¹¹⁰

1.7.3.2 Precipitation

Soluble silicates react almost instantly with multivalent metal cations such as Ca^{2+} and Mg^{2+} to form either insoluble metal silicate networks or hydrated silica with adsorbed metal oxides or hydroxides.¹⁰⁸ This mechanism is used to form pigments and surface coatings.

1.7.3.3 Gelation

Silicate solutions are stable to condensation above pH ~ 10.7 , due to the presence of repulsive highly charged anionic silicate species or stabilised ion-paired species.⁹² As the pH decreases fewer silicate anions are supported in solution, and the polymerisation of these species occurs with the expulsion of water due to a reduction in electrostatic repulsive forces.¹¹¹ There are three stages recognised in the polymerisation process:⁹²

1. Polymerisation of the monomer to form small particles

2. Growth of particles
3. Linking of particles into chains and then networks which extend through the solution, thickening it to a gel.

The extent of polymerisation is dependent on the solids concentration, salt content, the temperature and the pH of gelation. In general, the rate of gelation increases as the pH decreases to a maximum at pH 6-7.⁹² Initially small polymerised species are formed, maximising the number of internal siloxane bonds and minimising the number of surface silanol groups. The resulting small particles are the nuclei for larger particles which form the backbone of the silica gel. A dynamic equilibrium is present in which smaller more soluble particles dissolve releasing silica which can react with the nucleating particles resulting in growth of the particles in a process known as Ostwald ripening.⁹² The main driving force for this is the reduction in surface free energy. Both simultaneously with and following particle growth, aggregation of the particles may occur dependent on diffusion rates and electrostatic forces between the particles until a gel network is formed. During this process the gel continues on a macroscopic scale to have the same concentration of silica and water as the surrounding sol. However, if coagulants, such as polyvalent metal ions or substantial amounts of salts are present, a white precipitate or opaque gel will be formed.

The bond formed via gelation is usually not as strong as that caused by dehydration but can have a higher degree of water resistance.¹¹² A wide variety of different setting agents are available that can be used to induce gelation by reducing the pH of the solution. For controlled gelation a chemical that will be hydrolysed over time to induce acidity is often used.¹⁰⁹ For binding purposes a higher ratio silicate solution is often particularly valuable since less additional chemical is required to neutralise the solution to a pH below 10.7 and begin to induce gelation.

1.8 Utilising silica from biomass

Sodium silicate is generally formed by the fusing of sand (SiO_2) with sodium carbonate or 'soda ash' at around 1100-1200 °C. The resulting glass is then dissolved using high pressure steam.⁹² A large amount of energy is used during this process and there are environmental issues associated with the extraction of sand from mining or dredging, as

well as the release of CO₂ due to carbonate decomposition. It is only in the past few years that the extraction and use of silicon present in biomass has seriously been considered. The main resource studied has been rice husk ash (RHA) due its high content of relatively pure silica.

1.8.1 Dissolution of silica

Silica can either be dissolved by strong alkaline solutions or by HF. In alkaline solutions, the reaction that is occurring during dissolution is essentially depolymerisation, the reverse of the polymerisation reaction described in section 1.7.2. This reaction is also catalysed by hydroxyl ions which can react with silica to form a five co-ordinate centre, thereby weakening the other oxygen linking bonds. The rate at which dissolution occurs depends on the ability of the hydroxyl ion to catalyse this reaction, particularly the silica structure and the pH of the solution. At atmospheric pressure, the main crystalline silica phases formed are quartz, tridymite, cristobalite, with the transformation between them fully reversibly if the temperature change is slow (Figure 1.8).⁹² The structures of tridymite, cristobalite and silica melts (glass) will be preserved at low temperatures if they are quickly cooled beyond their transition temperature. Interestingly, as silica glass is heated it is transformed directly to β -cristobalite rather than quartz.⁹² Amorphous unstructured silicas, including glass, opal and biogenic silica, have much greater dissolution rates than the crystalline phases due to the openness of the structure, enabling greater access to hydroxyl ions.⁹² The dissolution rate and maximum saturation level for all silica phases increases with increasing alkalinity, particularly above a pH of 9, due to the increasing presence of silicate ions influencing the silica saturation equilibrium, with the rate of dissolution correlated to the density of the material.¹¹³ The dissolution rate and total solubility are also affected by surface area,¹¹³ temperature and pressure.¹¹⁴

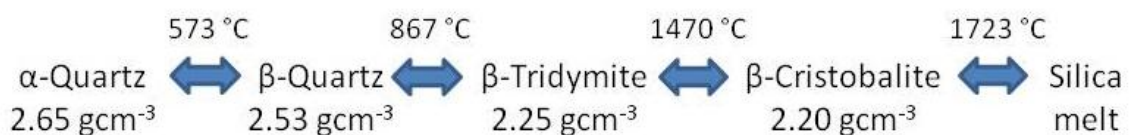


Figure 1.8: Silica phase transformations

1.8.2 Silica from Rice Hull Ashes (RHAs)

Most silica in biomass is thought to exist in inorganic linkages as amorphous silica. X-ray diffraction studies and solid state ^{29}Si NMR have identified amorphous silica in rice hull ashes (RHAs) up to 800 °C, with cristobalite and tridymite phases present at higher temperatures.⁷² Therefore, generally extraction of silica from RHAs uses material combusted, gasified or pyrolysed below 800 °C. By boiling RHAs in 1M NaOH for 1 h, Kalapathy *et al* demonstrated that 91% of the silica present could be extracted.¹¹⁵ This methodology is now being used by AgriTec Systems to produce sodium silicate solutions from gasified rice hulls with a high value activated carbon co-product.¹¹⁶ It has also been used to study the production of silicate thermal insulation material and the formation of flexible silicate films from RHAs.^{117, 118}

By purely heating RHAs to 700 °C for 6 h, Della *et al* found that they could produce a material that contained 95% amorphous silica with a surface area of 54 – 81 m² g⁻¹.¹¹⁹ This method was also used by Rodrigues to create a pozzolanic material for cement production.¹²⁰

Silica has also been formed from rice hulls, rice straw and wheat straw by chemical pulping of the material with H₂SO₄ followed by combustion of the residue at 500 °C. The materials formed contained 99% SiO₂ and had BET surface areas ranging from 186 – 291 m² g⁻¹.¹²¹ The only other studies that have examined the utilisation of silica in wheat residues have investigated, briefly, the use of ashes as an additive in cement production and for the formation of autoclaved mortar.^{76, 122, 123}

These studies found that wheat straw ash (WSA) or wheat hull ash can produce a pozzolanic material. However, once again these studies have not looked at the utilisation of WSA from a holistic and elemental sustainability perspective, understanding the interaction of all inorganic species and their use during combustion or other thermochemical processes. Specifically, the formation of alkali silicates utilising the inherent inorganic species has not been explored.

1.9 Composite materials

Alkali silicates have been utilised as adhesives in many applications including cardboard packaging and foil laminate.¹¹⁰ However, the use of alkali silicates in composite materials would be a novel application, particularly via the use of waste ash. There are additionally further environmental imperatives for the development of new binders.

Wood based panels are an ubiquitous part of office and home design with just over 6 million $\text{m}^3 \text{y}^{-1}$ used in the UK every year (Figure 1.9a).¹²⁴ The major types used are plywood, MDF and particleboard, with only the latter two produced in the UK (Figure 1.9b). These two materials are, therefore, most relevant to this study.

Particleboard has been defined as a “sheet material manufactured from small pieces of wood or other ligno-cellulosic materials (e.g. chips, flakes, splinters, strands, shreds etc.) agglomerated by use of an organic binder together with one or more of the following agents: heat, pressure, humidity, a catalyst, etc”.¹²⁴ MDF is defined as a “type of fibreboard with a density exceeding 0.50 g cm^{-3} but not exceeding 0.80 g cm^{-3} ”.¹²⁴ Fibreboard is “a panel manufactured from fibres of wood or other lignocellulosic materials with the primary bond deriving from the felting of the fibres and their inherent adhesive properties. Bonding materials and/or additives may be added. It is usually flat pressed but may also be moulded.”¹²⁴

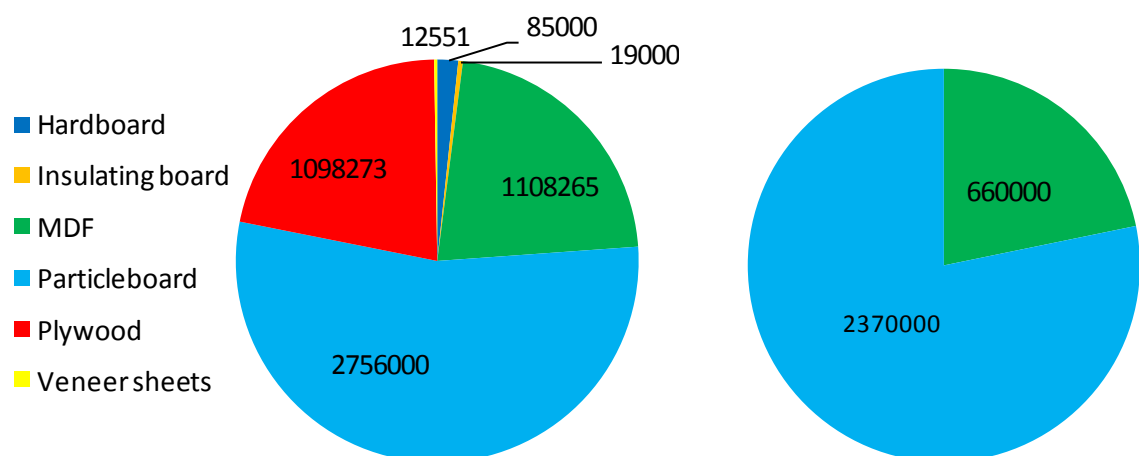


Figure 1.9: Volume (m^3) of wood-based panelling (a) used in the UK in 2009 and (b) produced in the UK in 2009 (Data from Ref 124) (Originally in colour)

The manufacturing methods for MDF and particleboard are shown in Figure 1.10. Although the overall processes are similar for both products, the manufacturing process for MDF requires the production of fine fibres prior to pressing.

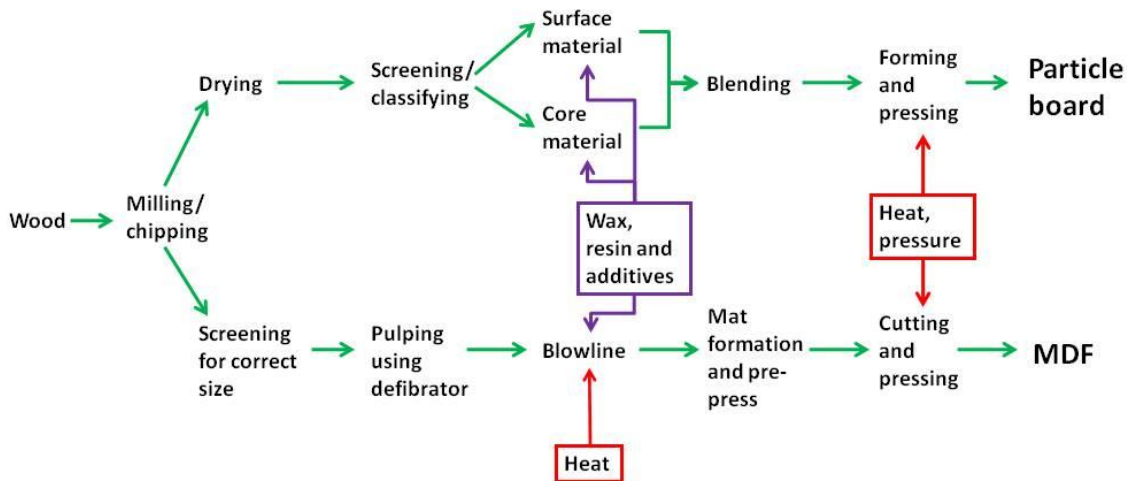


Figure 1.10: Main steps in the manufacture of particle board and MDF (Originally in colour)

1.9.1 Environmental impacts and challenges

There are three major environmental issues related to the current manufacture of these lignocellulosic construction materials: the binder; the use of wood as the substrate; and inefficiencies in the manufacturing process.

Urea formaldehyde (UF) is used as the binder for over 90% of particleboard and is also the main binder for many other wood-based panels due to the strong bonds formed at low cost.¹²⁵ However, formaldehyde has been classified as a ‘probable carcinogen’ by the International Agency for Research on Cancer,¹²⁶ is linked to eye, nose and respiratory irritation and can cause contact dermatitis,¹²⁷ thereby posing a significant health risk to people working in the composite board manufacturing industry. In addition, formaldehyde emissions continue to be released following manufacture due to the presence of free formaldehyde,¹²⁵ which has resulted in many countries applying stringent limits on formaldehyde release from composite boards.¹²⁸ Urea formaldehyde is also manufactured from fossil fuel sources.¹²⁹ With around 10% of urea formaldehyde

present in particleboard by weight,¹²⁵ and a higher content in MDF,¹³⁰ the production of boards worldwide puts pressure on the dwindling fossil fuel resources.

Currently, both particleboard and MDF are overwhelmingly made from wood-based material, usually waste from sawmills, although some virgin wood is used. However, with an estimated increase of MDF production of 4% year-on-year from 2006-2010 in Europe,¹³¹ competition from other products for the same raw material and environmental imperatives to reduce virgin wood consumption, the demand for non-wood lignocellulosic substrates will increase.

1.9.2 Alternative resins

Due to these challenges with conventional production, many researchers have been searching for alternative binders or production methods. Melamine modified urea formaldehyde,¹³² phenol formaldehyde,¹³³ and methylenediphenyl isocyanate all show reduced formaldehyde emissions. However, similar concerns remain as for UF since they are fossil-fuel derived and often require corrosive or irritating starting materials.

In search of sustainable alternatives, other researchers have looked to renewable binders based on for instance soy flour,¹³⁴ forest-floor biomass (depolymerised lignin),¹²⁶ cashew nut shell liquid,¹³⁵ and sugarcane bagasse lignin.¹³⁶ Mostly these are phenolic substitutes, although they usually cannot entirely replace the fossil fuel phenol source. An alternative approach is to eradicate the need for binders altogether. High strength-high density low cost binderless boards have been formed from coconut husk via the melting of the high lignin content pith residue binding the coir fibres.¹³⁷

Wood-plastic composites are a relatively new material based on a combination of a lignocellulosic substrate with either virgin or recycled thermosetting plastics.¹³⁸ However, around 40-50% of the composite by weight needs to be the thermoplastic in order to achieve good tensile and flexural strength, with these properties still worse than that of commercial MDF and particleboard.¹³⁹

Inorganic composites that are highly resistant to fire and insects have been developed using gypsum and Portland Cement.¹⁴⁰ These boards usually contain between 10-70wt%

wood particles and consequentially require 30-90wt% binder due to the high viscosity of the inorganic binders.^{140, 141} They can also require long cure times, although they are often set at ambient conditions. Research using potassium aluminosilicate as an alternative binder showed that with 70% binder by weight and curing at ambient temperature and pressure, highly fire-resistant materials could be formed.¹⁴²

1.9.3 Alternative substrates

In the past two decades interest in using alternative lignocellulosic material to replace wood-derived substrates has increased. The main focus of interest has been on the use of wheat straw for particleboards, but other alternatives are now beginning to be studied including cornstalks, corncobs,¹³⁹ Scottish pine needles,¹⁴³ and even aubergine stalks,¹⁴⁴ dependent on the particular renewable resources available locally. The composition and surface properties of these materials can be very different to wood, for instance straw has a very waxy surface.³ This can affect the binding of the substrate with the adhesive, so requiring additional research and development to produce boards with the same properties as traditional wood-based particleboard and MDF.

1.10 Project vision and thesis content

This project aims to draw together the different themes discussed above by approaching the study of the inorganic species within wheat straw and other biomass materials from a holistic perspective. This requires the study of the interrelation and interaction of all species during combustion and other treatment processes and how that can lead to recommendations and directions for the reutilisation of the inorganic species to ensure elemental sustainability. There is a particular focus on silica as it is the main inorganic species within wheat straw and has been relatively unstudied. In addition, there is a central motivation to study whether the hypothesised production of alkali silicates from biomass ashes and their utilisation as a novel inorganic binder for composite board manufacture is feasible. The latter process is significantly different from other attempts to produce inorganic composite boards, with the aspiration of utilising low levels of binder, similar to the concentrations of organic binders currently used for MDF production, whilst utilising only waste and renewable feedstocks throughout. This thesis therefore covers four main areas:

1. The lab-scale combustion of wheat straw and the impacts of wheat straw variety, year and combustion conditions on the mineralogical, chemical and textural properties of combustion residues.
2. The pretreatment of wheat straw by organic solvent, supercritical CO₂, water and acid and the impacts on the mineralogical and chemical properties of the combustion residues.
3. The lab-scale pyrolysis of wheat straw and the impacts on the mineralogical and chemical properties of the chars, and the impacts of inorganic removal on the combustion properties of chars.
4. The utilisation of combustion residues – fly ash and bottom ash – from commercial biomass facilities. The analysis of their composition, extraction and utilisation for the formation of alkali silicate binders for inorganic composite boards.

1.11 References for Chapter 1

1. L. L. Baxter, T. R. Miles, T. R. Miles, B. M. Jenkins, T. Milne, D. Dayton, R. W. Bryers and L. L. Oden, *Fuel Process. Technol.*, 1998, 54, 47-78.
2. D. C. Dayton, B. M. Jenkins, S. Q. Turn, R. R. Bakker, R. B. Williams, D. Belle-Oudry and L. M. Hill, *Energ. Fuel.*, 1999, 13, 860-870.
3. F. E. I. Deswarte, J. H. Clark, J. J. E. Hardy and P. M. Rose, *Green Chem.*, 2006, 8, 39-42.
4. United Nations, Report of the World Commission on Environment and Development, General Assembly Resolution 42/187, 11 December 1987.
5. Energy Information Administration, Short-Term Energy Outlook—January 2011, http://www.eia.doe.gov/steo/steo_full.pdf, Accessed 17/01/10.
6. R. L. Hirsch, R. Bezdek and R. Wendling, *Peaking of World Oil Production: Impacts, Mitigating and Risk Management*, Science Applications International Corporation, 2005.
7. P. Anastas and J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
8. Intergovernmental Panel on Climate Change, IPCC Fourth Assessment Report (AR4): The AR4 Synthesis Report, 17 November 2007.
9. S. Smith, Postnote No. 295: Climate Change Science, Parliamentary Office of Science and Technology, 2007.
10. D. Cohen, *New Scientist*, 2007.
11. C. A. DiFrancesco, M. W. George, J. F. Carlin Jr. and A. C. Tolcin, *Indium Statistics*, U.S. Geological Survey, 2010.
12. S. M. Jasinski, *Potash: Mineral Commodities Summary*, U.S. Geological Survey, January 2010.
13. P. Anastas and P. Tundo, *Green Chemistry: Challenging Perspectives.*, Oxford University Press, Oxford, 2000.
14. Great Britain, *Climate Change Act 2008: Elizabeth II, Chapter 27*, The Stationary Office, London, 2008.
15. European Parliament, *Promotion of the use of energy from renewable sources*, 2009/28/EC, 2009.

16. Department of Energy & Climate Change, 2008 final UK greenhouse gas emissions: data tables, London, 14 April 2010.
17. Department for Environment Food and Rural Affairs, UK Biomass Strategy, 2007.
18. Department of Energy & Climate Change, The UK Renewable Energy Strategy 2009, 2009.
19. L. Evans, S. Okamura, J. Poll and N. Barker, Evaluation of Opportunities for Converting Indigenous UK Wastes to Fuels and Energy, AEA report for the NNFFCC, July 2009.
20. G. Evans and L. Nattrass, Advanced Thermochemical Biofuels Roadmap and Challenge, NNFFCC Project 09/014, NNFFCC, York, 2009.
21. E4tech, Biomass supply curves for the UK, For DECC, March 2009.
22. A. J. Houghton, A. J. Bond, A. A. Lovett, T. Dockerty, G. Sünnerberg, S. J. Clark, D. A. Bohan, R. B. Sage, M. D. Mallott, V. E. Mallott, M. D. Cunningham, A. B. Riche, I. F. Shield, J. W. Finch, M. M. Turner and A. Karp, *J. Appl. Ecol.*, 2009, 46, 315–322.
23. E. M. W. Smeets, A. P. C. Faaij, I. M. Lewandowski and W. C. Turkenburg, *Prog. Energy Combust. Sci.*, 2007, 33, 56-106.
24. International Energy Agency, Key World Energy Statistics 2010, Paris, 2010.
25. J. Copeland and D. Turley, National and Regional Supply/Demand balance for agricultural straw in Great Britain, Central Sciences Laboratory, 2008.
26. A. Barneto, J. Carmona, J. E. Alfonso and L. Alcaide, *Bioresour. Technol.*, 2009, 100, 3963-3973.
27. J. M. Jones, M. Nawaz, L. I. Darvell, A. B. Ross, M. Pourashanian and A. Williams, in *Science in Thermal and Chemical Biomass Conversion*, ed. A. Bridgewater, Blackwell Science Ltd, Oxford, Editon edn., 2006, pp. 331-339.
28. A. Demirbas, *Prog. Energy Combust. Sci.*, 2004, 30, 219-230.
29. A. A. Khan, W. de Jong, P. J. Jansens and H. Spliethoff, *Fuel Process. Technol.*, 2009, 90, 21-50.
30. D. L. Klass, *Biomass for Renewable Energy, Fuels and Chemicals*, Academic Press, California, 1998.
31. J. Werther, M. Saenger, E. U. Hartge, T. Ogada and Z. Siagi, *Prog. Energy Combust. Sci.*, 2000, 26, 1-27.
32. Y. Q. Wu, S. Y. Wu, Y. Li and J. S. Gao, *Energ. Fuel.*, 2009, 23, 5144-5150.
33. S. Arvelakis, P. A. Jensen and M. Dam-Johansen, *Energ. Fuel.*, 2004, 18, 1066-1076.
34. D. Belle-Oudry and D. Dayton, in *Impact of Mineral Impurities in Solid Fuel Combustion*, ed. R. Gupta, Kluwer Academic / Plenum Publishers, New York, Editon edn., 1999, pp. 569-579.
35. A. B. Ross, J. M. Jones, M. L. Kubacki and T. Bridgeman, *Bioresour. Technol.*, 2008, 99, 6494-6504.
36. A. Pettersson, L. E. Amand and B. M. Steenari, *Fuel*, 2009, 88, 1758-1772.
37. C. Yin, L. A. Rosendahl and S. K. Kaer, *Prog. Energy Combust. Sci.*, 2008, 34, 725-754.
38. J. N. Knudsen, P. A. Jensen and K. Dam-Johansen, *Energ. Fuel.*, 2004, 18, 1385-1399.
39. R. P. van der Lans, L. T. Pedersen, A. Jensen, P. Glarborg and K. Dam-Johansen, *Biomass Bioenerg.*, 2000, 19, 199-208.
40. M. Blander and A. D. Pelton, *Biomass Bioenerg.*, 1997, 12, 295-298.
41. I. Obernberger, T. Brunner and G. Barnthaler, *Biomass Bioenerg.*, 2006, 30, 973-982.
42. B. Staiger, S. Unterberger, R. Berger and K. R. G. Hein, *Energy*, 2005, 30, 1429-1438.
43. M. L. Sander and O. Andren, *Water Air Soil Pollut.*, 1997, 93, 93-108.
44. B. M. Jenkins, R. R. Bakker and J. B. Wei, *Biomass Bioenerg.*, 1996, 10, 177-200.
45. B. Olanders and B.-M. Steenari, *Biomass Bioenerg.*, 1995, 8, 105-115.
46. T. R. Miles, T. R. Miles, L. L. Baxter, R. W. Bryers, B. M. Jenkins and L. L. Oden, *Biomass Bioenerg.*, 1996, 10, 125-138.

47. R. Gupta, T. Wall and L. Baxter, *Impact of Mineral Impurities in Solid Fuel Combustion*, Kluwer Academic / Plenum Publishers, New York, 1999.
48. N. O. Knudsen, P. A. Jensen, B. Sander and K. Dam-Johansen, in *Biomass for Energy and Industry*, eds. H. Kopetz, T. Weber, W. Palz, P. Chartier and G. L. Ferrero, *Centrales Agrar Rohstoff Mkt & Entwicklung Netzwerk*, Rimpär, Editon edn., 1998, pp. 224-228.
49. S. Arvelakis, H. Gehrman, M. Beckmann and E. G. Koukios, *J. Therm. Anal. Calorim.*, 2003, 72, 1019-1030.
50. P. Thy, B. M. Jenkins, C. E. Lesher and S. Grundvig, *Fuel Process. Technol.*, 2006, 87, 383-408.
51. D. Vamvuka, S. Troulinos and E. Kastanaki, *Fuel*, 2006, 85, 1763-1771.
52. J. M. Jones, L. I. Darvell, T. G. Bridgeman, M. Pourkashanian and A. Williams, *P. Combust. Inst.*, 2007, 31, 1955-1963.
53. M. J. F. Llorente and J. E. C. Garcia, *Fuel*, 2005, 84, 1893-1900.
54. R. W. Bryers, in *Impact of Mineral Impurities in Solid Fuel Combustion*, eds. R. Gupta, T. Wall and L. Baxter, Kluwer Academic / Plenum Publishers, New York, Editon edn., 1999, pp. 105-131.
55. S. Arvelakis, F. J. Frandsen and K. Dam-Johansen, *J. Therm. Anal. Calorim.*, 2003, 72, 1005-1017.
56. P. Thy, B. M. Jenkins, S. Grundvig, R. Shiraki and C. E. Lesher, *Fuel*, 2006, 85, 783-795.
57. A. Zolin, A. Jensen, P. A. Jensen, F. Frandsen and K. Dam-Johansen, *Energ. Fuel.*, 2001, 15, 1110-1122.
58. P. A. Jensen, F. J. Frandsen, K. Dam-Johansen and B. Sander, *Energ. Fuel.*, 2000, 14, 1280-1285.
59. D. N. Thompson, P. G. Shaw and J. A. Lacey, *Appl. Biochem. Biotechnol.*, 2003, 105, 205-218.
60. R. R. Bakker and B. M. Jenkins, *Biomass Bioenerg.*, 2003, 25, 597-614.
61. Defra, *Commodity Prices: Hay and Straw*, 7 July 2011.
62. P. A. Jensen, B. Sander and K. Dam-Johansen, *Biomass Bioenerg.*, 2001, 20, 431-446.
63. P. A. Jensen, B. Sander and K. Dam-Johansen, *Biomass Bioenerg.*, 2001, 20, 447-457.
64. S. Sarenbo, *Biomass Bioenerg.*, 2009, 33, 1212-1220.
65. A. Gómez-Barea, L. F. Vilches, C. Leiva, M. Campoy and C. Fernández-Pereira, *Chem. Eng. J.*, 2009, 146, 227-236.
66. A. Elliott and T. Mahmood, *Tappi J.*, 2006, 5, 9-16.
67. R. M. Pitman, *Forestry*, 2006, 79, 563-588.
68. P. Vesterinen, *Wood Ash Recycling: State of the Art in Finland and Sweden*, <http://www.cti2000.it/solidi/WoodAshReport%20VTT.pdf>, Accessed 01/02/2011.
69. K. Schiemenz and B. Eichler-Lobermann, *Nutr. Cycl. Agroecosyst.*, 2010, 87, 471-482.
70. S. Wang and L. Baxter, in *Science in Thermal and Chemical Biomass Conversion*, ed. A. Bridgewater, Blackwell Science Ltd., Oxford, Editon edn., 2006, pp. 325-330.
71. P. Janos, H. Buchtová and M. Rýznarová, *Water Res.*, 2003, 37, 4938-4944.
72. D. G. Nair, A. Fraaij, A. A. K. Klaassen and A. P. M. Kentgens, *Cement Concrete Res.*, 2008, 38, 861-869.
73. P. Chindaprasirt and S. Rukzon, *Constr. Build. Mater.*, 2008, 22, 1601-1606.
74. M. Frías, E. Villar-Cociña and E. Valencia-Morales, *Waste Manage.*, 2007, 27, 533-538.
75. W. Tangchirapat, T. Saeting, C. Jaturapitakkul, K. Kiattikomol and A. Siripanichgorn, *Waste Manage.*, 2007, 27, 81-88.
76. H. Biricik, F. Aköz, I. I. Berktaş and A. N. Tulgar, *Cement Concrete Res.*, 1999, 29, 637-643.
77. C. Leiva, A. Gomez-Barea, L. F. Vilches, P. Ollero, J. Vale and C. Fernandez-Pereira, *Energ. Fuel.*, 2006, 21, 361-367.

78. V. K. Gupta, I. Ali, V. K. Saini, T. Van Gerven, B. Van der Bruggen and C. Vandecasteele, *Ind. Eng. Chem. Res.*, 2005, 44, 3655-3664.
79. V. K. Gupta, A. Mittal, V. Gajbe and J. Mittal, *J. Colloid Interface Sci.*, 2008, 319, 30-39.
80. M. J. Hodson, P. J. White, A. Mead and M. R. Broadley, *Annal. Bot.-London*, 2005, 96, 1027-1046.
81. W. H. Casey, S. D. Kinrade, C. T. G. Knight, D. W. Rains and E. Epstein, *Plant Cell Environ.*, 2004, 27, 51-54.
82. H. A. Currie and C. C. Perry, *Annal. Bot.-London*, 2007, 100, 1383-1389.
83. K. Tamai and J. F. Ma, *New Phytol.*, 2003, 158, 431-436.
84. J. F. Ma, K. Tamai, N. Yamaji, N. Mitani, S. Konishi, M. Katsuhara, M. Ishiguro, Y. Murata and M. Ya no, *Nature*, 2006, 440, 688-691.
85. J. F. Ma, N. Yamaji, N. Mitani, K. Tamai, S. Konishi, T. Fujiwara, M. Katsuhara and M. Yano, *Nature*, 2007, 448, 209-212.
86. J. F. Ma and N. Yamaji, *Trends Plant Sci.*, 2006, 11, 392-397.
87. M. J. Hodson, A. G. Parker, M. J. Leng and H. J. Sloane, *J. Quaternary Sci.*, 2008, 23, 331-339.
88. J. Mecfel, S. Hinke, W. A. Goedel, G. Marx, R. Fehlhaber, E. Bäucker and O. Wienhaus, *J. Plant Nutr. Soil Sci.*, 2007, 170, 769-772.
89. E. Epstein, *Annu. Rev. Plant. Physiol. Plant. Mol. Biol.*, 1999, 50, 641-664.
90. K. Tamai and J. F. Ma, *Plant Soil*, 2008, 307, 21-27.
91. P. Hald, Technical University of Denmark, 1994.
92. R. K. Iler, *The Chemistry of Silica*, Wiley & Sons, New York, 1979.
93. C. T. G. Knight, R. J. Balec and S. D. Kinrade, *Angew. Chem., Int. Ed.*, 2007, 46, 8148-8152.
94. M. J. Mora-Fonz, C. R. A. Catlow and D. W. Lewis, *J. Phys. Chem. C*, 2007, 111, 18155-18158.
95. T. T. Trinh, A. P. J. Jansen and R. A. van Santen, *J. Phys. Chem. B*, 2006, 110, 23099-23106.
96. M. J. Munoz Aguado and M. Gregorkiewitz, *J. Colloid Interface Sci.*, 1997, 185, 459-465.
97. G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel and W. Wieker, *A. Anorg. Allg. Chem.*, 1975, 418, 17-28.
98. G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley, New York, 1987.
99. J. L. Bass and G. L. Turner, *J. Phys. Chem. B*, 1997, 101, 10638-10644.
100. C. F. Weber and R. D. Hunt, *Ind. Eng. Chem. Res.*, 2003, 42, 6970-6976.
101. I. L. Svensson, S. Sjoberg and L. O. Ohman, *J. Chem. Soc. Farad. T. 1*, 1986, 82, 3635-3646.
102. J. L. Provis, P. Duxson, G. C. Lukey, F. Separovic, W. M. Kriven and J. S. J. van Deventer, *Ind. Eng. Chem. Res.*, 2005, 44, 8899-8908.
103. I. Halasz, M. Agarwal, R. Li and N. Miller, *Catal. Today*, 2007, 126, 196-202.
104. I. Halasz, M. Agarwal, R. Li and N. Miller, *Catal. Lett.*, 2007, 117, 34-42.
105. J. S. Falcone Jr, J. L. Bass, P. H. Krumrine, K. Brensinger and E. R. Schenk, *J. Phys. Chem. A*, 2010, 114, 2438-2446.
106. J. Osswald and K. T. Fehr, *J. Mater. Sci.*, 2006, 41, 1335-1339.
107. C. T. Kirk, *Phys. Rev. B*, 1988, 38, 1255.
108. PQ Corporation, *Sodium Silicates: Liquids and Solids*, PQ Corporation, USA, 2004.
109. P. M. Gill, *Bulletin 9: Environmentally Safe Binders for Agglomeration*, PQ Corporation, USA, 1997.
110. PQ Corporation, *Bulletin 12-31: Bonding and Coating Applications of PQ Soluble Silicates*, PQ Corporation, 2006.

111. H. A. Nasr-El-Din and K. C. Taylor, *J. Pet. Sci. Eng.*, 2005, 48, 141-160.
112. M. McDonald and J. LaRosa Thompson, *Sodium Silicate a Binder for the 21st Century*, PQ Corporation.
113. W. Vogelsberger, A. Seidel and G. Rudakoff, *J. Chem. Soc. Faraday T.*, 1992, 88, 473-476.
114. N. Zotov and H. Keppler, *Chem. Geol.*, 2002, 184, 71-82.
115. U. Kalapathy, A. Proctor and J. Shultz, *Bioresource Technol.*, 2000, 73, 257-262.
116. USA Pat., 6524543, 1998.
117. U. Kalapathy, A. Proctor and J. Shultz, *Ind. Eng. Chem. Res.*, 2003, 42, 46-49.
118. U. Kalapathy, A. Proctor and J. Shultz, *Bioresource Technol.*, 2000, 72, 99-106.
119. V. P. Della, I. Kuhn and D. Hotza, *Mater. Lett.*, 2002, 57, 818-821.
120. F. A. Rodrigues, *Cement Concrete Res.*, 2003, 33, 1525-1529.
121. M. Ubukata, S. Mitsuhashi, A. Ueki, Y. Sano, N. Iwasa, S. Fujita and M. Arai, *J. Agr. Food Chem.*, 2010, 58, 6312-6317.
122. J. Zhang, J. M. Khatib, C. Booth and R. Siddique, in *Excellence in Concrete Construction through Innovation*, eds. M. C. Limbachiya and H. Y. Kew, Crc Press-Taylor & Francis Group, Boca Raton, Editon edn., 2009, pp. 517-521.
123. N. M. Al-Akhras and B. A. Abu-Alfoul, *Cement Concrete Res.*, 2002, 32, 859-863.
124. FAOSTAT, ForesSTAT, <http://faostat.fao.org/site/630/default.aspx>, Accessed 03/02/11.
125. G. Nemli and I. Öztürk, *Build. Environ.*, 2006, 41, 770-774.
126. A. Ghosh and M. Sain, *Polym. Polym. Compos.*, 2006, 14, 217-227.
127. Z. E. Isaksson M, Bruze M, *J. Occup. Environ. Med.*, 1999, 41, 261-266.
128. California Air Resources Board, Fact Sheet: Airborne Toxic Control Measure (ATCM) to Reduce Formaldehyde Emissions from Composite Wood Products.
129. H. Xu, Q. Li, L. F. Shen, W. Wang and J. P. Zhai, *J. Hazard. Mater.*, 175, 198-204.
130. Environment Protection Agency, An Introduction to Indoor Air Quality, <http://www.epa.gov/iaq/formalde.html>, Accessed 03/02/2011.
131. S. Halvarsson, H. Edlund and M. Norgren, *Ind. Crop. Prod.*, 2008, 28, 37-46.
132. H. Chung-Yun, F. Feng and P. Hui, *Forest Prod. J.*, 2008, 58, 56-61.
133. R. M. Rammon, in *Proc. 31st Inter. Particleboard and Composite Materials Symp.*, Washington State Univ., Pullman, Washington, Editon edn., 1997, pp. 177-181.
134. Columbia Forest Products, PureBond: Formaldehyde-Free Hardwood Plywood <http://www.columbiaforestproducts.com/products/prodpb.aspx>, Accessed 12/08/08, 2008.
135. M. Lubi and E. T. Thachil, *Polym-Plast. Technol.*, 2007, 46, 393-400.
136. W. Hoareau, F. B. Oliveira, S. Grelier, B. Siegmund, E. Frollini and A. Castellan, *Macromol. Mater. Eng.*, 2006, 291, 829-839.
137. J. E. G. van Dam, M. J. A. van den Oever and E. R. P. Keijsers, *Ind. Crop. Prod.*, 2004, 20, 97-101.
138. A. Ashori, *Bioresource Technol.*, 2008, 99, 4661-4667.
139. S. Panthapulakkal and M. Sain, *Compos. Pt. A-Appl. Sci. Manuf.*, 2007, 38, 1445-1454.
140. B. English, *The National Institute of Environmental Health Sciences (NIEHS)*, Editon edn., 1994, vol. 102, pp. 168-170.
141. M. H. Simatupang and R. L. Geimer, *Wood Adhesives*, Wisconsin, 1990.
142. J. Giancaspro, C. Papakonstantinou and P. Balaguru, *Compos. Sci. Technol.*, 2008, 68, 1895-1902.
143. G. Nemli, S. Yildiz and E. D. Gezer, *Bioresource Technol.*, 2008, 99, 6054-6058.

144. E. Guntekin and B. Karakus, *Ind. Crop. Prod.*, 2008, 27, 354-358.