



Determination of verifiable programmes for heat treatment of Welsh larch

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1. Introduction

1.1 Background

The objective of this study was to answer some simple questions:

1. At what temperature does larch resin become cured or permanently hardened? And does it have to remain at this temperature for a specific length of time?
2. What is the minimum temperature larch planks need to be heated to in order to achieve this effect in practice? And, does the thickness and moisture content of the planks influence the length of time needed?

Two related questions were also asked at the scoping stage of the work:

3. What effect does this have on properties such as glueability, paintability, hygroscopicity, durability, machinability.
4. Does the larch resin contribute to the durability of larch timber

However, question 3 has been addressed within the CIRP A4B funded project on upgrading Welsh timbers (COL 1023). It was shown that glueability of larch which had been thermally modified using the Welsh process was less influenced than is reported for the other commercial thermally modified woods. Performance with PVA and PU glues was similar to that in untreated larch. Paintability was also unaffected, standard surface preparation by sanding for both gluing and painting are assumed.

During the COL 1023 project a range of different timbers were treated, and a mild and a moderate thermal treatment process was explored. The level of reduction in hygroscopicity was related to the intensity of the treatment. That is, treatments conducted at higher temperatures or for longer time periods were more intense than those conducted at lower temperatures or for shorter time periods. In both the mild and the moderate treatments, the machining properties of larch were improved, although care was required to achieve this without inducing stresses within the timber, so treatment runs were well controlled to avoid defect formation.

Question 4 requires dedicated durability testing which was too costly for inclusion in the study.

1.2 Outline of work packages

Having established the focus of the study as questions 1 and 2, the following six tasks were agreed and undertaken in order to observe the behaviour of the wood, and its resin constituents, on different scales of treatment and testing.

- Literature review
- Lab scale experiments
- Analytical chemistry
- Pilot scale (1m³) capacity oven
- Commercial scale oven
- Reporting

The experimental work has been reported with reference to the relevant literature. A basic introduction to larch chemical composition and the concept of thermal modification are given in the literature review section. This forms the foundation for

further discussion of relevant scientific papers or texts at the relevant stages in experimental reporting.

The work of the six diverse and highly technical work packages has been conducted and drawn together to boost understanding of:

- Larch resin composition and observable thermal changes
- Larch timber changes in the presence and absence of resin
- Data relevant to thermal treatment as a practical process
- Data relating to plank dimensions, and kiln dimensions, and the influence on thermal modification regimes for different loads and ovens.

In the conclusions section the two primary questions are answered in the light of the whole array of test results and data analysis. A basic thermal modification schedule for a mild modification to cure larch resin is given. The parameters which must be considered before transfer from one oven to the next are highlighted in the accompanying text. It is assumed that any timber for treatment will be below fibre saturation point (FSP, approx. 30% moisture content), otherwise additional drying stages are required, and the likelihood of drying degrade is increased.

Also within the conclusions, but for reference only, a schedule based on the continuous treatment process is also provided. Transfer of this to a large kiln should be undertaken only after suitable preliminary tests based on the individual steps within the three day process.

The mild thermal modification systems tested and scaled up here allows preparation of timber in which the majority of resin pockets have been dried or partially dried (e.g. in a tacky not liquid state) to a point where no liquid seepage is anticipated in service. It is believed that this timber has a greater suitability for joinery applications than the untreated timber, and shows potential for lamination.

2. Literature review

2.1 Introduction

Thermal treatment of timber has gained a great deal of interest during the past twenty years. Much has been learnt about the effects of thermal treatment on the main commercially treated species (namely spruce and pine) since early commercial work was reported in the 1990s (Militz 2002). The improvement in dimensional stability and durability, and the temperatures necessary to achieve beneficial effects in these properties, are now well understood. Similarly, the alteration in mechanical properties, and the use of weight change as an indicator of the level of dimensional stability, durability or strength change achieved for a given set of kiln parameters are widely known (Hill 2006, Esteves and Pereira 2009). The efforts of the Finnish Thermowood Association to create a set of products with predictable and uniform quality from a large number of licensed kilns (Mayes and Oksanen 2002), and later in scale up when taken on by large companies such as Stora Enso (Stora Enso 2014) have demonstrated the adaptability and potential of the product for small to large scale production given suitable guidance and protocols.

Knowledge of the effect of heat on the chemical composition of the thermally treated wood has emerged, although generally this data relates to the treatments at temperatures of 180 to 240°C, and have identified the main alterations in hemicelluloses or lignin (Table 2.1). In the more mild treatment temperature range, chemical composition effects have been less extensively published, for example Popescu *et al.* (2013) reported the effect of thermal treatment at 140°C, but over very long time periods (4 to 21 days). Due to the more subtle effects at lower temperatures, data from this temperature range is also more specific to the timber species in question, thus for larch (the species of interest in Wales), and the temperatures used in the mild modification process, a significant quantity remains for study.

Let us first summarise the general trends and processes which are known to occur during full thermal modifications (Table 2.1), e.g. where weight change is greater than 5% as defined by the standard DD/CEN TS15679 (BSI 2007). The hemicellulose is frequently mentioned as the first of the structural components of the wood to be decomposed by the action of heat, it is also generally the most significantly altered component (Hill 2006). Changes in the hemicellulose have been reported from approximately 140°C, whereas lignin is generally thought to begin to change at 180°C or higher, with the nature of such changes being very dependent on the atmosphere in which the modification is performed. Cellulose is usually last to show chemical change, with degradation beginning at 210°C and this only in the amorphous regions.

Hemicellulose is a polysaccharide, containing glucose, mannose, galactose, xylose and arabinose. It has a branched chain resulting from the variety of different sugar monomers within it (Sjöström 1993). The precise characteristics of hemicelluloses vary with tree species, and the hemicellulose may also contain a number of acetate groups and carboxylic acid groups within its structure. The acetate groups are highly susceptible to the action of heat, and liberate acetic acid when deacetylation occurs, formic acid and methanol can also be generated at the same temperature range, along with non-condensable gases such as carbon dioxide. The onset of deacetylation in larch hemicelluloses (when studied in pure form) was 154°C

(Shimizu *et al.* 1989) Higher temperatures result in more significant changes, increasing the level of carbon monoxide and carbon dioxide evolved, and, leading to depolymerisation, and the formation of furfural or hydroxymethyl furfural (Fengel and Wegener 1989). The loss of polysaccharides becomes significant at 180°C.

Component	Main changes
Hemicellulose	Deacetylation Depolymerisation Dehydration Degradation to form formaldehyde, furfural, hydroxymethyl furfural and other aldehydes
Lignin	Apparent increase as a percentage of the wood Structural changes, including an increased carbonyl group content Free molecules Condensation reactions, including polycondensation with other cell wall components Cross-linking
Extractives	Emission of many original extractives as VOC during treatment New extractible compounds formed
Cellulose	Increased crystallinity Degradation of amorphous the cellulose component

Table 2.1. General chemical changes due to thermal modification of wood

The onset of chemical changes in lignin occurs at slightly higher temperatures than hemicellulose (e.g. from 180°C), and results in some increases in carbonyl structures and ether linkages. Bonds within the lignin are broken, liberating short fragments of the polymer, but bonds also reform during condensation reactions, including reactions forming bridges to hemicellulose or cellulose. Under a nitrogen atmosphere cleavage of alkyl-aryl bonds occurs from 220°C upwards, whereas in a steam atmosphere the cleavage of β-aryl ether linkages is reported from 180°C by Nuopponen *et al.* (2004). Steam processes can increase the quantity of lignin which can be extracted by water, and increase the phenolic hydroxyl content, which is likely to relate to the cleavage of the β-aryl ether linkages, leaving hydroxyl on the aromatic ring structure.

The cellulose shows the greatest degree of resistance to thermally induced changes, with reactions occurring only in the amorphous region, and most likely at temperatures of 210°C or higher. The result is an apparent increase in cellulose crystallinity, which is likely to relate to the degradation of the amorphous cellulose, and to the alteration of conformation of amorphous cellulose to assume a more crystalline form (this process is reported to be accelerated in the presence of water).

In the same way, changes in extractive content have primarily been studied for the species of greatest commercial interest including spruce and pine, rather than for larch. For example, Nuopponen *et al.* (2003) investigated the distribution of fats, waxes and resin acids within thermally treated pine. The fats and waxes migrated to the surface of the plank during the treatments in the 100 to 160°C temperature range. These compounds were fully driven off or not detected in the higher temperature runs (180 to 240°C). The migration of the resin acids along the length of the 1.5metre long batten was studied by FTIR, with thermal treatments up to 180°C revealing resin acids throughout the batten, while 200°C showed that the resin acids had migrated

from the centre of the batten, but were still present in the region towards the ends of the planks. These thermal treatments used a 3 hour hold period, but took a 36 hour period including a very slow steady increase of temperature up to the treatment stage.

For UK grown larch, where resin is a noticeable component, and the beneficial effect of resin cure during mild thermal modification has been observed, the mechanisms have yet to be fully established. The altered handling during machining operations, and greater surface quality resulting from planing or finishing have been demonstrated in a previous project (Spear *et al.* 2014). Additionally, larch contains an interesting form of hemicellulose, arabinogalactan, which is known to yield soluble xylans if the timber is soaked in water. Certain aspects of the thermal treatment effects on the larch hemicellulose may therefore also be specific to this species of timber.

2.2 Thermal treatment

In simple terms thermal modification, or heat treatment, involves treating timber at elevated temperatures (typically 180 to 240°C) for a sufficient period of time to alter the chemical composition of the hemicellulose within the wood cell wall. This results in a colour change, a reduction in density, an increase in dimensional stability and may also result in elevated durability or reduced strength depending on conditions (Esteves and Pereira 2009). The extent of decay resistance is largely governed by the duration and the temperature achieved during this treatment stage.

Steam can be used during thermal treatment to limit the influence of oxygen, by inducing a steady positive pressure of gases (air and steam) through the thermal treatment kiln. The steam is intended also to facilitate the physical changes in dimensions of the timber (throughout the thickness of the planks) which will result from change in equilibrium moisture content of the kiln, and the ameliorate any negative effects or stresses developing due to rapid evaporation from the heated timber surfaces. The presence of steam during the high temperature stage also contributes to re-ordering of the hemicellulose, to allow the wood structure to assume a slightly more compact, stable form after treatment. Others have suggested that the presence of steam (which, as the gaseous form of water, is a highly reactive molecule with the ability to form hydronium ions H_3O^+ by autonionization) may alter the chemistry of thermally induced reactions (Garrote *et al.* 1999), and potentially increase strength loss.

The thermal treatment system developed in Wales typically uses steam throughout the initial heating stage, and the dwell at high temperature, and a significant quantity of water is present condensing from the atmosphere throughout the cooling stage. Typically the temperatures used are at the lower end of the range used throughout Europe, and a benefit in machining and in resin cure has been seen for various treatments of different intensities (temperature and duration).

The thermal treatment process uses elevated temperature, and a controlled atmosphere to induce thermal changes in the chemical constituents of the wood, as shown in Table 2.1. One of the main aims of the process is the increase in dimensional stability which results when the number of hydrophilic (moisture-loving) hydroxyl functional groups on the wood surface is reduced. These groups are predominantly located in the hemicellulose. The reduction in hydroxyl groups reduces the propensity of the wood to swell by taking up moisture, for example the equilibrium

moisture content of Thermowood is reported to be 5 to 6% at 60% relative humidity, while untreated timber would be 12-14% (Mayes and Oksanen 2002). The level of inhibition of swelling increases with the temperature of treatment, or the duration of the treatment. In low temperature mild treatments such as the one described in the experimental sections of this report, some swelling remains likely.

The main commercial processes have been reviewed elsewhere, however a short summary of the Thermowood process here allows a better understanding of the differences in approach. The Thermowood schedule has been developed to run continuously (Figure 2.1), with Phase 1 requiring approx. 18 hours, prior to the ramp to the target treatment temperature in Phase 2 (Mayes and Oksanen 2002). Precise details such as hold duration are not shown, however the treatment is concluded in approximately three days.

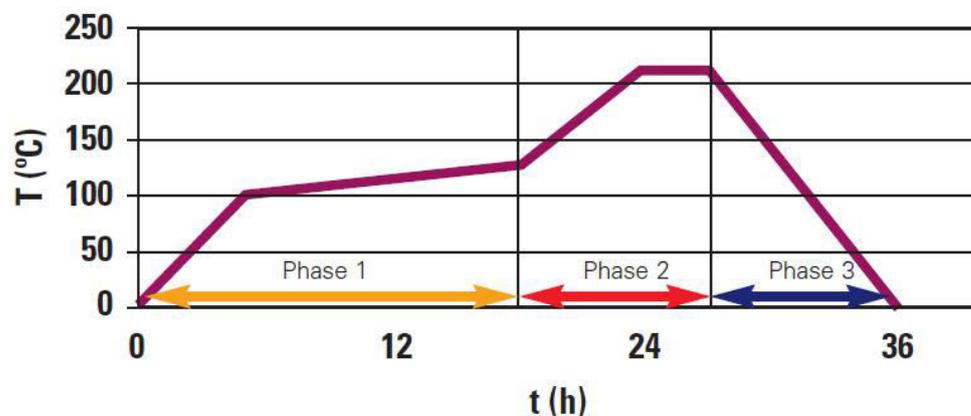


Figure 2.1. Schematic of the Thermowood D schedule, showing temperature increase in Phase 1 and 2, leading to a plateau at the treatment temperature of 210°C before cooling.

The Welsh system has been devised primarily to heat the timber to achieve a mild or moderate thermal modification, therefore the timber experiences temperatures considerably lower than for the commercial thermal treatments. For example the beneficial effects in machining are observed with temperatures of 150°C or above, and for shorter treatment times. The main characteristic of the Welsh system is its development for use in workshops with limits on the operating hours, either due to number of employees, or to insurance or practical time limits on operation at the premises. The continuous three day process is not suited to this method, so a system using three working days to achieve a drying stage, and treatment stage and a conditioning stage was developed (Figure 2.2).

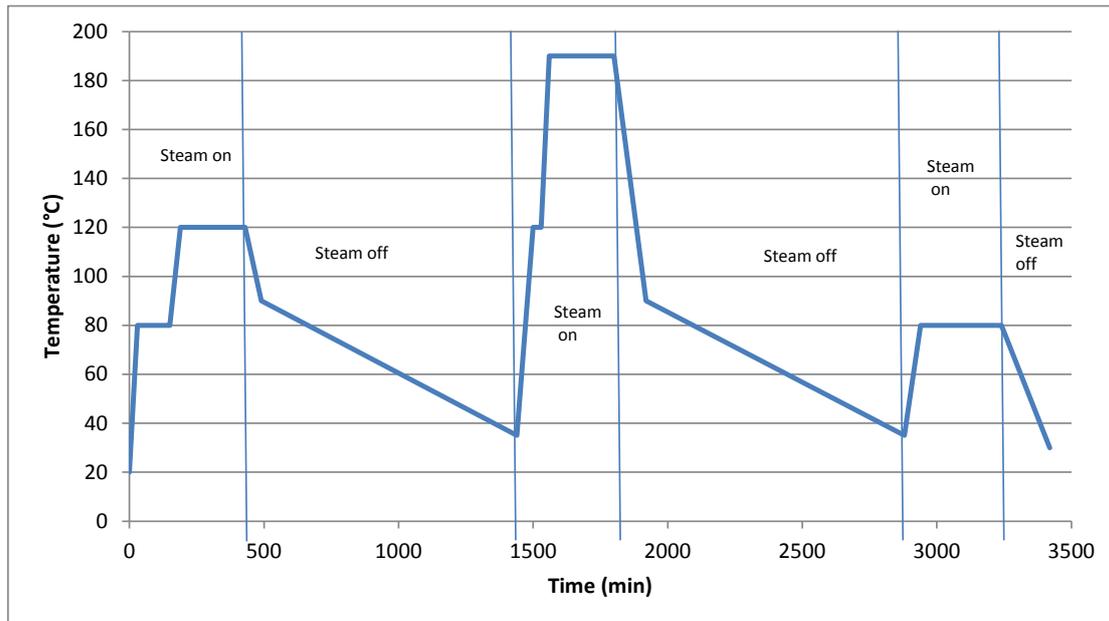


Figure 2.2 Schematic showing a typical three day treatment, where each day is kept within working hours for a small enterprise.

2.3 Larch composition

The focus of this study is larch, due to strong interest in upgrading this timber; current availability due to phytosanitary fellings to control the *Phytophthora ramorum* tree disease within Wales; and previous success in thermally treating this timber for joinery.

Larch is the third most common softwood grown in UK forestry, and can be divided into two groups – the European larch (*Larix decidua*), which is grown on the Eastern side of the UK, and Japanese larch (*Larix kaempferi*) and hybrid larch (*Larix x eurolepis*), which are more commonly found on the wetter Western side of the country. The focus of this study is the Japanese larch local to Wales, and for the remainder of the document, unless otherwise specified, larch will refer to the Japanese larch (*Larix kaempferi*).

British grown larch typically contains 23.5 to 30.1% lignin, and the holocellulose component comprises 62.8 to 71.8% glucose (predominately in cellulose, but also a constituent of hemicellulose), 14.2 to 21.5% mannose, 6.0 to 8.0% xylose, 1.6 to 2.6% arabinose and 3.9 to 6.8% galactose (Packman 1966). Based on a typical cellulose content of 41 or 42% in softwoods, the hemicellulose content may be between 27 and 35%.

Packman (1966) reported that the hot water extractable components are significant in larch, and can be up to 8.3% of the total material, in addition to between 1.3 and 3.7% alcohol/benzene extractable substances. This includes the resin, and various higher molecular weight organic compounds, which are grouped together under the title “extractives”, due to the method by which they are removed for analysis. The chemistry of the extractives will be considered in the next section.

The water soluble fraction of larch is dominated by arabinogalactan, a type of hemicellulose which occurs in much higher levels in larch than other softwoods. In

fact, it is known that the quantity of arabinogalactan may actually range from 5 to 30% (Côté *et al.* 1966). Within the arabinogalactan polymer, the galactose to arabinose ratio is 6:1, with approximately two thirds of the arabinose being in the furanose (five membered ring) conformation, and the other one third being a pyranose. The backbone is (1→3) linked β-D-galactopyranose units. On this backbone, almost every unit is grafted at the 6 position with a (1→6) galactose residue, but also (1→6) α-L-arabinose. In addition there are a small quantity of glucuronic acid residues within the molecule ((Côté *et al.* 1966, Sjöström 1993). It is commented that the heartwood contains more arabinogalactan than the sapwood (Côté *et al.* 1966), but trends with height within the tree, distance from the pith or bark, and age have also been suggested. The quantity appears to be greatest at the region closest to transition from sapwood to heartwood.

More recent research has continued to show that the extractives within larch are highly variable, for example, Geirlinger *et al.* (2003) in a NIR study of 278 larch trees (both *L. decidua* and *L. kaempferi*) from plantations and natural forest at a range of locations across Europe, reported hot water extractives ranging from 3.1 to 27.0%, acetone extractives from 0.8 to 4.3%, and a phenolic content (from the combined hot water and acetone extractive samples) of 0.3 to 4.8%. The acetone extractives are predominantly flavonoids (Ohmura *et al.* 1999, Grabner *et al.* 2005). The extractive content changes with distance from pith to bark, reaching a maximum at a layer of heartwood adjacent to the sapwood. This region may be referred to as the transition zone, as it is the region of xylem which has been most recently been closed off to sap flow, and subjected to the deposition of heartwood extractives.

When investigating the reasons for changes in termite feeding between steamed and unsteamed larch, Ohmura *et al.* (1999) reported the complete disappearance of arabinose from the hot water extract of steamed larch, and a near 50% reduction in galactose. It appears that the arabinogalactan is removed or chemically altered by the steaming process, and similar effects may be expected in the thermal modification of wood in a steam atmosphere. In addition, the increase in mannose and xylose in the hot water extracts of steamed larch (Ohmura *et al.* 1999) indicates additional changes may have occurred to other hemicelluloses within the larch during exposure to steam, rendering them more soluble. In later work, Ohmura and coworkers studied the flavonoids of larch, and found that they are depleted during steaming at 170°C for 60 minutes. Four flavonoids were investigated, as these are reported to occur in Japanese larch: taxifolin, aromadendrin, quercetin and naringenin. After hydrothermolysis various products were studied, only quercetin showed no change after the reaction, with flavanones undergoing isomerization, epimerization and dehydrogenation, except in naringenin, where only epimerization occurred, and quercetin which did not react (Ohmura *et al.* 2002).

2.4 Larch resin

Larch is one of the four main softwood genera which contain prominent resin pockets (along with pines, Douglas fir and spruces, (Desch and Dinwoodie, 1981)). While all softwoods may produce resin as a defence mechanism in living tissue, the species from these four genera are prone to forming significant pockets of resin, which pose a problem in sawing or machining the timber, or in paint quality for finished joinery. The resin pockets may be formed in response to injury, but larch (like all softwoods) also contains resin ducts which can readily supply resin throughout the xylem in smaller quantities. While these are smaller than the resin pockets, the spotting due

to resin migration from these ducts may be seen with a hand lens after a section of larch has aged for a period of time, or has been heated in a timber drying kiln.

The larch resin is predominantly composed of terpenes, with some fatty acids or other compounds present in small quantities (Sjöström 1993). It has been reported that flavonoid content of the resin increases if the resin is produced in response to injury (sometimes termed callus resin, Holmbom *et al.* 2008), and these flavonoids are likely to provide additional protection to the growing tree. The oleoresin, which is produced by the healthy tree contains a very rich mix of terpenes and terpenoids, with different molecular weights (mono-, sesqui- and diterpenes are seen), and different functionalities (alkane or alkene type terpenes, and acid, alcohol and ester functionalised terpenoids). As a result, these compounds have a wide range of properties – melting and boiling point, polarity. Many would be solid at room temperature if they were not held in a solution with the fatty acids and linear alkanes.

Much can be discovered by looking at the physical properties of some of the main components of the oleoresin (Table 2.2). The compounds within the table are not an exhaustive list, but give insight into the variety of components present.

Name	Type	Formula	Molecular wt (Da)	Mpt (°C)	Bpt (°C)	FP (°C)
α-pinene	monoterpene	C ₁₀ H ₁₆	136.23	-55	155	32
β-pinene		C ₁₀ H ₁₆	136.23	-61	163	34.9 ¹
longifolene	sesquiterpene	C ₁₅ H ₂₄	204.35	46.04 ²	252.2 ¹	101.1 ¹
germacrene		C ₁₅ H ₂₈	208.38	-3.83 ²	268.0 ¹	114.4 ¹
thunbergene	diterpene	C ₂₀ H ₃₂	272.47	56.93 ²	365.2 ¹	166.8 ¹
abietadiene		C ₂₀ H ₃₂	272.47	94.25 ²	360.3 ¹	162.0 ¹
thunbergol	diterpene	C ₂₀ H ₃₄ O	290.48	107.75 ²	392.7 ¹	169.8 ¹
epimanool	alcohol	C ₂₀ H ₃₂ O	288.47	127.46 ²	378.7 ¹	128.4 ¹
epi-torulol		C ₂₀ H ₃₄ O ₂	306.48	143.58 ²	409.1 ¹	176.3 ¹
torulol acetate		C ₂₄ H ₃₈ O ₄	390.56			
abietic acid	diterpene acid (resin acids)	C ₂₀ H ₃₀ O ₂	302.45	173	250	208.1 ¹
dehydroabietic acid		C ₂₀ H ₂₈ O ₂	300.44	159.73 ²	425.1 ¹	202.5 ¹
pimaric acid		C ₂₀ H ₃₀ O ₂	302.45	154.45 ²	413.2 ¹	198.7 ¹
undecane	linear alkane	C ₁₁ H ₂₄	156.31	-26	196	60
linoleic acid	fatty acid	C ₁₈ H ₂₈ O ₂	280.45	-12	230	110
water		H ₂ O	18.02	0	100	

Table 2.2. Some typical components of larch resin, and their physical properties.

Mpt, melting point; Bpt, Boiling point; FP, Flash point

Notes ¹ predicted data from ACD/Labs Percepta Platform, average of experimental data from EPISuite.

The lower molecular weight compounds, such as monoterpenes, are liquid at room temperature, while the majority of components are solids until heated. Similarly, the higher the molecular weight, and the higher the level of functionalization (e.g. alcohol or acid) then the higher the boiling point for the compound is likely to be. It may be expected that the low boiling point compounds (monoterpenes) will be driven off during the heating process, either during drying prior to thermal modification, or during modification.

Studies from drying softwoods, and from drying sawdust for bioenergy pellets, have indicated that the processes governing mono- and sesquiterpene evaporation is influenced by the presence of water. The actual temperature for driving the compound off may not be equal to the boiling point listed in Table 2.2, rather the process is more gradual and time dependent. For example the presence of water in the timber may influence the rate of loss of the mono and sesquiterpenes with temperature (Banerjee and co-workers, 1998, 2001). The solubility in water may be assisted by the presence of fatty acids and resin acids. While dissolved in water, the terpenes (especially monoterpenes) are better able to migrate through the wood, although mobility of sesquiterpenes is thought to occur more readily at moisture contents below fibre saturation point (Granström 2009).

The composition of the resin present in untreated larch has been studied, as has the composition of various resin pockets and deposits observed on thermally treated larch produced in the various kiln runs. This will be reported in the Analytical Chemistry section.

2.5 Thermal modification and chemical composition

In addition to the processes by which mono and sesquiterpenes are driven off from softwoods during drying, several chemical reactions also occur within the wood structural components (Table 2.1) at elevated temperatures. This can lead to differences in resin and volatile organic compound (VOC) content of thermally modified woods, which is an important consideration if using the timber in interior fittings. For example, a study of thermal modification of Scots pine timber by the Thermowood process showed distinct differences in the type of volatiles before and after treatment (Manninen *et al.* 2002). As expected, the monoterpenes were the dominant component of volatiles gathered from air dried Scots pine, e.g. α -pinene, and 3-carene, as well as hexanal. These three compounds contributed 74% of the total volatiles observed for air dry pine, but dropped to only 1% in the thermally treated samples. Instead, the thermally modified wood volatiles contained 2-furancarboxaldehyde (28.37%), acetic acid (23.91%) and 2-propanone (7.34%) as the dominant components. Note that the thermally treated timber had been treated at 230°C with steam for one day, which is a high intensity treatment, and the level of chemical change is therefore likely to be more significant than occurs in mild and medium intensity treatments studied here.

It is known that hemicellulose, and in particular xylan (pentosan) is very susceptible to thermal degradation (Kotilainen 2000, Manninen *et al.* 2002), and volatiles may be generated from this degradation process. An abundance of acetic acid is often released from thermally treated wood during treatment, which relates to hydrolysis of the acetyl groups on hemicellulose as a result of thermal and steam processes (Kotilainen 2000, Manninen *et al.* 2002). Peters *et al.* (2008) showed that the VOC content of spruce is dramatically reduced after thermal treatment at 180 or 200°C,

whereas hardwoods (beech, sycamore and ash) showed an increase in VOCs collected by the SPME method after thermal treatment. Untreated hardwoods do not contain terpenes, and generally had a significantly lower initial VOC content, including aldehydes (pentanal, hexanal and furfural), carboxylic acids (acetic acid) and esters, ketones, aliphatic and aromatic compounds. After thermal treatment, the type of aldehydes changed, with furfural and 5-methyl furfural becoming dominant.

The hexanal, which was observed by Maninen *et al.* (2002) for untreated pine, is known to be formed during oxidation of unsaturated fatty acids present in the wood, and is often observed from solid wood products such as parquet (Risholm-Sundman *et al.* 1998) and panel products. In summary, Manninen *et al.* (2002) reported that the alcohol, aldehyde, ketone and carboxylic acid content of timber increases as a result of thermal modification, while terpene content is markedly reduced. Aliphatic and aromatic hydrocarbon content is also increased by a small amount.

The extractive content of spruce was also shown to change as a result of thermal modification (Peters *et al.* 2008) with the level of dehydroabietic acid, linoleic acid campestrol, and β -sitosterol decreasing slightly, while levels of lignin degradation products increased. These included coniferyl aldehyde, vanillin, and a stilbene. The hardwoods were reported to include a greater number of lignin degradation products, additional stilbenes and resinols. Polyaromatic hydrocarbons such as phenanthrene, acenaphthylene, and phenanthrene derivatives have been reported by Kamdem *et al.* (2000) in heat treated maritime pine.

The extractive content of thermally treated larch has also been investigated and revealed many trends in common with the above data. Full details are reported in the Analytical Chemistry section.

3. Lab scale experiments

3.1 Initial study

A sample of larch was selected with fresh resin on the surface which had oozed from a resin pocket cut open during planing. The perimeter of the resin on the surface was marked using pencil before the sample was cut into three segments. The first segment was retained at room temperature, the second was placed in an oven at 50°C overnight, and the third was placed in an oven at 105°C overnight.

The next day, the room temperature sample still had sticky resin, which had not changed since the previous day. The 50°C piece still had tacky resin on the surface. The 105°C piece had dried, leaving a greasy stain in the location outlined by the pencil margin. The patch where the resin had been was no longer tacky, and the surface was dry to the touch. This initial study prompted the use of set temperature of 50°C and 105°C in the Stepwise DSC runs, and confirmed that the use of temperatures above 100°C in the kiln-based thermal modification process was likely to be a significant contributor to the drying effects reported by timber users receiving thermally treated timber.

3.2 Pressure reactor experiments

In a second experiment, with small samples of solid wood (no visible resin pockets), the effect of heating in the presence of a steam rich atmosphere was investigated. Sample blocks were approx. 50mm length and 15 x 25mm cross section, with no specific growth ring orientation or region of the trunk being sampled. Several samples were taken from juvenile wood, but others were from the mature wood region.

The objective was to study the changes occurring under mild thermal conditions (110°C, 120°C and 140°C) which had been suspected to occur in colder regions of the stack during preliminary trials in the pilot scale oven. The presence of steam was essential to this, and a sealable pressure reactor was used in order to generate and retain steam around the samples during treatment (Figure 3.1).

Test runs were conducted to establish which set point would achieve the required temperatures (110°C, 120°C and 140°C) within the reactor during the early stages of the heating process. These set points were 104°C, 109°C and 122°C respectively, due to the tendency of the high power heater element to overheat near the boiling point of water (latent heat of vaporization). The duration of the treatment was selected as 1 hour. 300ml of deionised water was added to the base of the reactor, and wood blocks were placed in a basket suspended above this reservoir of water. The valve at the top of the reactor was left slightly open to avoid large pressure build up within the reactor, but a condenser system was designed to fit to this steam outlet, to cool and retain the water, thus slowing the rate of loss from the system. This had a self-regulatory effect on the moisture loss from the reactor, and allowed the full treatment time to be achieved without the reactor drying out.



Figure 3.1. Pressure reactor during thermal treatment of small larch blocks, trapping and measuring steam loss from treatment vessel.

	Moisture content before (%)	Moisture content after (%)	Weight change (%)
110°C			
A1-A	11	19	-3
B8-A	12	25	-2
C2-A	11	24	-2
D3-A	11	25	-2
120°C			
A2-A	11	9	-3
B2-A	11	12	-3
C3-A	11	29	-2
D2-A	11	29	-2
140°C			
A6-A	11	7	-3
A7-A	11	8	-3
B7-A	11	8	-3
C1-A	11	8	-2

Table 3.1. Initial and final moisture content of sample blocks, and weight loss due to the hydrothermal treatment.

The treated blocks gained colour, becoming a pale brown rather than the pinkish colour of untreated larch. This was in line with the expected changes for low

temperature and steam. Despite the different temperatures used, there was very minor change in the weight loss seen in the blocks, which ranged from 2 to 3% in each batch (Table 3.1). The treatment at 110°C and 120°C still contained liquid water at the end of the run time, whereas the 140°C run left very little moisture in the vessel after the treatment had finished. This may explain the lower final moisture content of the blocks from this higher temperature run.

Samples cut from these blocks were observed using FTIR spectroscopy (method details described in Section 4.6). An example spectrum for the untreated and three levels of treated blocks is shown in Figure 3.2. Changes due to the different treatment temperatures (110°C, 120°C and 140°C) were relatively minor. The most noticeable change occurred at 1588 cm^{-1} which relate to C-O stretches and conjugation with α -carbonyl groups and at 1637 cm^{-1} relating to the presence of adsorbed water in hemicellulose (marked with the red arrow in Figure 3.2). The change in the 140°C treatment spectrum (uppermost line) is greater than for the 120°C and 110°C lines (next lines down). The magnitude of the changes in the FTIR spectrum was in line with expectations, as the treatment temperatures had been selected to be below the main onset of thermal degradation of the hemicellulose.

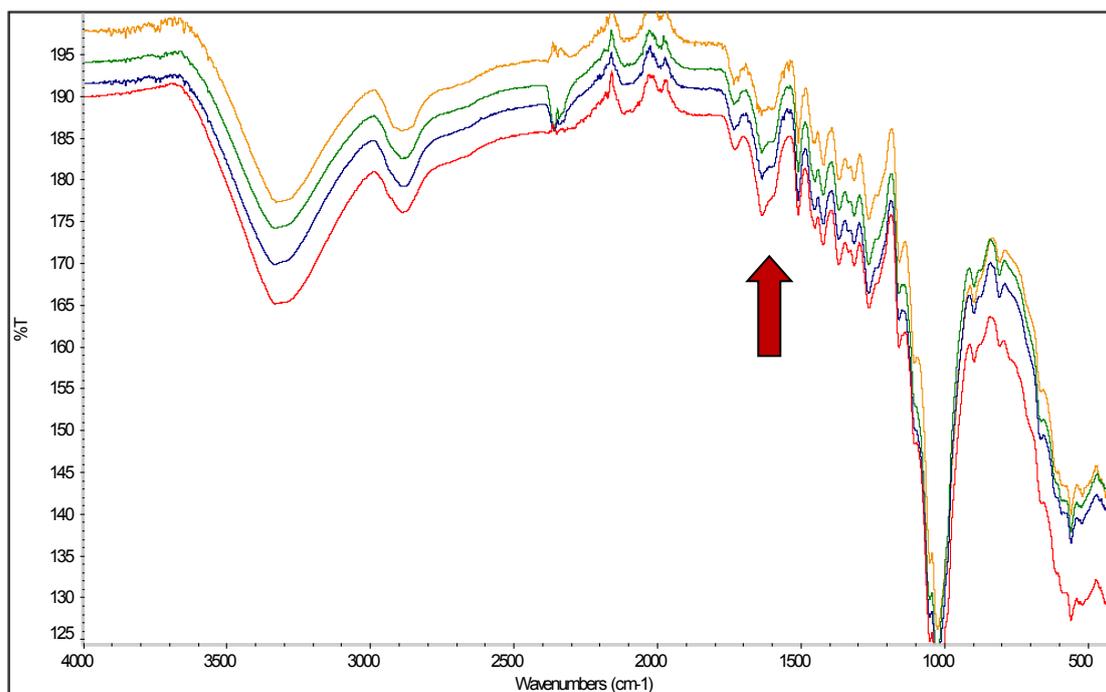


Figure 3.2. Comparison of control samples (red) with samples treated in the pressure reactor experiments at 110°C (blue), 120°C (green) and 140°C orange.

3.3 Pressure reactor samples containing resin

Strips of larch in which small pockets or large resin canals had been identified were placed in the pressure reactor on a treatment run using the same steam rich atmosphere and 140°C schedule.

The larch had been machined to a good surface, and was approx. 5mm thick, meaning that good thermal transfer was expected throughout the piece. The relatively thin dimension also allowed the sample to be placed on the ATR unit of the

FTIR and held sufficiently well to record a spectrum without damaging the sample prior to treatment. This permitted sampling from identical locations before and after treatment.

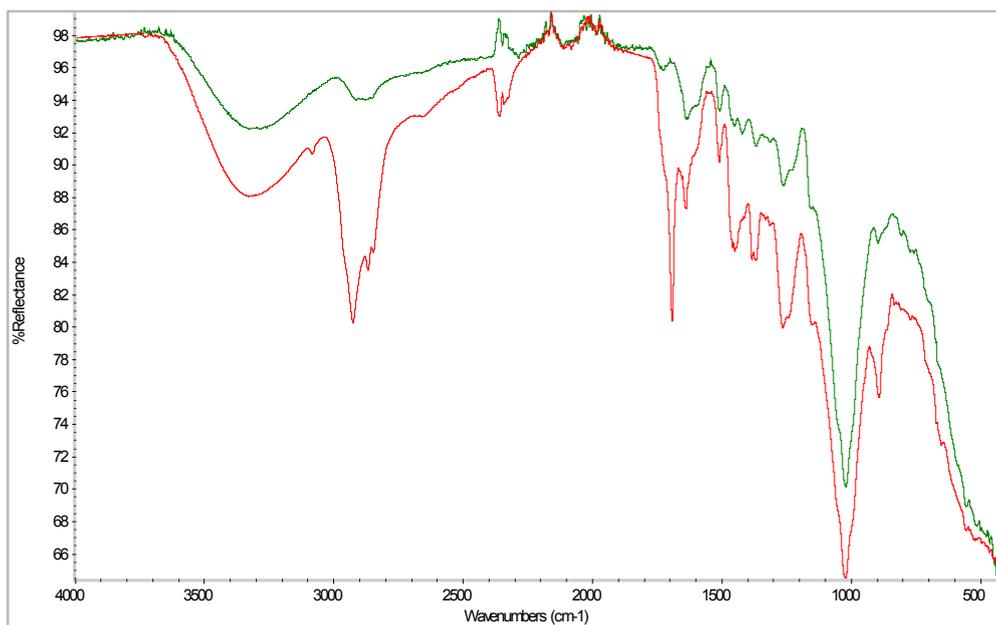


Figure 3.3. FTIR spectra for earlywood (green line) and resin pocket (red line) in sample Larch 7 prior to treatment.

Once again, changes in the spectrum for the wood was very minor. The resin pockets prior to treatment had spectra which clearly distinguished them from the wood (Figure 3.3), confirming the visual identification.

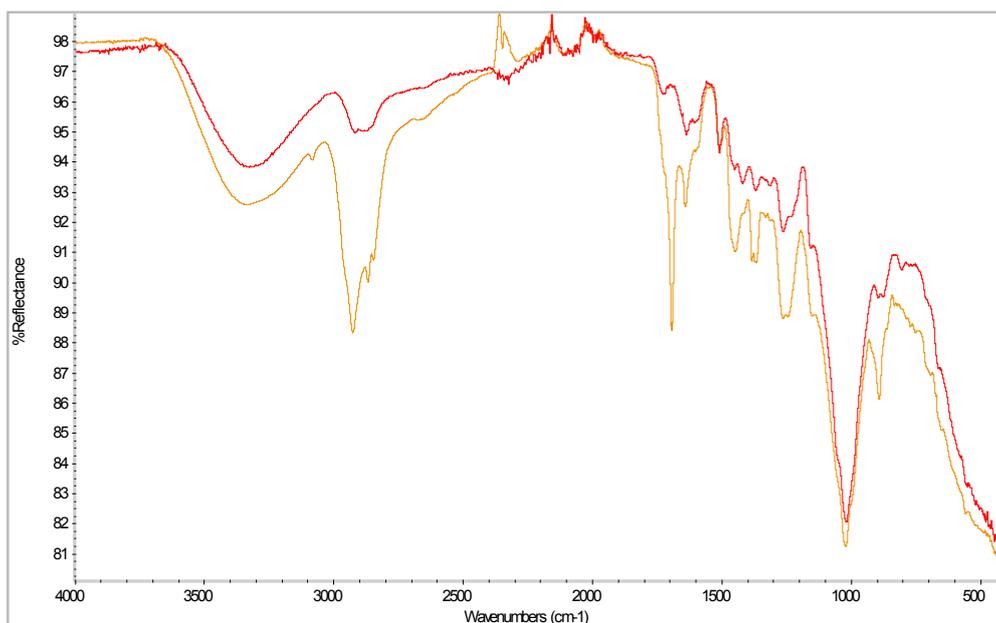


Figure 3.4. Resin pocket before treatment (orange line), and after 140°C treatment in pressure reactor (red line)

Large differences were seen in the spectra for the resin pockets before and after treatment (Figure 3.4). The spectrum for the resin pocket after treatment showed that carbonyl absorptions at 1721 cm^{-1} and 1230 cm^{-1} were lost, and there was also a

strong change in the C-H stretch region at 2900-3000cm⁻¹. Similar effects were seen in all seven of the resin pockets studied.

The spectrum for the dry resin pocket retained many of the peaks but at a much lower level than in the untreated resin pocket spectrum. It appears that significant changes, possibly by driving off or loss of compounds occurred within the pressure reactor at 140°C. These results will be discussed further in the analytical chemistry section (Section 4.6).

4. Analytical chemistry

4.1 Overview

The resin composition of larch was evaluated before thermal treatment, and in various states after several thermal modification processes. Larch resin is often associated with the pith or juvenile wood, in addition to its formation in callus tissue resulting from wounding or insect attack of the tree. The callus resin is richer in lignans than the oleoresin (Holmbom *et al.* 2008). These experiments have focused on the oleoresin, which is more abundant in the freshly sawn timber, especially the juvenile wood near the pith. Here the dominant components are mon-, sesqui- and diterpenes, and these will form the majority of the chemical studies reported.

Some planks were seen to have significant resin on cut surfaces prior to thermal modification, and this was collected in the liquid or viscous state, as this best represents the material encountered by the sawmiller. Older, dried material from less recently cut surfaces was avoided as far as possible to avoid detection of the effects of ageing.



Figure 4.1. Larch oleoresin in the juvenile wood of a freshly cut plank. The cracks visible in the resinous plank are radially aligned, and the pith would originally have been to the left of this plank.

Resin was frequently found to be associated with the pith, or juvenile wood, as shown in Figure 4.1. In thermally treated larch planks, this resin was frequently observed to have solidified on the plank surfaces, as will be discussed later. This

material was collected by scraping, or by dissolution with solvent followed by transfer onto a clean glass plate, from which the solution of resin could then be gathered and prepared for chromatographic analysis.

The untreated, and the thermally treated larch resin samples were analysed by gas chromatography mass spectrometry (GC-MS). This couples the separation of molecules by size and polarity in a gas chromatograph with the mass spectrometry technique which can be used to detect molecular weight and typical fragmentation patterns characteristic of different organic molecules. The combination of these two techniques gives a powerful tool to identify the composition of the resin, and to observe changes which occur in the resin composition due to the thermal modification processes.

In addition, the extractive content of the larch is expected to change with the thermal modification process. This area emerged from the literature review as an under-investigated topic. In the mild thermal modification process it may be more instructive than full chemical composition analysis or quantification of hemicellulose loss. Resin components are expected to form a significant portion of the initial extractive content, relating to their widespread distribution within the resin canals and parenchyma. On thermal modification was expected to alter depending on thermal modification conditions. The change in extractive composition resulting from thermal modification was also studied by GC-MS, as an increase of some compounds (relating to changes in cell wall polymers) and a potential decrease in other compounds (due to the evaporation) may indicate the effect of heat in regions away from resin pockets. In addition it was expected that some chemical changes may occur to the compounds which typically comprise the extractive fraction.

All GC-MS analysis was performed on a Perkin Elmer Clarus, using a VF5 column in splitless mode. After injection at 60°C, the temperature was maintained for 1 minute then increased at 6°C/minute to 300°C where the temperature was held for 10 minutes. Mass spectra were analysed using TurboMass, and compared with reference spectra from the NIST library. Retention index information for common plant terpenes and terpenoids compiled by Babushok *et al.* (2011) was used to assist in identification amongst closely related structures, e.g. the C₁₅H₂₄ sesquiterpenes. The solvent system used for the resin was either heptane, dichloromethane, or methanol.

4.2 Composition of larch resin

Samples of freshly oozed larch resin were collected from various planks of untreated wood. This resin was used in experiments on the GC-MS and the TGA-DSC. Resin A was sourced from Coed Cymru in timber of the same batch as used in Runs B to E. Resin was also sampled from freshly cut material used at Coed Cymru in the summer of 2015 (UT, Dia1 and Dia2). Samples were also sourced from Coed Mon and Aberbargoed, however these samples from larger kilns were used only in GC-MS analysis.

The chemical composition of the resin was studied by gas chromatography-mass spectrometry (GC-MS). Samples of approx. 5mg were dissolved in the selected solvent (hexane, dichloromethane or methanol) and run on a Perkin Elmer Clarus GC-MS using a VF5 column.

The chromatograph revealed many components, including mono-, sesqui- and diterpenes as expected based on the literature survey. Note that due to the method used, the majority of the diterpene resin acids (which are compounds with organic acid functional groups) may have only been detected in limited quantities on the column used. However the majority of the compounds reported by Mills (1973), for example are the resin acids like abietic acid, pimaric acid, palustric acid, were seen. Various diterpenes without acid functional groups were also detected, e.g. epimanol and thunbergene. Any fatty acid compounds, also known to be present in softwood resins, were not detected in the GC-MS experiments, and this is likely to the selected column polarity.

For the purposes of this experiment, the comparison of chromatography profiles before and after the various treatments can still reveal much about the drying process amongst the compounds which were detected.

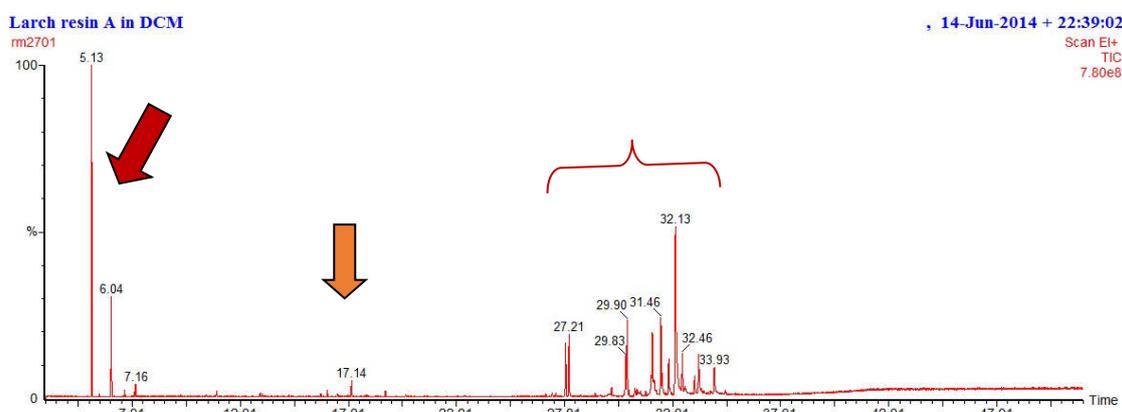


Figure 4.1. Gas chromatograph for Resin A in dichloromethane. Red arrow indicates the monoterpene region, orange arrow indicates the sesquiterpene region and the bracketed section contains the diterpenes.

Figure 4.1 shows a typical chromatograph for the larch resin. The main three monoterpenes identified were α -pinene, β -pinene and 3-carene, all were seen before 10 minutes. The main sesquiterpenes were longifolene, γ -elemene, Germacrene D, β -cadinene and Germacrene B. These were seen between 15 and 19 minutes. The diterpenes were identified at higher retention times, above 25 minutes, this region contained a mixture of many compounds, including diterpenes (thunbergene), diterpene alcohols (e.g. epimanol, isopimarol, torulosol), acetates of some diterpene alcohols (e.g. torulosol acetate) and diterpene resin acids (palustric acid, abietic acid, neoabietic acid).

4.3 Composition of larch resin after controlled heating in a DSC

The unheated larch resin was also studied using a differential scanning calorimeter (DSC). The instrument is also a thermogravimetric analyser (TGA), and records the weight change of samples during exposure to a temperature profile. This was used in order to observe the behaviour of small samples of resin on heating to temperatures similar to those used in the thermal modification programmes investigated. In one set of experiments, the untreated resin was heated using a profile which ramped to a set point selected to equate to the hold temperature on the drying day (Day 1) or on the treatment day (Day 2). A series of different temperatures for Day 2 were chosen

(150°C, 170°C and 190°C). These equated to the set point used in kiln schedules developed for the pilot and large scale timber ovens. This gives insight into the weight change due to heating to each set temperature, which can be used to estimate the proportion of the different resin components driven off by heat.

In addition, a simplified stepwise programme was used, which ramped the temperature through a series of increments. This mimicked the step by step approach taken in the kiln schedules, but used a simplified series of set points: 50°C, 105°C and 200°C. Each one used a one hour hold period at the isothermal set point. During each isotherm, and each ramp stage, it was possible to observe how much material had been driven off or evaporated. The first set of samples exposed to the stepwise schedule did not use a hold at 200°C, but later experiments added this (20 minutes), as a result of observations in the isothermal studies.

Samples of approx. 5mg resin were placed in unsealed aluminium pans, and heated using a Mettler Toledo TGA/DSC 1 STAR^e System. The pan and an empty reference pan were heated on one of the schedules listed in Table 4.1. The experiment was conducted under 50cm³/min nitrogen as purge gas. The weight loss during this thermal procedure was recorded over time, and thermal input to each pan was recorded, allowing endotherm or exothermic processes to be detected.

Stepwise	Stepwise hold 200	Day 1	Day 2 190°C	Day 2 170°C	Day 2 150°C
10°C/min to 50°C	10°C/min to 50°C	10°C/min to 120°C	10°C/min to 190°C	10°C/min to 170°C	10°C/min to 150°C
30 min hold	30 min hold	60 min hold	60 min hold	60 min hold	60 min hold
5°C/minute to 105°C	5°C/minute to 105°C				
30 min hold	30 min hold				
5°C/minute to 200°C	5°C/minute to 200°C				
No hold	20 min hold				

Table 4.1. DSC schedules used in the larch resin experiments

From the TGA/DSC output it was possible to calculate the mass lost due to each step of the sequence. For the graph shown in Figure 4.2 the stepwise schedule was used. The weight change for hold periods at 50°C and 105°C are visible in the upper line (sample weight), and the percentage of weight lost by the sample at each step has been calculated. The lower line refers to heat flow, and is approx. horizontal during hold periods, but increases steadily during temperature ramps.

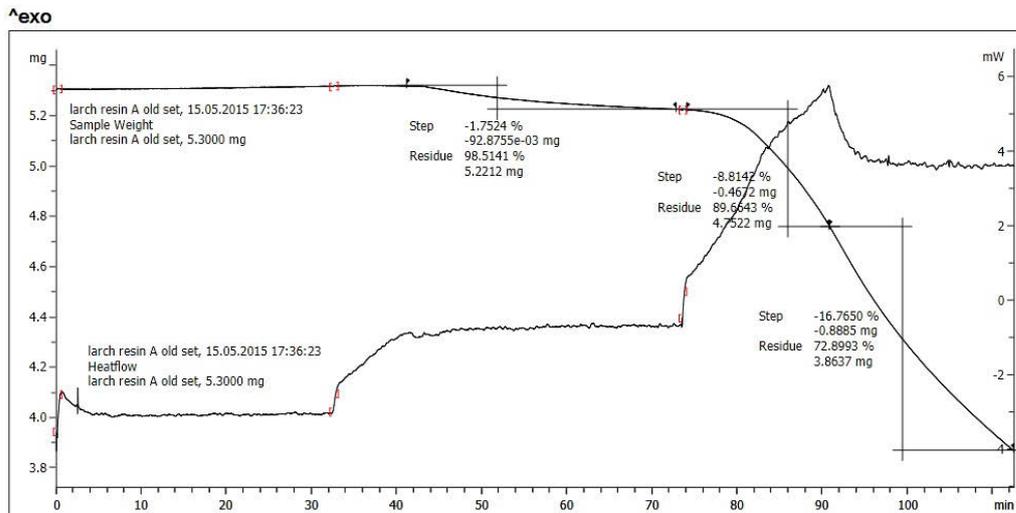


Figure 4.2. DSC and TGA output for resin A old, run on the stepwise hold 200 schedule

The weight loss seen for larch resin on the stepwise schedule is recorded in Table 4.2. It is possible to see that the 200°C hold period contributes significantly to the degree of weight loss – this the initial samples run without the 20 minute hold at 200°C record much lower total weight losses.

	Stepwise hold 200 schedule			
	50°C	105°C	ramp	200°C
Resin A old	negl.	-1.752%	-8.814%	-16.765%
Resin D old	-0.210%	-1.727%	-9.504%	-21.900%

Table 4.2. Weight loss for samples on stepwise hold 200 schedule

The weight loss for schedules which used the Day 1 and Day 2 set points as isotherms are recorded in Table 4.3. Example TGA-DSC outputs are shown in Figures 4.3 to 4.6 for the four different isothermal temperatures. The lower temperature runs showed small mass losses during the ramp and the isotherm (Table 4.3). The quantity of resin driven off was clearly related to temperature of the isotherm, with significant increase in weight loss for the 170°C and 190°C programmes.

		Day 1 (120°C)	Day 2 (150°C)	Day 2 (170°C)	Day 2 (190°C)
Resin A	ramp		-2.3270%	-3.6629%	
	isotherm		-12.5246%	-23.1080%	
	residue		3.9153mg	4.5632mg	
UT	ramp	-1.0444%	-2.0191%	-7.1936%	-10.5407%
	isotherm	-9.5621%	-14.8054%	-31.0611%	-48.5842%
	residue	3.6678mg	3.5724mg	3.9861mg	1.0196mg
Dia1	ramp	-3.0689%	-3.1069%	-7.3155%	-11.9764%
	isotherm	-8.2138%	-15.5338%	-27.6076%	-60.5482%
	residue	3.8123mg	3.5788mg	2.7895mg	0.5186mg
Dia2	ramp	-2.6315%	-4.8903%	-6.4693%	
	isotherm	-8.1963%	-11.3445%	-28.0898%	
	residue	2.8580mg	5.6884mg	4.4709mg	

Table 4.3. Weight loss due to simple isothermal DSC runs (1 hour at 120°C, 150°C, 170°C or 190°C)

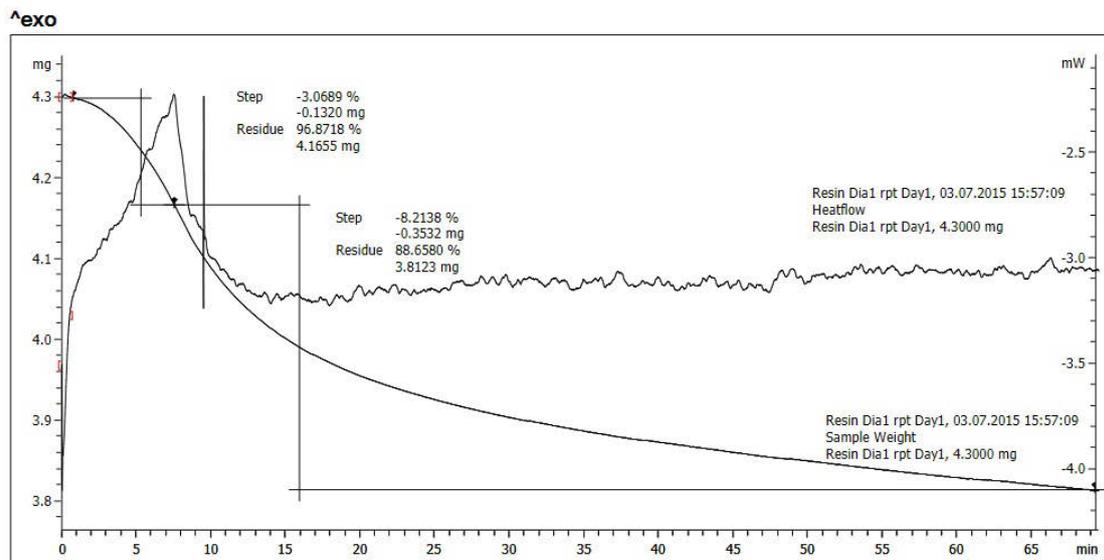


Figure 4.3. TGA-DSC output for Day 1 run, showing 3% weight loss on the ramp and 8% loss on the isotherm

The 120°C schedule (representing the Day 1 drying type schedule) had the greatest residue remaining after the 60 minutes, it also appeared to be nearing a plateau after 60 minutes (Figure 4.3). The 150°C and 170°C programmes showed steep weight loss curves up to the end of the run, indicating that mass loss would be likely to have continued at a similar rate had the isotherm been held for longer. The 190°C Day 2 programme began to approach a plateau after significant steady weight loss during the isotherm, although this varied between samples of resin and sample size in the DSC crucible.

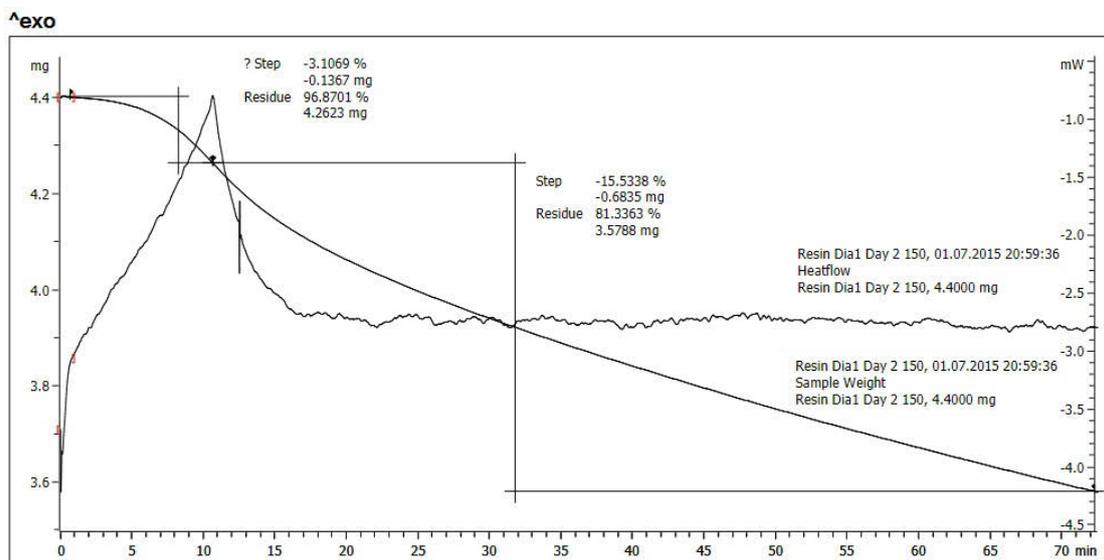


Figure 4.4. TGA-DSC output for Day 2 150°C run, showing 3% weight loss on the ramp and 15% loss on the isotherm

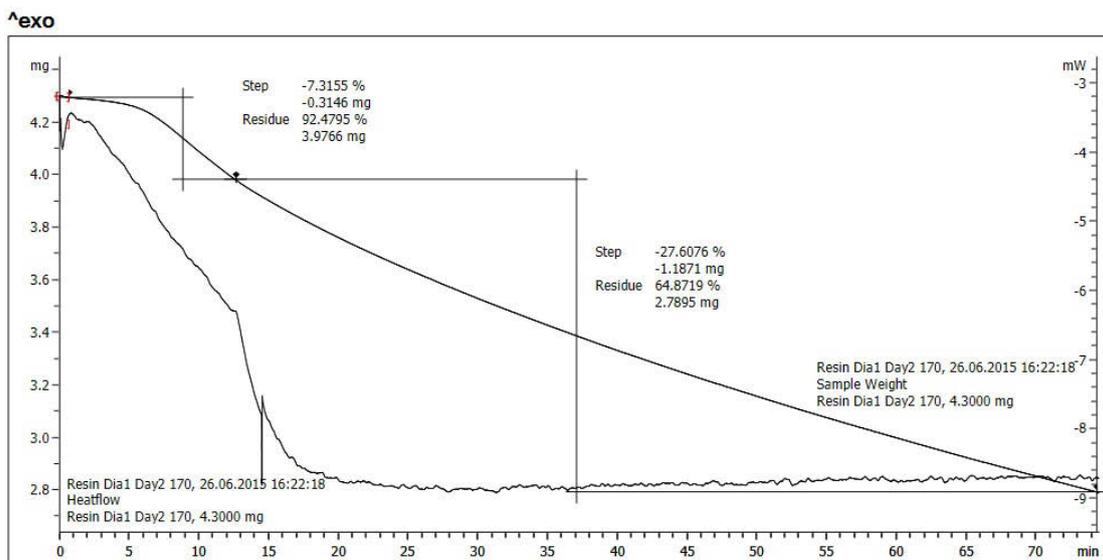


Figure 4.5. TGA-DSC output for Day 2 170°C run, showing 7% weight loss on the ramp and 27% loss on the isotherm

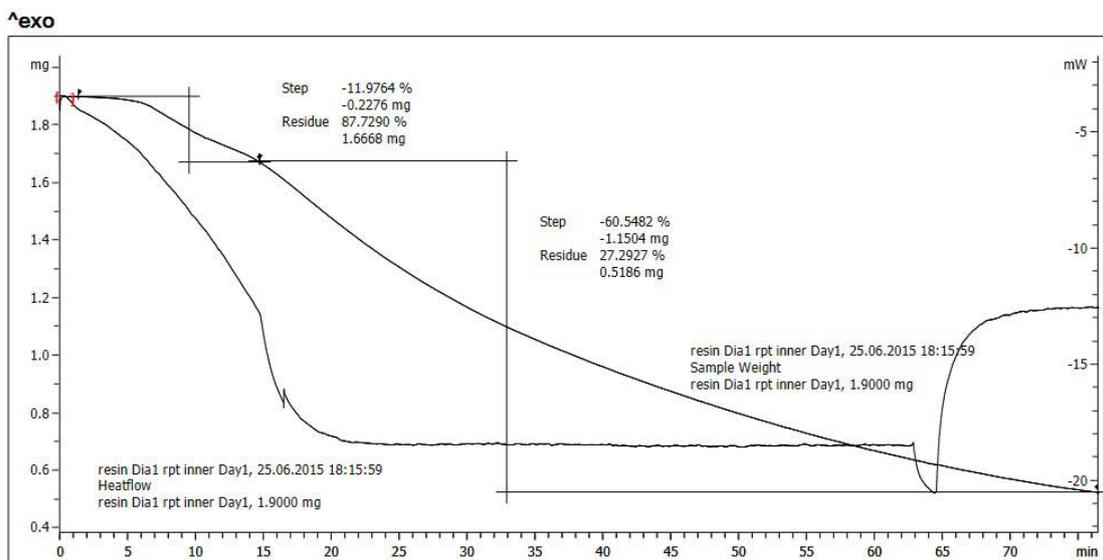


Figure 4.6. TGA-DSC output for Day 2 190°C run, showing 12% weight loss on the ramp and 60% loss on the isotherm

After the DSC thermal sequences, the resin residue was dissolved using dichloromethane and transferred to a vial for GC-MS analysis using approx 1ml of solvent. The residue of some DSC runs was too small to allow detection on the mass gas chromatograph (e.g. due to high mass loss at 190°C). However in most cases a good chromatogram was obtained and mass spectrometry was used to identify the components, except where too weak. In these cases it was sometimes possible to recognise previously identified compounds due to their elution time (in comparison with samples run within the same batch on the same column).

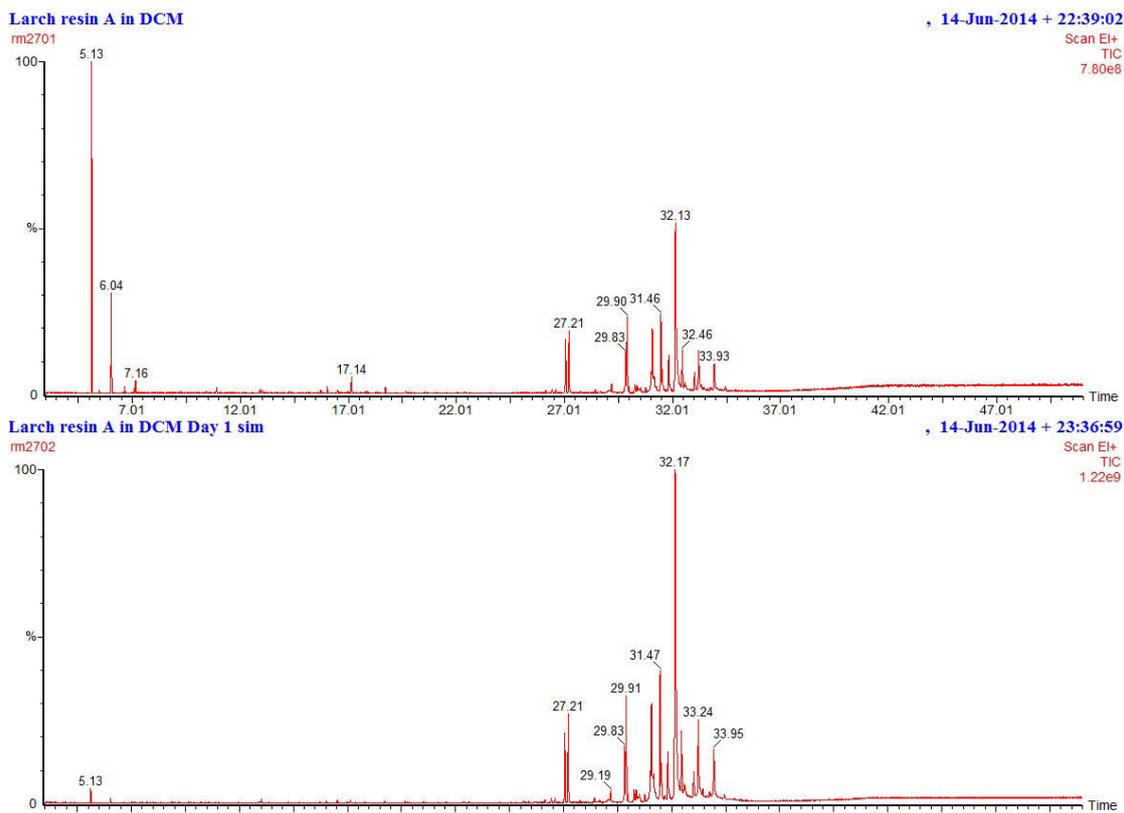


Figure 4.7. Gas chromatograph of Resin A (a) before and (b) after heating on DSC to 120°C.

When larch resin A was heated to 120°C using the DSC/TGA to simulate a Day 1 heating cycle, the GC/MS trace showed a clear reduction in monoterpenes. The β -pinene and Δ -carene peaks (4.35 and 5.45 minutes) were not present, and only a very small α -pinene peak (3.72 min) remained. Similarly the sesquiterpene peaks normally observed at 16 to 21 minutes were almost undetectable. The diterpenes and higher melting point sesquiterpenoids, were still present, for example thunbergol and epimanol (38.75min, 40.42min) as well as the suspected torulosol and torulosol acetate (44.05min and 44.09min). Minor peaks in the very high retention index range were also still present, e.g. 47.35, 49.97 and 53.24min.

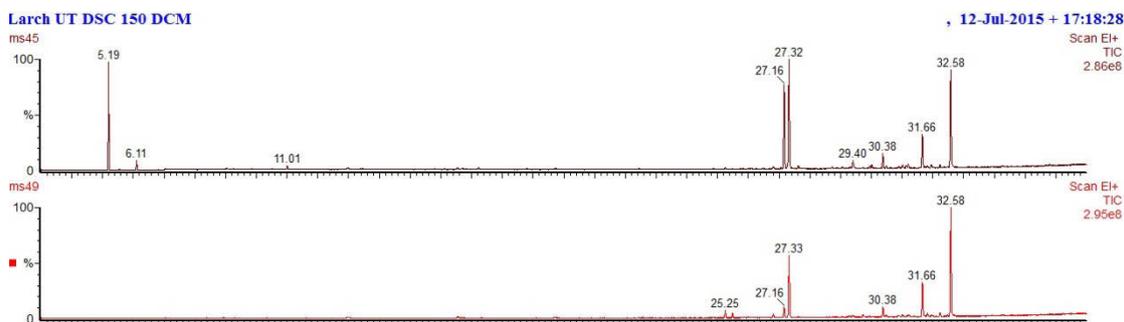


Figure 4.8. Gas chromatographs for resin (UT) and the same resin after the Day 2 150°C DSC programme.

The resin used in Figure 4.8 has been taken from a plank which was in the wood pile for a number of months prior to sampling. It was still tacky, but probably older than the fresh resin seen in Figure 4.7a. The difference in diterpene profile may reflect some ageing processes which occur on exposure to ambient conditions, however the

pair of peaks at 27.16 and 27.32 minutes equate to the thunbergol and epimanool seen near 17.21 minutes in the earlier study. The strong peak at 32.58 minutes equates to the peak seen at 32.13 in the fresh Resin A sample. Because of these differences, data are presented as pairs of samples.

The main difference seen in Figure 4.8 is the total removal of the α - and β -pinene peaks at 5.15 and 6.11 minutes for the heated resin. In the DSC, with an open pan, the volatile monoterpenes were easily driven off from the sample during the temperature schedule used, despite the conditions being lower than the boiling point of for example 155°C (α -pinene). The sesquiterpene peaks for the raw resin were very weak, but present at 15.81 to 18.81 including germacrene D and γ -elemene. In the sample exposed to the 150°C hold temperature all sesquiterpenes were also missing. The boiling point for these is higher, e.g. 268°C for germacrene.

In the diterpene region the most noticeable change was the formation of two new peaks at 25.25 and 25.48 minutes. The untreated resin did not contain these peaks. These were identified as thunbergene and a pimaradiene, which are likely to have been formed by dehydration of the thunbergol and epimanool during heating. The dehydration of thunbergol to thunbergene is widely known in museum and fine art curation, where Venice turpentine (Larch resin from European larch) was widely used in oil paintings of old masters. Dehydration of epimanool to pimaradienes is less widely reported, however the mass spectrum of the second new peak observed at 25.48 min contained the characteristic mass fragments for pimaradiene.

In the UT sample exposed to 170°C the same effects were observed, the monoterpene and sesquiterpene peaks were completely removed, and small changes appeared to have occurred in the profile of diterpenes. However, the sample was not sufficiently concentrated to confirm the presence of all compounds, as the total mass lost during the 170°C DSC run was 38% of the initial sample weight, leaving only a very small residue for analysis in the GC-MS.

The most noticeable effect was the near elimination of the monoterpenes by the DSC run. This occurred for the Day 1 schedule (120°C isotherm) as well as the Day 2 simulations (150, 170 and 190°C). The boiling points of the α - and β -pinene are reported to be 155 and 163°C, which are above the temperature of the isotherm used for the Day 1 study. However it is possible that the relatively low enthalpy of vaporisation (37.8 and 38.6 kJ/mol respectively (similar to that of ethanol 38.6)) may lead to volatilisation of individual molecules from the surface before the boiling point. In addition, pinene is known to show azeotropic behaviour in mixtures with various alcohols and carboxylic acids, so prediction of its behaviour in the complex mixture present in oleoresin is difficult, even though the vapour pressure of the two compounds is known (3.5 for α -pinene and 2.4mmHg for β -pinene at 25°C respectively. These values are lower than the vapour pressure of water (17.5mmHg, i.e. the pure pinene is less likely to volatilise).

In the TGA output from the TGA-DSC runs (Figure 4.3-4.6) it is obvious that the weight change is not sudden relating to a sharp evaporation event (which would be accompanied by an endotherm for the latent heat consumed to boil off that specific compound at its boiling point). Neither is it a series of such endothermic events indicating a sequence of components from a separable mixture. Instead, the TGA records a gradual weight loss over the full 60 minutes. This implies a strong interaction between the components, which is also likely given the azeotropic tendencies of the various monoterpenes mentioned above.

The 120°C isotherm showed an interesting tendency towards a stable weight, with rate of mass loss dropping from 0.1mg/4s to 0.1mg/23s. This may correspond with the exhaustion of the compounds which are mobile at this temperature (e.g. moisture and low molecular weight organics), and the inability of other compounds (which require higher energy) to volatilise. By comparison the 150°C and 170°C isotherms generated steady state rates of mass loss: approx. 11s and 3.25s to evaporate 0.1mg of resin respectively. This equates to 0.545g/min at 150°C and 1.846g/min at 170°C. These temperatures are therefore able to mobilise a greater proportion of the compounds present in the oleoresin. The 190°C isotherm generated a rapid loss of mass, followed by a slowing rate as the supply of mobile material was exhausted.

It is worth noting that in the full sized planks, the rate is likely to be altered based on the surface area available for evaporation and volatilisation of these resin components to occur. A resin pocket of for example 2cm x 4mm dimensions will have relatively low rates of evaporation, whereas the splits occurring near the pith may provide two faces of over a metre length and several centimetres depth. Resin drying here is likely to be efficient, but the timber quality poor.

4.4 Composition of larch resin from thermally treated planks

Various thermally treated planks which had naturally oozed resin during thermal modification, or in which resin pockets were discovered later during cross cutting or other machining operations were selected for study (Table 4.4). These were taken from thermal treatment runs at the pilot and large scale. In these planks the oleoresin was present either in a solid or a more liquid state, depending on the thermal conditions used within that treatment run. The thermal treatment runs to which these relate will be described in Section 5, and can be identified by the numbering system in Table 5.1. Sample CMT relates to the commercial scale runs reported in Section 6.

Plank sample	CC treatment run number	Plank size	Planks treated in the batch
8D	C	Small	6 to 10 A to E
35E dark 'F'	E	Small	30 to 35, blank to E
35E light 'E'	E	Small	30 to 35, blank to E
35B dark	E	Small	30 to 35, blank to E
35B light	E	Small	30 to 35, blank to E
1D	F	Large	1 to 5 A to E
4E	F	Large	1 to 5 A to E
12A	G	Large	11 to 15 A to E
23C	H	Large	21 to 25 A to E
CMT	CM5, CM6 or CM7 (low intensity)	Thin	

Table 4.4. Planks selected for resin sampling

Samples of resin were removed using a razor blade or spatula, and were prepared for GC-MS analysis. In a few cases, where resin had spread over the surface of the plank but taken a thin glassy form which was difficult to sample by blade, a sample

was washed with solvent onto a clean glass plate, from which the dissolved resin was transferred to the GC-MS vial.

The resin which was harvested from treated planks was more variable in its composition than the raw resin, and the samples analysed from the DSC experiments. Some of this reflected species variation, and it was clear that the majority of the large planks contained resin with a different composition of diterpenes than the thin planks (while a few of the large ones were more similar to the thin set). This was detected in the balance of larixol and torulosol (and their derivatives) seen in the diterpene region of the chromatogram. Mills (1973) reports that hybrid larch has both compounds present, whereas Japanese larch has only torulosol and its derivatives. Larch is known to hybridise readily so the inclusion of a small amount of hybrid larch in the pack of sawn wood is entirely possible. European larch would have only larixol. The pair of peaks which evolved at 31.58 and 31.66 minutes indicate the presence of both larixol and torulosol in planks 12A and 23C, whereas plank 4E contained only torulosol, and was Japanese larch, as were planks 35B and 35E from the thin batch. The torulosol acetate content of resin from plank 4E was also strong, while in the dried resin from this plank, both the torulosol and torulosol acetate peaks had increased prominence, as the levels of other diterpene components had altered.

In addition to the species differences above, there were differences relating to the quantity of monoterpenes which remained after the thermal treatment. This data has been compiled in Table 4.5 to demonstrate the effect. The total diterpene content and total sesquiterpene content have been used to avoid spurious effects such as the resin composition differences between larch species.

	α -pinene	β -pinene	sum of sesqui	sum of diterpene
Untreated CC RM2701	20.67%	6.66%	2.37%	70.30%
CC 8D (RM2715)	6.41%	1.14%	2.51%	89.9%
CC large 4E liq MS36	10.71%	0.67%	0.66%	87.96%
CC large 4E dry MS37	9.48%	0.60%	0.98%	88.94%
Untreated CM RM3024	35.19%	2.94%	3.04%	58.84%
CMT RM3025	31.7%	3.64%	4.52%	60.14%

Table 4.5. Proportion of α - and β -pinene relative to total terpene content. Sesquiterpenes and diterpenes presented as aggregate figure to variability of compounds within these groups.

It is interesting that although there is a clear difference between the untreated larch (20% α -pinene) and the resin from treated planks (11% or lower), the difference between the liquid resin and the dry resin from the same treated plank is relatively minor (e.g. plank 4E). This is a further confirmation of the outcome of DSC studies, where although monoterpene loss occurs, it is clearly connected to loss of closely associated moisture. It may be the moisture which is the factor which determines the physical state (solid or liquid) of the resin, although the moisture content will closely track the monoterpene content due to their interactions in vaporization.

One interesting example is plank 4E, in which both solid resin and liquid resin were sampled from the same region (Figure 4.9). The dry resin had oozed to the surface during thermal treatment, and formed a glassy solid on drying. The liquid resin had remained protected within the thickness of the plank and been revealed when the plank was cross cut at a later date. Both had very similar α -pinene content, considerably lower than in untreated resin, however the dry sample contained 9.48% and the liquid sample contained 10.71%. It is possible that the dryness of the resin does not relate to the reduction in pinene content, but the removal of moisture which accompanies this process. The timber of plank 4E had a colour which indicated that it had been mildly thermally treated.



Figure 4.9. Resin in three locations on plank 4E – where a resin pocket was cut longitudinally during rip sawing, and resin dried on thermal treatment; where the end of the same resin pocket was cross cut after treatment, revealing liquid resin; resin associated with the pith which dried on the plank face.

The resin sampled from untreated planks at Coed Mon had a very high α -pinene content (35%) compared to the planks sampled at Coed Cymru. This possibly relates to the age of the resin (duration since the plank was cut). It is clear that the α -pinene dominates, but that both α - and β -pinene are lost steadily during drying, either in the log yard, or in the thermal treatment oven. The treated Coed Mon sample (which was a liquid resin found within a plank section which had received a relatively mild thermal treatment) still had a very high pinene content, indicating only minor changes in composition during the thermal treatment step.

Sample CC 8D was a resin pocket which was cross cut during sample preparation, and the resin inside had a hybrid consistency, more like a waxy solid than a liquid. It

is interesting to see that this sample contained 6.41% α -pinene, again confirming that the thermal treatment had partially driven off the monoterpenes (and we can assume associated moisture). This resin pocket was completely embedded within the plank, with no easy pathway for the resin or its moisture rich components to migrate to the surface, however drying was partially completed via the cellular structure of the wood.

In most of the samples the dehydration of thunbergol to thunbergene was again seen, generating additional peaks at a slightly early elution time than the diterpenes of untreated resin, this was most noticeable in the wet and the dry resin samples taken from plank 4E. Similarly the pimaradiene peak for dehydration of epimanol was also seen strongly in this sample. This reaction under the action of heat is not well studied, however the mass spectrum of the second new peak did contain the characteristic mass fragments for pimaradiene. As this was seen in both the liquid and the dry resin within plank 4E (i.e. despite the incomplete removal of moisture), it can be inferred that the transformation of the diterpene monoalcohols to diterpene alkenes occurred under the action of heat, rather than the total absence of water. This is interesting as it is a dehydration reaction.

It is worth noting the variety of different forms of resin deposit from which the resin was sampled. Some resin pockets were very small and entirely contained within the plank until revealed by cutting or planing, e.g. the sample from 8D. Other patches of resin had been brought to the surface by the primary sawing into planks, which revealed either star shake with resin closely associated with the pith (23C had this origin), or a ring shake within resin-rich interface within a growth ring, which tended to split during thermal modification revealing a smooth resin rich surface (planks 35B and 35E were of this type).



Figure 4.10. The end grain of plank 23C reveals resin rich growth rings in the juvenile wood near the pith. While resin has collected in a star-like pattern where small radial

splits are present, it is also preferentially located in the earlywood of each growth ring.



Figure 4.11. Ring shake, with resin cured on both faces of the split of plank 35B.

4.5 Extractive composition

In addition to the resin, larch contains various extractive compounds (non-structural chemical components) which may be dissolved using water, or various solvents. A sample of untreated larch, and samples of thermally treated larch from two thermal treatment batches (Run C and Run E) were prepared by milling to a powder to allow soxhlet extraction in a mixture of toluene:methanol:acetone (4:1:1 v/v). The extract was dried by rotary evaporation and prepared for GC-MS analysis using dichloromethane or methanol as solvent.

The extractives in untreated wood include some terpene components similar to those present in resin, in particular the diterpenes and resin acids at 24 to 32 minutes (Figure 4.12), but also short chain alkanes such as undecane and compounds such as lignans and flavonoids from the heartwood of the timber.

HEAT TREATMENT OF LARCH TIMBER

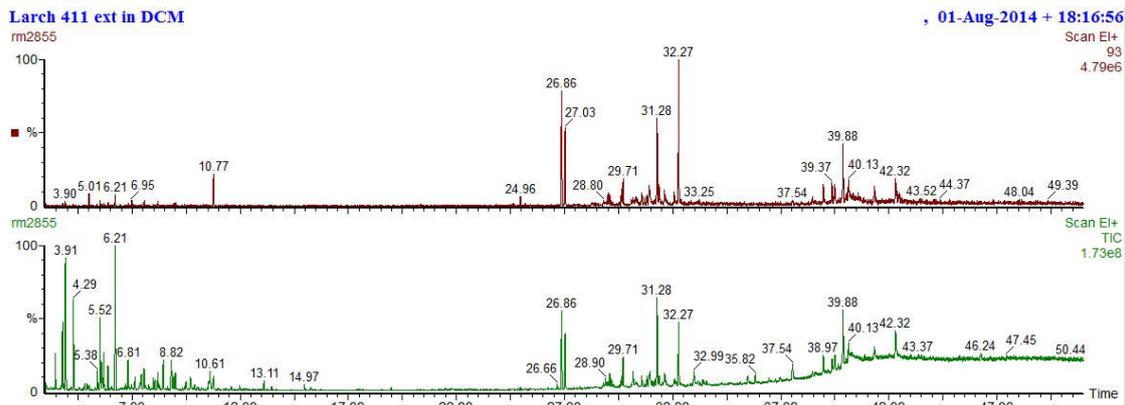


Figure 4.12. 4:1:1 extract of untreated larch in dichloromethane as a gas chromatograph, showing the total ion count (lower line, green) and showing only the 93 Da mass fragments which are indicative of terpenes (upper line, brown).

The thermal treatment introduced several new strong peaks to the chromatogram, including phenylpropane derivatives such as hydroxymethoxyphenyl propane (21.71 minutes) and hemicellulose degradation products such as hydroxymethyl furfural (11.42 minutes). The original terpene peaks were greatly reduced, this has not been previously shown but is in keeping with results of VOC studies – where monoterpene content decreases on thermal modification.

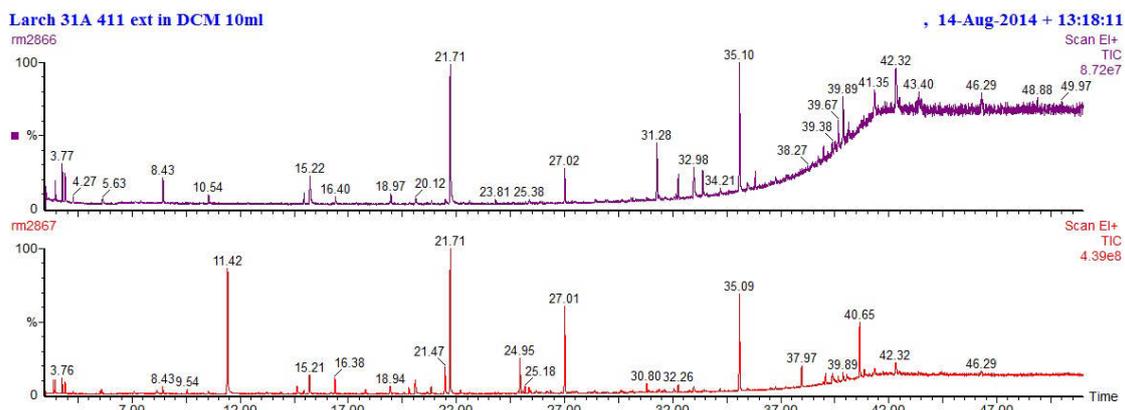


Figure 4.13. GC chromatogram for two 411 extracts of larch (31A upper chromatogram and 34A lower chromatogram), in dichloromethane.

It was interesting to observe for the two planks from Run E presented in Figure 4.13 that the one from lower in the oven (31A) showed no evidence of hydroxymethyl furfural (HMF, the product of degradation of hexoses from the hemicellulose) but did contain fragments from lignin degradation. This plank may have received a shorter dwell period in the treatment zone than plank 34A, in which the HMF content was significant. Similar results were seen in Runs B and C, where planks which had received higher thermal conditions for more sustained periods of time had extractive compositions which included HMF (e.g. plank 4E) whereas those which were on the cooler side of the oven did not. In Batch C, the samples which had received Day 1 only did not contain either HMF or hydroxymethoxy phenylpropane (HMPP) or HMF, whereas the samples which received the full treatment did contain HMPP.

These GC results for extractives confirm that the thermal modification system under development here is on the border between the onset of changes in the structural components of the cell wall, and the simple act of 'drying' or driving off resin

components. The formation of HMF and HMPP are indicative of thermal changes induced at temperatures commonly reported as in the region of 180°C. It is possible that isolated regions of the oven during these early treatment runs have reached similar temperatures, while other regions in which drying was less efficient did not. The process of improving air flow, and developing the mild treatment schedule is reported in the next section.

4.6 Fourier Transform InfraRed (FTIR) of changes in the wood and the resin

The resin, the untreated timber and the thermally treated timber were also observed using FTIR spectroscopy. A Thermo Nicolet 8000 FTIR was used with a Pike Industries GladiATR Vision unit, allowing spectra to be recorded in Attenuated Total Reflectance (ATR) mode. This allowed non-destructive sampling of timber before and after thermal treatment in the samples treated in laboratory scale pressure reactor experiments (see previous Section 3.2 and 3.3). Planks of thermally treated timber from the large scale were also analysed.

In the pressure reactor samples, very little change was seen with spectra for the heartwood and sapwood of untreated larch. An example spectrum for untreated larch is shown in Figure 4.14 and reveals typical absorptions for wood, e.g. the hydroxyl content of the cellulose, hemicellulose and lignin (broad absorption centred on 3335cm⁻¹); CH stretches in all three components (which are superimposed in the region 2800-2910cm⁻¹); ester carbonyls in the cellulose and hemicellulose (1729cm⁻¹); aromatic skeletal vibrations within the lignin (several absorptions including 1426, 1510, 1590cm⁻¹); several C-O stretches and deformations, largely due to the hemicellulose and cellulose (several absorptions including the strong 1030cm⁻¹, and nearby 1060, 1160cm⁻¹) as well as the cellulosic OH association at 1110cm⁻¹ and OH bend at 1205cm⁻¹.

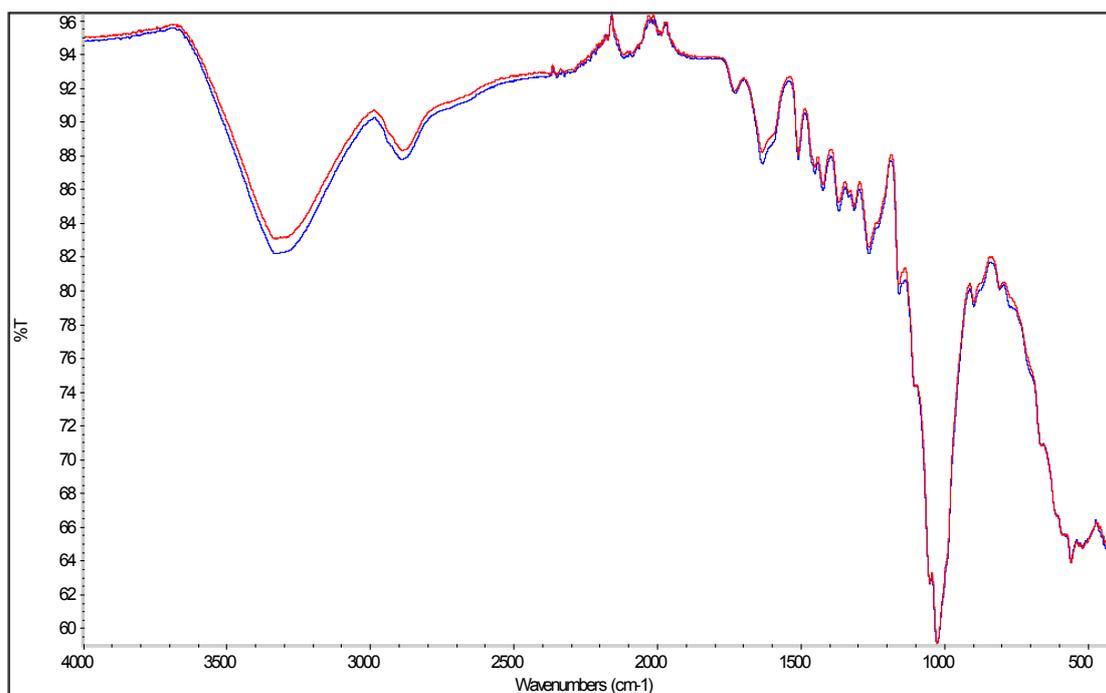


Figure 4.14. FTIR-ATR spectra for two untreated control samples from the pressure reactor experiment.

The effect of thermal treatment on the wood itself showed very limited changes in FTIR spectrum. Figures 4.15 and 4.16 show the changes observed for earlywood and latewood of sample Larch 1 on thermal treatment at 140°C. Changes in the spectrum were concentrated on the pair of peaks at 1588 and 1637cm⁻¹ which relate to aromatic C-O stretches, and conjugation with α -carbonyl groups, and to the presence of adsorbed water in hemicellulose. Changes in this region were previously reported by Kotilainen *et al.* (2000) for thermal modifications performed at higher temperatures, however in that case the lower wavenumber absorption increased (possibly indicating condensation of lignin), while the higher decreased (due to moisture being driven off from the wood). It is clear that the changes in lignin are not seen here, but the decrease of both peaks together reflects the loss of moisture. Note that the latewood showed a stronger 1637cm⁻¹ absorption, but that this was diminished in the same manner on thermal treatment (Figure 4.16).

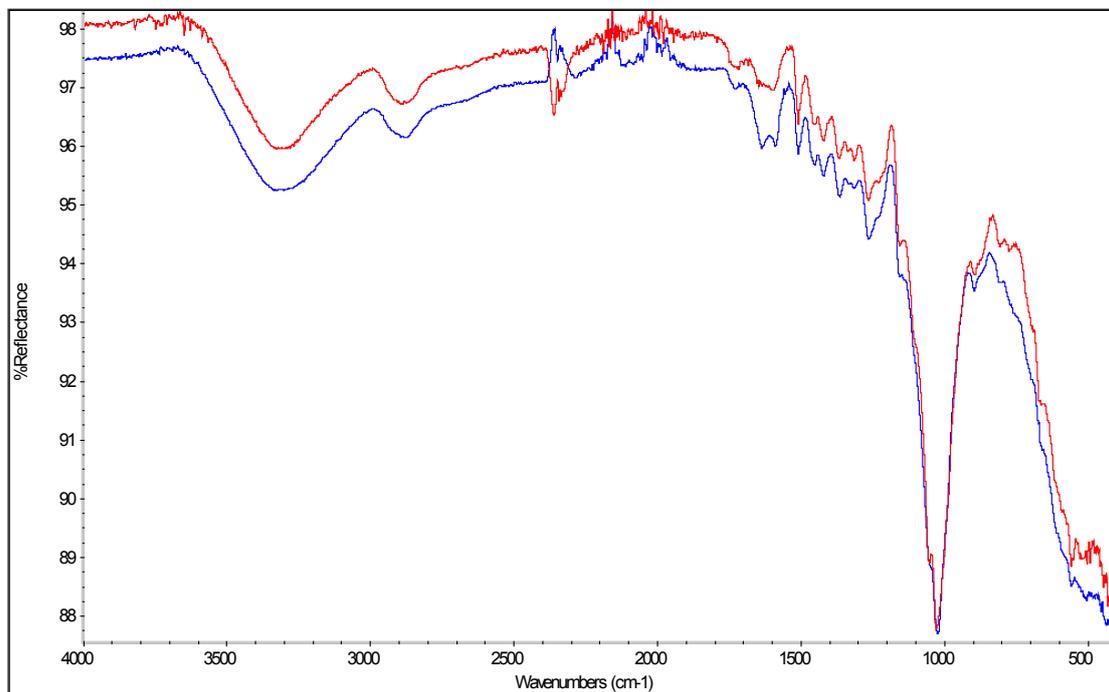


Figure 4.15. FTIR spectra for Larch 1 earlywood before (blue line) and after (red line) thermal modification at 140°C

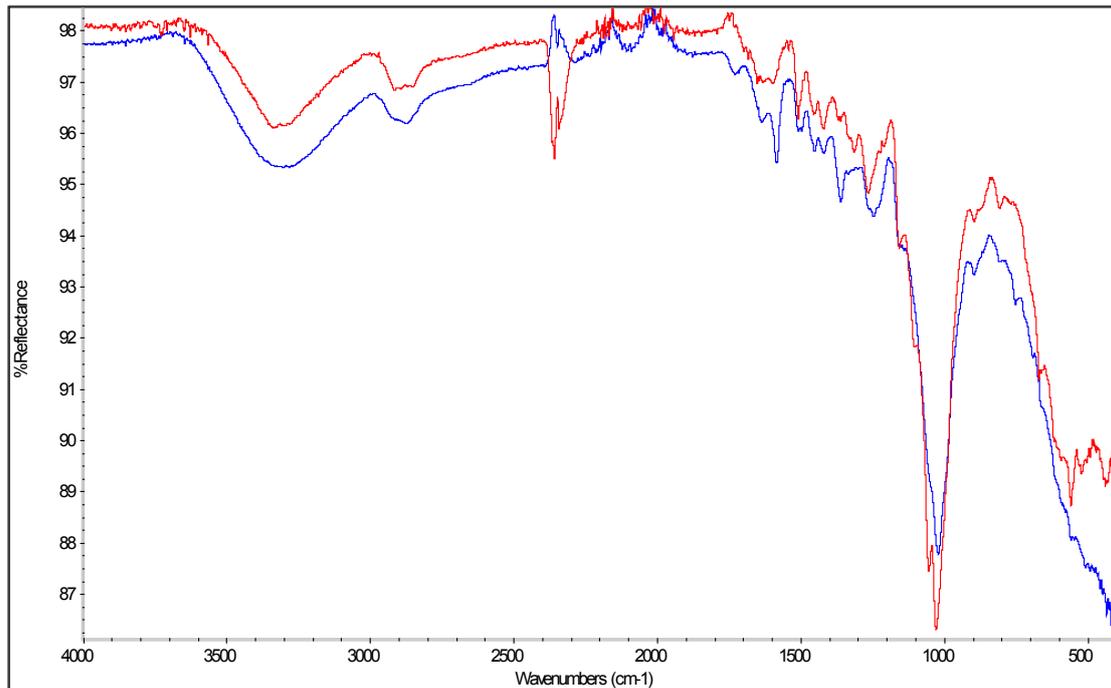


Figure 4.16. FTIR spectra for Larch 1 latewood before (blue line) and after (red line) thermal modification at 140°C

When the spectra prior to treatment were compared with spectra after thermal modification, relatively small changes were observed in the wood itself (Figures 4.15 and 4.16), but larger differences were seen in the resin pockets (Figure 4.17).

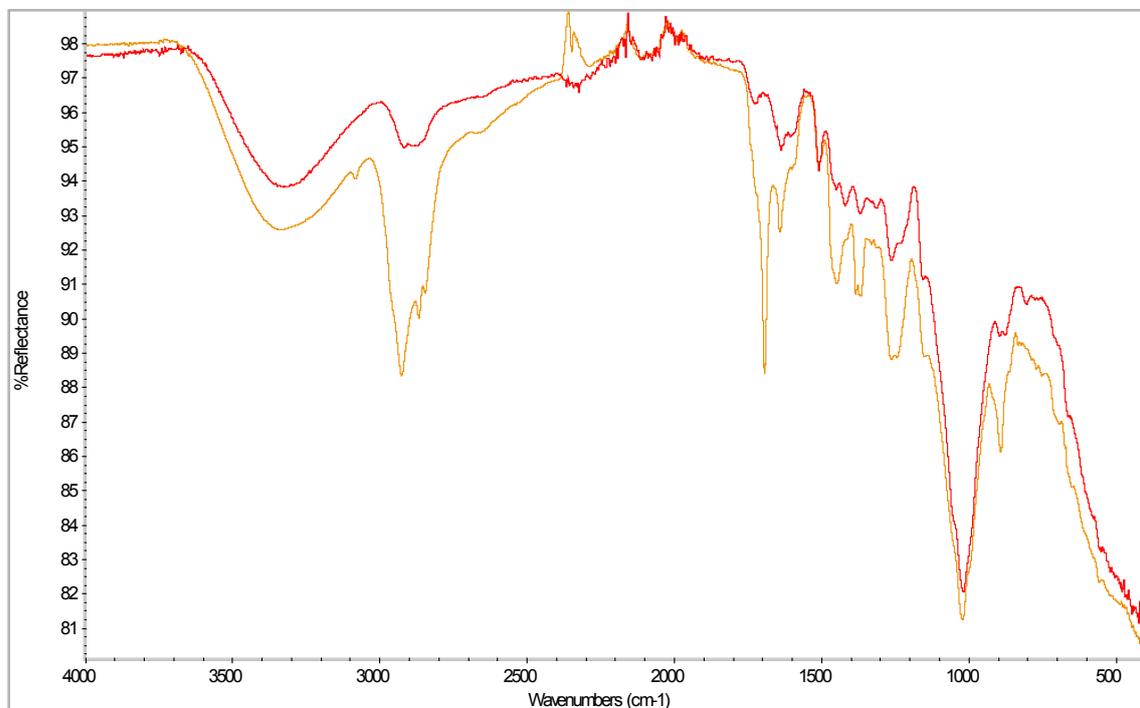


Figure 4.17. Resin pocket before treatment (orange line), and after 140°C treatment in the pressure reactor (red line)

The spectrum for the resin pocket before and after treatment showed that carbonyl absorptions at 1721 cm⁻¹ and 1230 cm⁻¹ were lost at relatively low temperature of

140°C (Figure 4.17). There was also a strong change in the CH stretch region at 2900-3000cm⁻¹ with the loss of the terpene compounds. The shape of the spectrum which remained in this region was more typical of wood when observed in ATR mode. Notably the small absorption at 3085cm⁻¹ which is typical for C-H stretches in sp² hybridized alkenes, such as terpenes. In fact, many of the peaks in the untreated resin pocket spectrum prior to thermal treatment correlate with the spectra for α - and β -pinene (1721, 1638, the overlapping peaks at 1455 and 1444; the pair at 1388 and 1361; the overlapping pair at 1262 and 1240; and the absorption at 889 cm⁻¹). This is unsurprising given the abundance of pinene in the raw resin, and the chemical structural similarity between these cyclic monoterpenes and the cyclic sesqui- and diterpenes also present.

Carboxylic acid functional groups on the dipterene resin acids would provide absorptions near 1650-1700 and 1274cm⁻¹, which are within the heavily populated fingerprint region. Nuopponen *et al.* (2003) used the 1697cm⁻¹ absorption as a characteristic band for resin acids in their study of extractive migration during a Thermowood style process. This is close to the 1690cm⁻¹ absorption which was so strongly reduced in the resin pockets, but which is likely to correspond with the pinene, thus the resin acid spectrum probably contributes to the absorptions which remain after the thermal treatment, some of which are not characteristic for resin-free wood. In addition, oxidation reactions are known to occur in abietic acid (Ren *et al.* 2015) which would result in ketone or other carbonyl functionalities, further altering the profile. Due to the complexity of the mixture further detailed analysis of composition was not performed, being more appropriate in the GC-MS studies, but Figure 4.17 clearly shows the loss of terpenes from the oleoresin during its volatilisation.

4.7 FTIR of thermally treated wood from the pilot scale

Samples of thermally treated larch were selected from the pilot scale treatment batches for FTIR-ATR analysis. A selection of these have been presented here to demonstrate the main trends. The changes in the spectrum for the wood were again relatively small, for example in Figure 4.18 the untreated wood has a wider compound peak for the CH stretches, which changes shape for the two thermally treated samples – losing the definition of the 2923cm⁻¹ absorption, but retaining a weaker shoulder centred on 2940cm⁻¹. Popescu *et al.* (2013) also identified subtle changes in this region for low temperature thermal modification experiments.

The absorption at 1417cm⁻¹ changed in dominance (Figure 4.18), but this varied between samples of treated wood – in commercial Thermowood an increase in this absorption would be expected, correlating with aromatic skeletal vibrations in the lignin (Kotilainen *et al.* 2000). It is possibly interesting therefore that the absorption decreased in the sample taken from the more mild location in the stack, but had strengthened slightly in the sample from the hot side of the stack (23E). The absorption at 773cm⁻¹ on the other hand is steadily lost from the untreated sample to the sample taken from the centre of the stack (23C) to the sample from the hottest side (23E). The shoulder at 1052cm⁻¹ became more prominent in the heat treated samples than it had been in the untreated larch. This is likely to relate to aliphatic alcohols and ethers (in the carbohydrates).

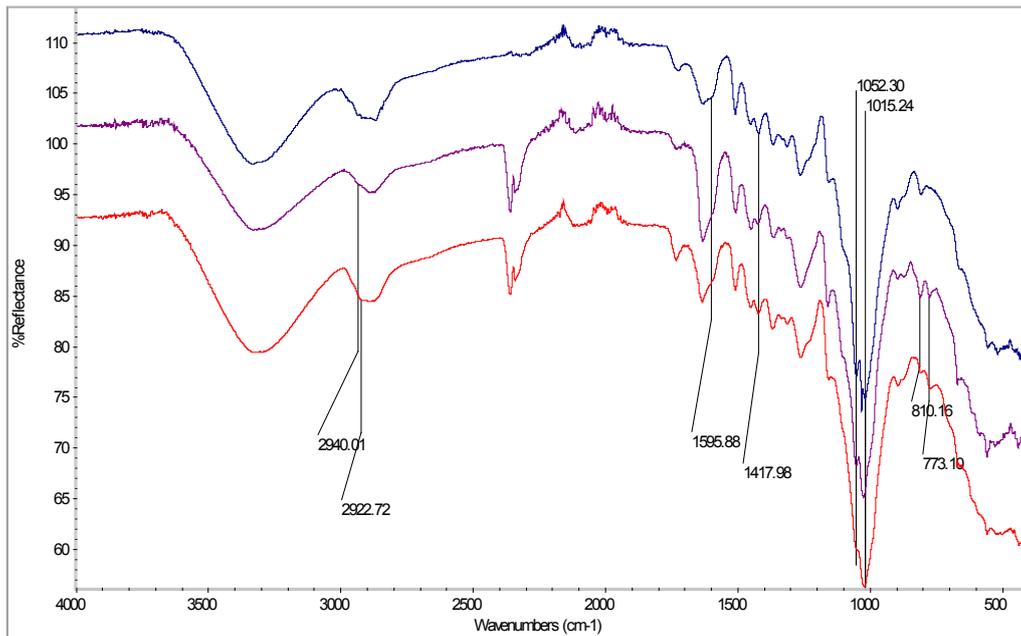


Figure 4.18. FTIR spectra for wood sampled from 23E (navy line), 23C (purple line) and untreated larch (red line). Planks 23E and 23C were taken from Run H.

Similar effects and levels of change were seen when samples from different treatment batches were compared, including when comparison was made between Runs B-E on thinner planks and Runs F to J on thicker planks. A sample from the hot side of Run E (which was also a more intense level of thermal treatment due to the treatment phase at 190°C) showed a very similar spectrum to that seen for sample 23E in Figure 4.19. Here there was a decrease in the 1630cm⁻¹ absorption, relating to either conjugated double bonds or to adsorbed water, this second explanation makes the greater sense in the mild thermal modification process.

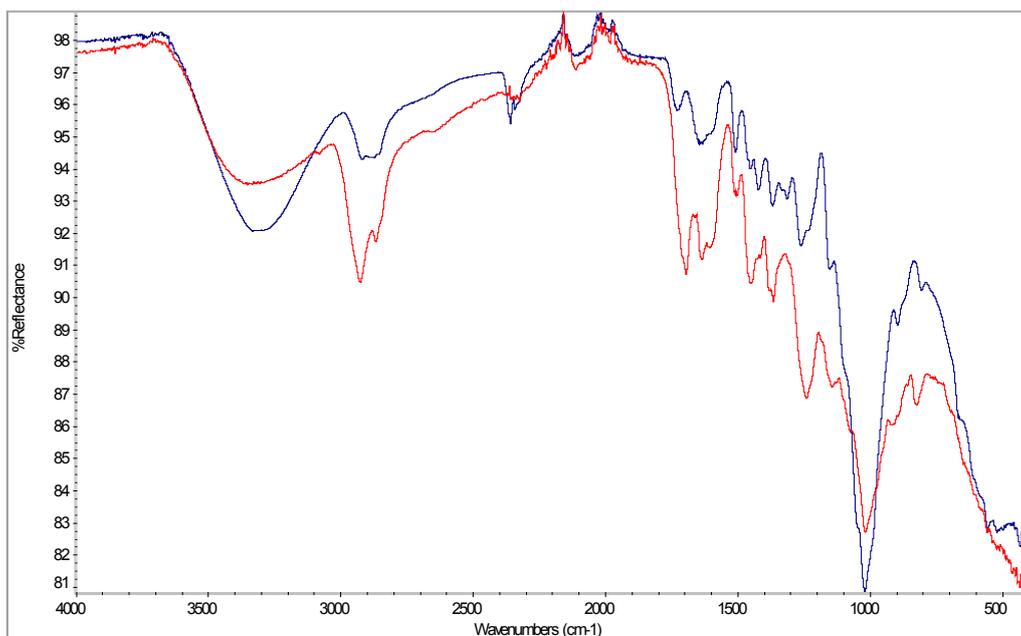


Figure 4.19. FTIR spectra for a sample of wood (navy line) and of dry resin (red line) from thin plank 20E (Run D).

Samples containing regions of dried resin were observed, for example Figure 4.19 shows the dried resin spectrum still containing many characteristic terpene absorption peaks, including prominent CH stretches at 2918, and 2873 cm^{-1} , a strong resin acid carbonyl absorption at 1690 cm^{-1} , and at 1230 cm^{-1} . On the other hand many of the characteristic features from the pinene-rich spectrum previously presented (Figure 4.17) were not present (e.g. the small 2843 cm^{-1} CH stretch, the strength of the 1690 cm^{-1} absorption, the clarity of the pair at 1388 cm^{-1} and the sharp 889 cm^{-1} absorption). These differences reflect the shift in composition of the resin which has accompanied its change into a dry product, with a greater proportion of higher molecular weight terpenes. This resin has hardened, but remains on the surface of the resin pocket.

In another sample of solidified resin, located on the surface of plank 23C (Run H), a similar spectrum was obtained. This is presented with the spectrum for the wood of the same plank in Figure 4.20. This plank experienced slightly lower temperatures during treatment than plank 20E from Run D. Here a greater level of pinene is suspected in the resin, as can be seen from the strength of the carbonyl absorption, the presence of the 3085 cm^{-1} CH stretch, and the strong 887 cm^{-1} absorption.

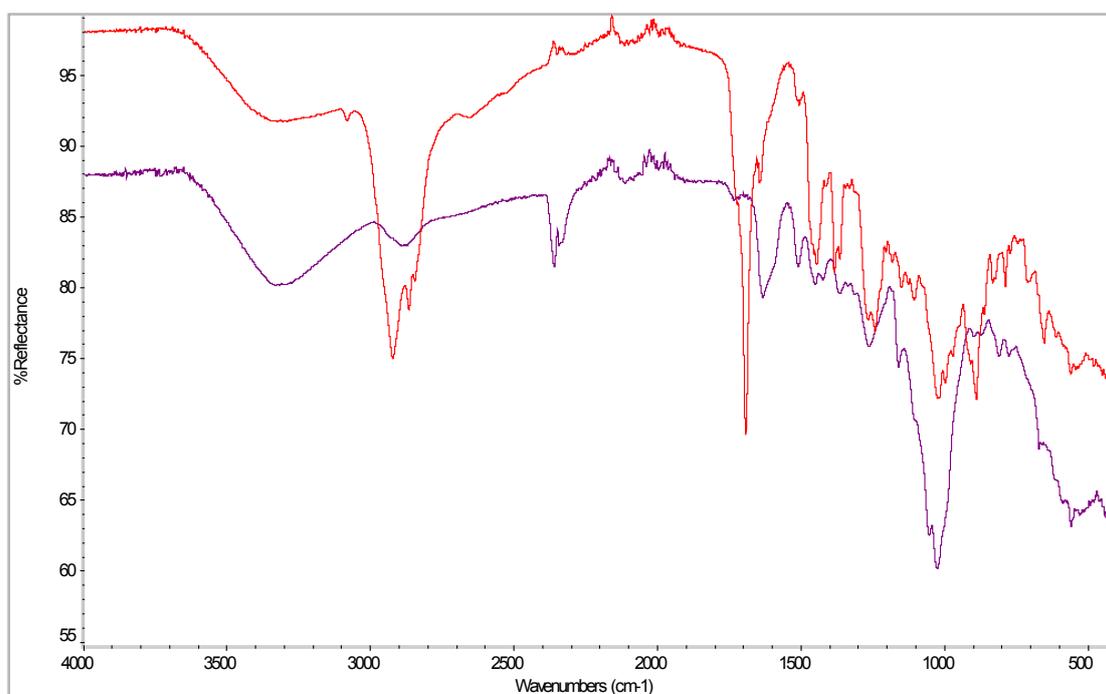


Figure 4.20. FTIR spectrum of dried resin (red line) and wood (purple line) from plank 23C (Run H).

It can be seen that while the resin pockets can be characterised by presence of (and potentially a reduction in) carbonyl absorption at 1721 cm^{-1} , the carbonyl absorption for the hemicellulose within the wood is seen at 1738 cm^{-1} . This absorption may also show changes in some samples of treated wood. In planks where both sapwood and heartwood were present the 1738 cm^{-1} carbonyl absorption could be observed to have increased if the location of the spectrum collection was located near to the edge of the heartwood (Figure 4.21). In Thermowood samples this absorption has been reported to increase (Kotilainen *et al.* 2000). In the larch samples, the locations with the unusually strong carbonyl signal were often seen to have an increase in absorption at 1366 and 1228 cm^{-1} . As this phenomenon occurs within the plank,

rather than being a symptom of the thermal conditions experienced by the plank, this phenomenon will not be considered further here.

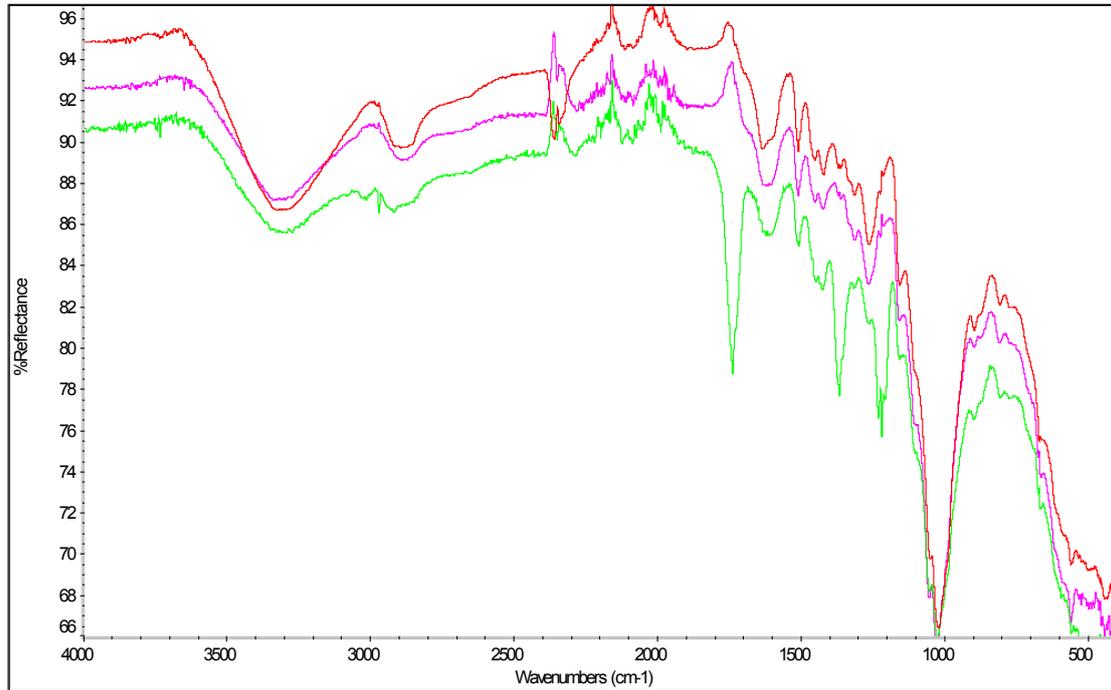


Figure 4.21. Spectra from three different sampling locations within the same plank 31C, taken from Run E

5. Pilot scale 1m³ capacity oven

5.1 Introduction

A series of treatment runs were conducted on small (110 x 30 mm cross section) and large (155 x 38mm cross section) planks using a pilot scale oven. The oven was controlled using a Eurotherm control panel, which could be programmed with a series of steps, ramps and dwell periods. The oven was equipped with a steam generator which was switched on for several or all of the thermal treatment steps, providing steam at 4 to 6 kg/hour.

The majority of kiln schedules tested used a three day system (Figure 2.2, Table 5.1), where Day 1 was a drying day, reducing moisture content and generating a more uniform load for treatment. Day 2 was the treatment day and used a higher temperature than the other two days to effect the changes within the timber. Day 3 was the conditioning day, using a lower temperature and high humidity to restore some moisture content within the timber prior to unloading from the kiln. The three day system was designed specifically for the working conditions in small enterprises within Wales, where a single shift operating pattern was appropriate due to low staff numbers.

The maximum temperature, and the duration of time spent at this temperature, will be referred to as the treatment phase for Day 2 (Figure 5.1). Observation of the thermocouple data however reveals that the temperature within the timber lagged behind the oven temperature, and that the peak temperature within the wood varied to a small extent with location in the stack (and with the level of drying which had occurred in that stack during the drying day). It is therefore also necessary to define a treatment zone – which for this report will be considered the duration for which the temperature of the wood was greater than 150°C. As several of the treatment runs showed considerable variability in temperature distribution across the stack, the data have also been analysed using 160°C and 170°C as the threshold temperature (and selected sub-sections of the stack) to investigate changes relating to a moderate intensity treatment – i.e. one with greater effect on the wood cell wall material in addition to the resin cure effects and mild changes seen in mild treatments. In fact the objective of treatments C-E was to investigate higher intensity treatments, while runs F-J returned to the objective of optimizing the parameters for the mild treatment.

As can be seen in the schematic, the treatment zone typically began at a similar time to the treatment phase, with the degree of lag relating to dryness of the stack at the end of Day 1, and the ramp rate used to elevate the oven temperature to the treatment phase. The duration of the treatment phase varied, again relating to the initial dryness of the stack. Short treatment zones were generally seen for stacks with non-uniform drying, or long initial lags, whereas more uniformly dried stacks tended to have treatment zones which extended for a period beyond the end of the treatment zone (as shown in Figure 5.1). This was due to the low thermal conductivity of wood, which resulted in relatively slower cooling by the stack than the kiln air temperature.

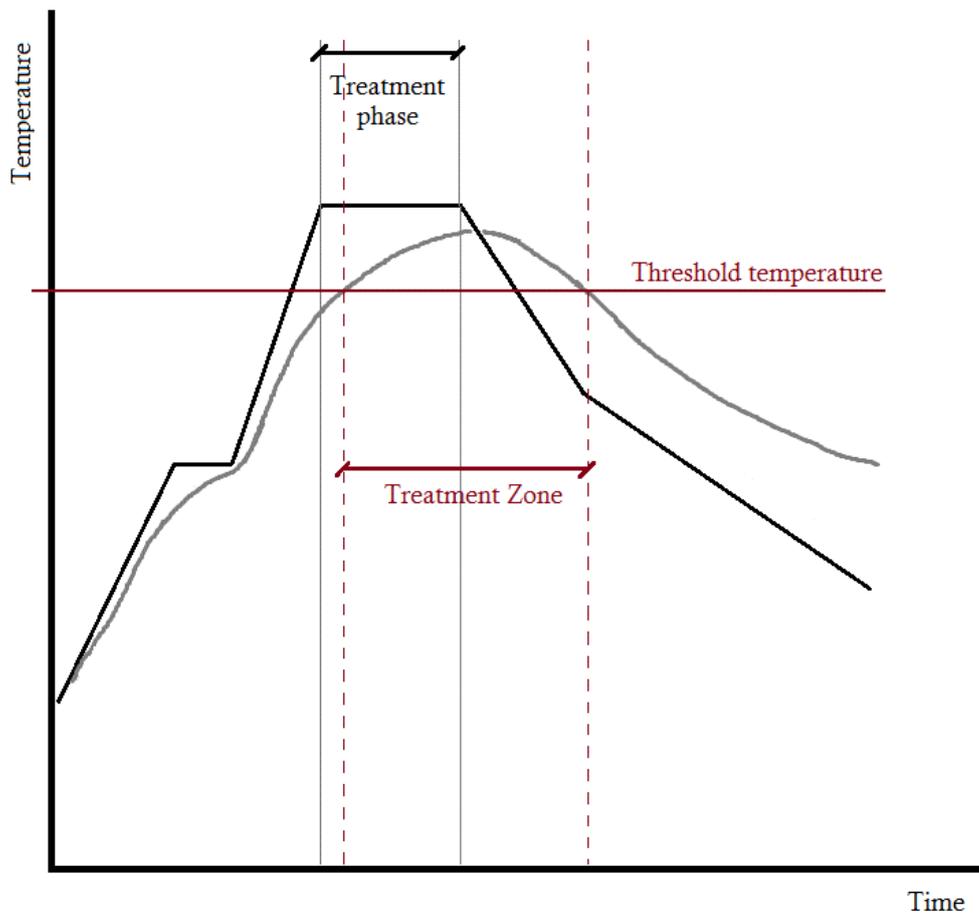


Figure 5.1. Schematic showing the treatment phase (controlled by the oven programme), and resulting treatment zone (above the threshold temperature).

By altering the kiln set point and duration for the treatment phase, the duration for which the timber was in the treatment zone can be controlled. Conditions were selected for Run B to achieve mild conditions, and for Runs C to E to achieve more intense treatment. For Run B a three hour treatment zone at 180°C resulted in 1¾ hours in the treatment phase (above 150°C) while Runs C to E achieved 1½ to 4½ hours within this treatment zone, and 1 to 2½ hours at a temperature of 160°C. The darker colour of planks from Runs C to E increased with increasing treatment zone duration, and these can be considered to have received a moderate rather than mild thermal treatment. The initial moisture content of the timber prior to the treatment step contributes to the stability of the relationship between treatment phase parameters and the treatment zone that results. Replicability of this treatment zone conditions relies on efficient pre-conditioning of the timber on Day 1, which for the process used here generated a moisture content of 9 to 11.5% in the planks (when the initial moisture content prior to the day 1 step was 18% and above).

In later experiments (Runs H, I and J, Table 5.1) a single continuous run was developed, in which the time lost in cooling and then re-heating timber between Day 1 and 2, and between Day 2 and 3 was removed, allowing a cycle which completed in roughly 40 hours. This system retained a conditioning or drying step prior to the temperature increase to the treatment phase. After this the temperature was reduced but to a moderate temperature with high humidity in order to recondition the timber.

In practice, after this adaptation, it was found that considerable drying effect had been lost by the removal of the cooling period of Day 1. Although the timber was conditioned to a higher temperature lower relative humidity state, the timber appeared to have dried less than after the Day 1 sequence of the three step process, see Section 5.4). Subsequent adjustments between Runs H, I and J did not address the treatment phase, but more usefully altered the initial drying step which leads into the treatment stage, to optimise the level of drying in the timber.

5.2 Method details

Table 5.1 shows the pilot scale runs which have been analysed here to gain insight into the process of optimising the thermal treatment process. Schematics of the main schedule types tested, and graphs of thermocouple data recorded during the treatment schedules are compiled in the Appendix.

Run ID	Date	Plank size	Day 1	Day 2	Day 3
Run B	July 2013	110 x 30mm	120°C	180°C 3 hours	80°C
Run C	August 2013	110 x 30mm	120°C	190°C 3 hours	80°C
Run D	December 2013	110 x 30mm	120°C	190°C 4 hours	60°C
Run E	April 2014	110 x 30mm	120°C	190°C 5 hours	60°C
Run F	February 2015	155 x 38mm	120°C	180°C 5 hours	60°C
Run G	March 2015	155 x 38mm	120°C	190°C 6.4 hours	60°C
Run H	April 2015	155 x 38mm	110°C 5 hours 180°C 3 hours		
Run I	May 2015	155 x 38mm	120°C 5 hours 180°C 3 hours		
Run J	June 2015	155 x 38mm	120°C 5 hours 180°C 3 hours		

Table 5.1. Oven conditions tested for mild and moderate modification of larch relating to resin drying.

A standardised thermocouple arrangement was developed which recorded the temperature within planks distributed across the stack, and additionally recorded the temperature in the surface of the planks at each side of the stack. For the thin planks, thermocouples were located left to right across the stack, plus the uppermost layer and lowest layer, see Figure 5.2a. This altered slightly when additional planks were introduced to the oven for Run E, which used a stack which was 7 planks wide rather than 5 planks wide, see Figure 5.2b. Further changes were made when treating the larger planks Figure 5.2c.

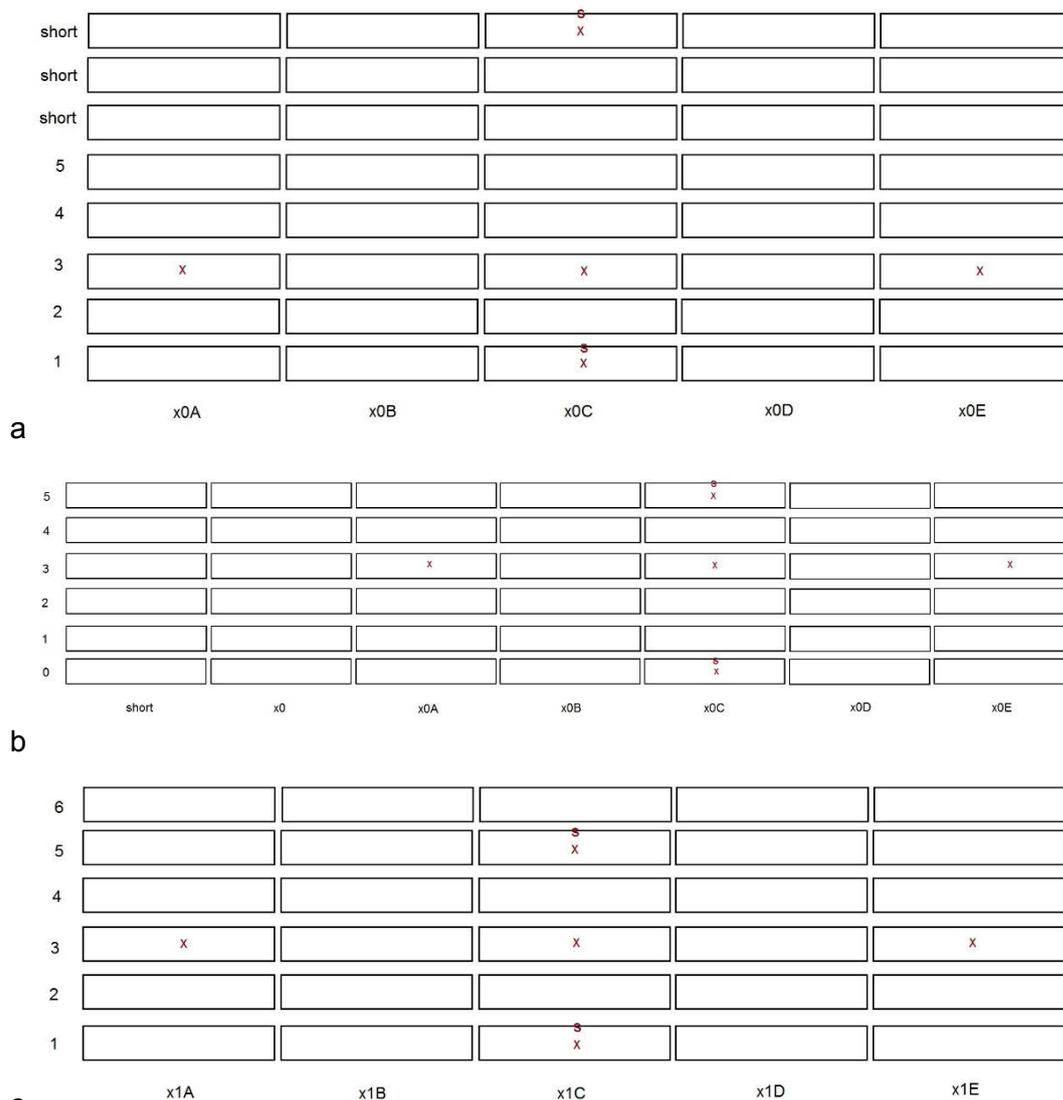


Figure 5.2. Schematics showing locations of thermocouples drilled into the core of the plank (red x) and on the surface of the planks (red s). A generic numbering scheme is indicated, where x can be altered with the run identifier. In Figure 5.2a planks are identified A to E from left to right and x1 to x5 bottom to top. Figure 5.2b, the wider stack for Run E was created by placing additional planks on the left. Short planks on top of stack not shown for simplicity. Figure 5.2c shows locations for the five by six stack of thicker planks used in runs F to J.

Moisture content of the planks was recorded before and after treatment using a radio frequency moisture meter. Samples for gravimetric determination of the moisture content were also cut from the planks in runs B to E. Before treatment a single sample was cut a distance of approx. 28 cm from the end of each plank, leaving the 90 cm plank for treatment. The comparison of the moisture meter data with gravimetric data confirmed that the correlation was sufficient for day-to-day operation of the oven, however the moisture meter underestimated the moisture content (Figure 5.3). In addition, for the initial batches of timber the precise gravimetric moisture content data was useful in estimating oven dry weight prior to treatment, to evaluate weight change on a plank by plank basis.

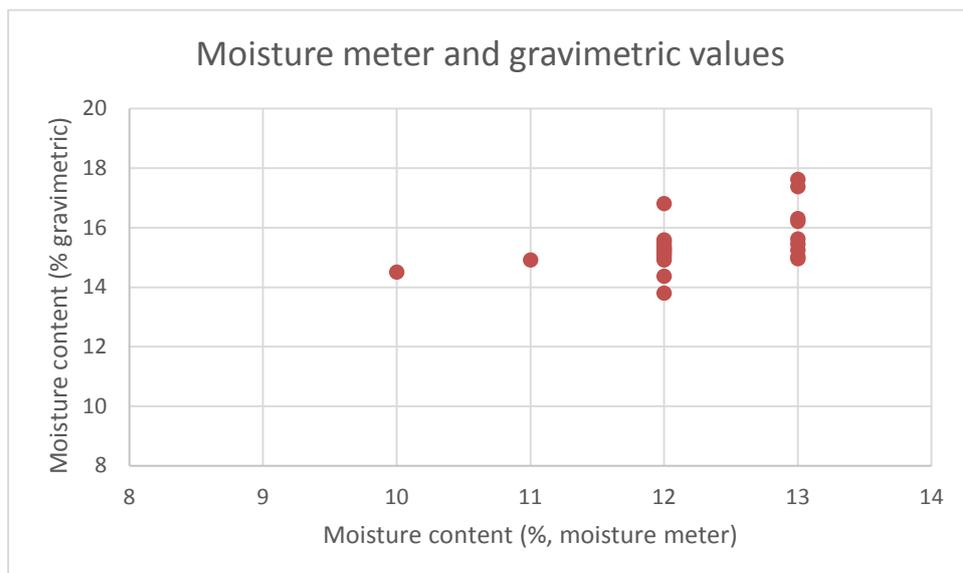


Figure 5.3. Correlation between moisture meter readings and true moisture content as determined by oven drying small samples.

After treatment, the three moisture content samples were taken from locations 8cm from the plank ends and in the centre. Whole plank weight was recorded before cutting, and the weights of all sections were recorded immediately after cutting. Moisture content samples were then dried in an oven at 105°C and re-weighed. Using the moisture content of the treated plank segments it was possible to estimate the treated dry weight of the planks, to evaluate whether any weight change had occurred.

5.3 Summary data from three step thermal treatment runs

Due to the large number of treatment runs, planks handled and large number of effects at work, within the thermal treatment oven, only the dominant trends will be presented here, using sufficient data to give useful examples and explanations. Thermocouple data from the kiln runs was of greatest interest in order to evaluate the efficiency of drying across the kiln from right to left (the direction of air circulation) and from top to bottom. The level of drying achieved on Day 1 was found to clearly influence the outcome from Day 2, as only planks which were sufficiently dry would be heated sufficiently fast to the higher temperatures to achieve the desired treatment phase on the treatment day.

The moisture content of the initial runs gave baseline data – as planks were removed from the oven and weighed after Day 1 and Day 2 of Runs B and C. This allowed gross estimation of the effect of drying and of thermal treatment. As a result it is possible to confirm that the thin planks dried to between 9 and 11.5% moisture content during Day 1, having started at a moisture content of 18% or above. The planks in the top row of the stack were found to be slightly drier, 6.9 to 8.9% (these values were based on whole plank weight and estimated oven dry plank weight). This result correlates well with the observed colour of the treated planks from this part of the kiln.

Data for the duration spent at a temperature of over 95°C during the Day 1 schedule are presented in Table 5.2. These are average values, and mask different levels of variability between batches. In Run B, which did not use a baffle for example, there

was a strong decrease in temperature and duration across the oven from right to left, which resulted in timber of very different intensities of treatment from the single batch. The plank furthest from the infeed of hot air recorded a temperature of over 95°C for only 91 minutes on Day 1, while the plank nearest the hot air spent 280 minutes above 95°C. Figure 5.4 shows that although all planks converged on the same temperature at the end of the 2 hour hold at 80°C, the drier planks increased in temperature rapidly when set point increased to 120°C, whereas the wetter planks further from the heat input took considerably longer to reach 100°C, and some did not achieve this temperature.

As a result of this large variability in dryness, the average time spent above 150°C on Day 2 (Table 5.2) for Run B was also low. Some planks spent three hours at 150°C or above, while one thermocouple did not achieve this temperature – recording a maximum of 143°C. This thermocouple was in the plank furthest from the hot air inlet. The thermocouples across this row of the kiln read maximum temperatures of 143°C, 156°C and 167°C, showing clearly the necessity of good drying in preparation for the thermal treatment day.

The gradient of temperature across the stack was corrected in later batches by measures such as inclusion of a baffle above the timber to force air through the stack, and locating the base of stack lower in the oven for the same reason. Despite this, a significant difference remained in Run F, being 90 minutes above 95°C on the cold side and 408 minutes on the hot side. In the experiments on thick planks the dwell time on initial stages was increased to further optimise drying.

Run ID	Initial mc (%)	Vol wood (m ³)	Day 1		Day 2			
			time > 95°C	T _{max} oven (°C)	time > 150°C	time > 160°C	T _{max} oven (°C)	T _{max} wood core (°C)
B	12.4	0.099	227.2	122.91	105.8	47	181.82	163.28
C	15.45	0.099	141.6	125.06	196.0	139.4	191.78	180.64
D	19.53	0.099	100.8	122.96	85.4	57.4	192.72	177.53
E	18.04	0.140	33.2	122.90	273.4	209.6	191.66	184.60
F	16.98	0.154	255.6	---*	250.4	148.2	182.32	174.63
G	16.3	0.154	174.6	123.49	372.6	273.2	173.4	183.48

Table 5.2. Summary data from the three-step thermal modification runs. * indicates data not reported due to short term overshoot of temperature.

In Run B and C the steam was on during the first 5 hours of the drying day, but switched off for the final hour of the 120°C hold, and the cool down (Figure 5.4 and Appendix). In Runs D and E the steam was on throughout the high temperature hold but turned off for the cooling stage.

In Run E the initial ramp was altered to try to follow a slower ramp, closer to the temperature of the timber, prior to the 2 hour hold at 80°C (Figure 5.5). The intention was to avoid over-drying the hot side of the stack while the cooler side slowly increased in temperature. Difficulties were encountered with the holdback settings on the oven for this control mode, although the temperature profile of the timber follows the oven temperature much more closely in this control mode than it did in the previous examples. The use of a ramp rather than a stepped temperature increase is

preferred for the commercial scale operations where stack size is greater, and lag on the cold side of the stack may be significant.

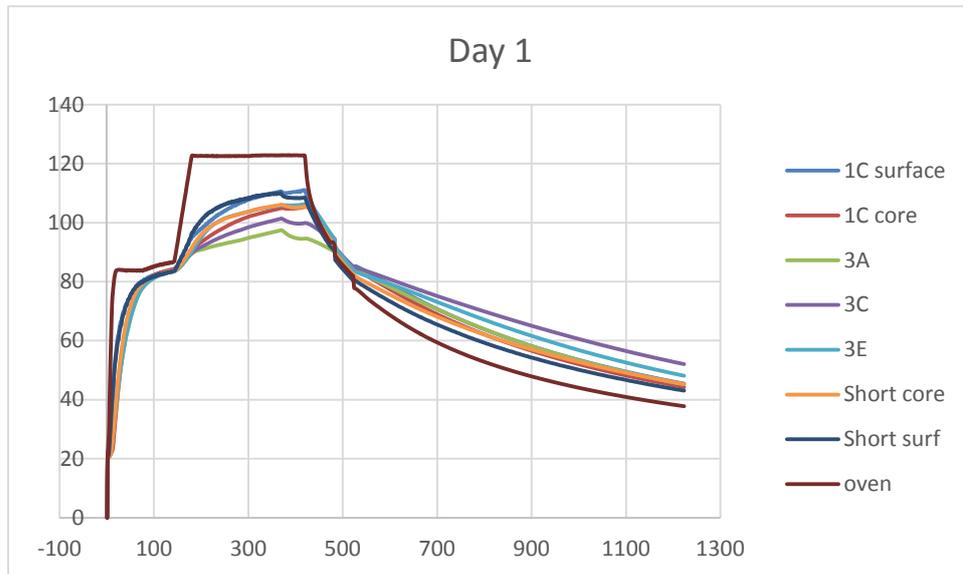


Figure 5.4. Temperature profile for oven and timber during Run B, showing rapid temperature increase to 80°C, 2 hour hold, then ramp to the 120°C set point, resulting in most planks achieving temperatures above 100°C.

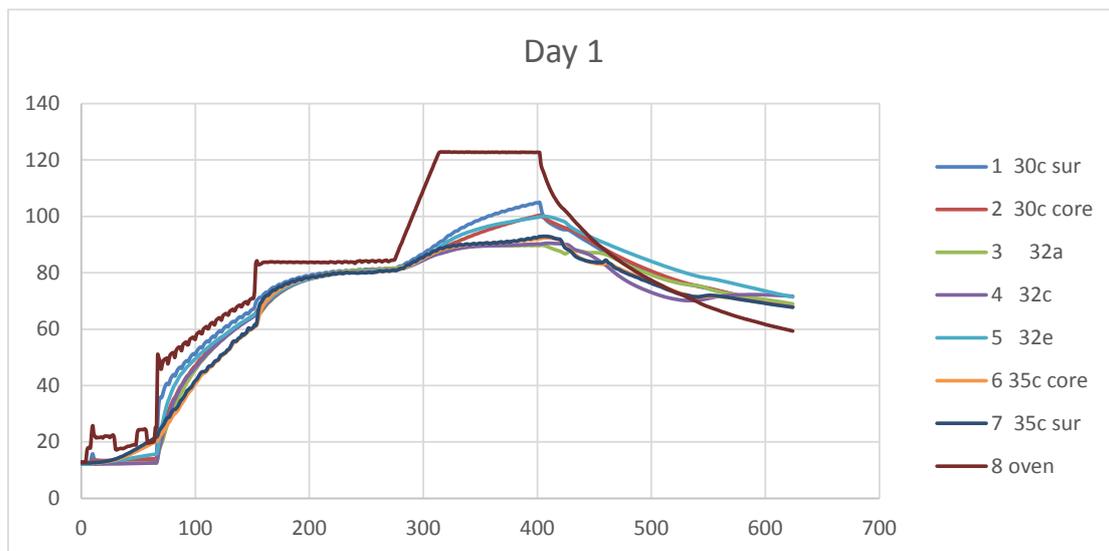


Figure 5.5. Temperature profile during Day 1 for Run E, using a temperature ramp rather than step in the first temperature increment.

In Run E the delays due to holdback controls during the initial stages resulted in a shorter than normal hold period at 120°C (90 minutes), so unfortunately only two of the planks achieved temperatures above 95°C. On Day 2 the majority of the stack did reach the treatment zone for a significant time (approx six hours) but the cold side of the oven achieved a temperature over 150°C for only 104 minutes. The aim of this treatment run was in fact the more intense level of modification, using a 5 hour treatment phase and 190°C set point. In the majority of the stack this was successful, and using the criterion of 170°C for treatment zone most planks achieved a four hour treatment level. It is this batch which showed the greatest levels of hydroxymethyl furfuraldehyde in the GC-MS analysis of extractives for example, indicating

degradation of the hemicellulose has begun (see previous section). Weight loss due to the treatment was still low, estimated between 0.8 and 2.6%, meaning that the objective of a moderate treatment, which is below the thermal intensity range used in other commercial systems was achieved.

Thicker planks: February and March 2015

The average moisture content of sample planks from the February set (Run F) was 5.46% after treatment and conditioning. Planks 5c and 3e were drier than the others, possibly indicating a temperature gradient still exists across the oven. This is a likely effect of increasing the plank thickness, and was borne out by examination of the thermocouple data. The middle of plank 3e was almost completely dry, while its end segments were 5 and 9% moisture content. Plank 5c was more uniformly dry, all segments were between 1.5 and 2.5% moisture content.

The average moisture content of the March set (Run G) was 3.76%, and this was more uniform across all planks and all locations in the planks. There was generally only 0.5 to 1% difference between the plank ends and the plank centre.

In both batches, the drying day used 30 minutes at 80°C and 5 hours at 120°C, with steps in between. The drying day graphs indicate that plank x3a generally lags behind the others in drying, for example in Run G plank 13a did not reach 100°C, whereas 13e spent four hours at this temperature (Figure 5.6). The primary challenge in achieving a uniform thermal treatment remains the distribution of temperature and therefore dryness of the wood across the oven.

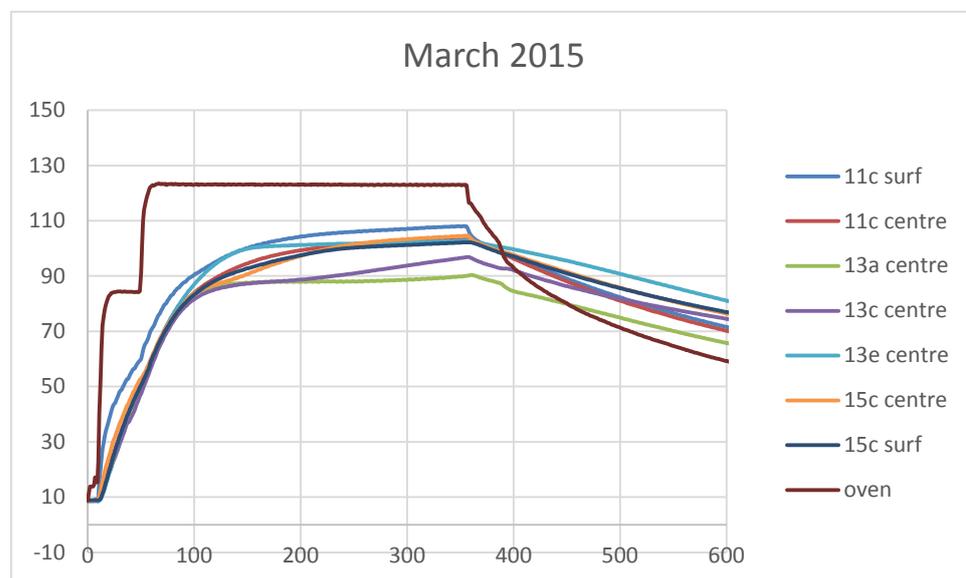


Figure 5.6. Thermocouple data for Day 1 of Run G showing slow increase towards 100°C for planks 13a and 13c.

The discrepancies in dryness at the end of Day 1 influence the rate of heating on Day 2. Figure 5.7 shows the thermocouple data for Day 2 of Run F, where dry timber in plank 3e heated more rapidly than the still damp timber of plank 3a. The resulting effect on the shape of the temperature profile for the three planks was very interesting, with a long delay in reaching the threshold temperature of 150°C for plank 3c (shown by the red bar along the x axis) compared to plank 3e (indicated by the purple bar). Plank 3e barely attained the threshold temperature, as the end of the

treatment phase coincided with the moment at which it reached 150°C, giving a dwell time of just 7 minutes in the treatment zone.

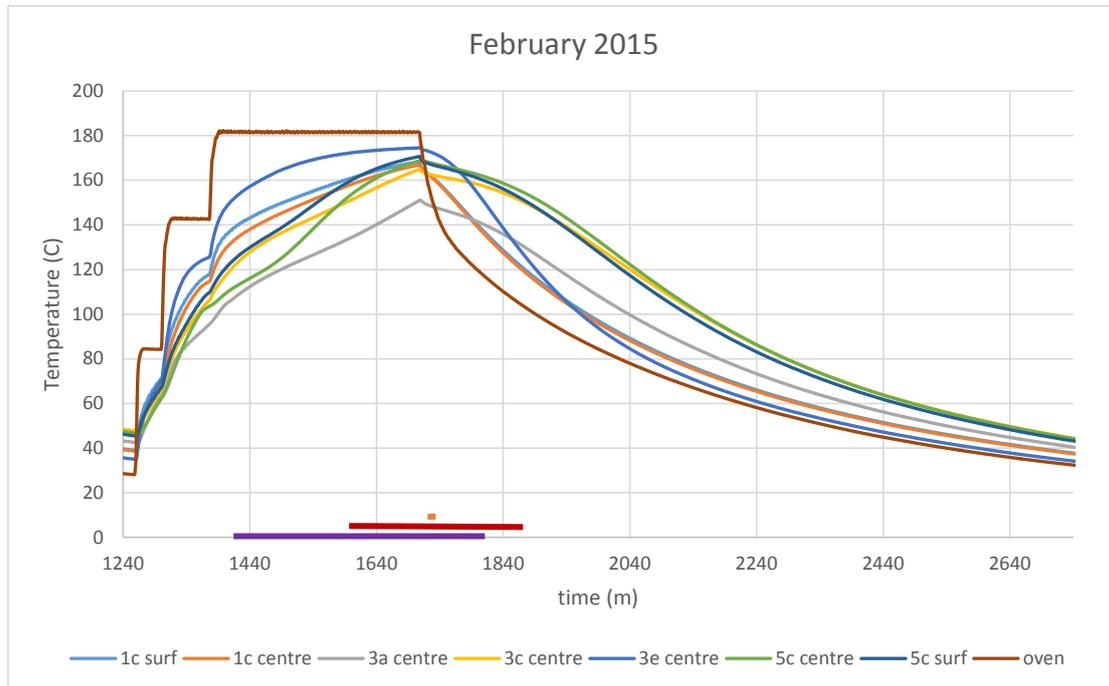


Figure 5.7. Treatment day for Batch F, showing the different treatment duration in the treatment zone (150°C) for plank 3a (orange bar on x axis), plank 3c (red bar on x axis) and plank 3e (purple bar on x axis).

The use of a stepped change in temperature may contribute to this challenge, as can be seen in the graph for this oven run. In Figure 5.6, the step to 80°C took only 10 minutes, while stepping from 80 to 120°C took 8 minutes. Heat output from the oven is high for this short interval to achieve an oven thermocouple reading of the new target temperature. After this, the transfer of heat to the wood occurs slowly, and only small increments of energy are required to top up the energy transferred to the wood. So although the energy transfer is driven well by the temperature difference between the air and the wood, this exacerbates premature drying of the surface regions and leads to a high temperature difference between the surface and the core.

If temperature control is done by ramping, the oven provides a lower portion of thermal energy initially and is required to monitor minute by minute the output required to remain on target, while this thermal energy is used by the wood. As wood is known to have a low thermal conductivity, the expected time taken to warm across a width of 75cm is long, so a slow ramp which allows the timber temperature to rise in synch with the oven may achieve similar or better results than a step followed by a long hold period. It is unfortunate that the one run with a ramped schedule had such a short hold period, and was performed with thinner planks than Runs F and G, so proper numerical comparisons cannot be made. When ramping, it does appear that although a significant temperature difference may still develop between the temperature of air in the oven and the wood temperature, but this is in the region of 10 to 20°C rather than 30°C or more.

The rate at which the timber temperature itself increased was therefore analysed across the various treatment processes. This was split into 30°C segments for ease of identifying main trends. The window either side of the boiling point of water was

avoided as each plank has high variability at this point depending on its moisture content. Quantification of this effect would not be useful without paired values of actual moisture content at that moment in time. The temperatures at which the oven temperature was held (e.g. 80°C) were also avoided, to minimise sources of variability. Example data for Run F and Run G are shown in Table 5.3, where the slowing of temperature increase between the first stages and the later stages of Day 1 and of Day 2 can be easily seen.

Rate of temperature increase (°C/minute)		Day 1		Day 2			Day 3
		30 to 60°C	50 to 80°C	30 to 60°C	50 to 80°C	110 to 140°C	30 to 60°C
Run F	ch1	0.97	0.71	1.76	0.77	0.41	0.97
	ch2	0.88	0.70	1.20	0.75	0.31	0.86
	ch3	0.94	0.70	0.91	0.63	0.14	0.77
	ch4	0.88	0.65	1.07	0.61	0.23	0.77
	ch5	0.91	0.94	1.43	0.81	0.48	0.88
	ch6	0.97	0.68	0.81	0.58	0.21	0.86
	ch7	0.91	0.70	1.20	0.65	0.25	0.75
	oven ch8	15	7.5	10	7.5	3.75	10
Run G	ch1	0.86	0.75	1.3	1.0	0.35	0.97
	ch2	0.91	0.75	0.81	0.91	0.19	0.75
	ch3	0.97	0.81	0.86	0.79	0.17	0.86
	ch4	0.94	0.71	0.81	0.68	0.21	0.86
	ch5	0.97	0.79	0.79	0.88	0.34	0.73
	ch6	0.83	0.67	1.07	0.79	0.24	1.15
	ch7	0.94	0.73	0.86	0.79	0.25	0.97
	oven ch8	15	5.0	10	6.0	3.33	2.73

Table 5.3. Rate of temperature increase for 30°C intervals for each thermocouple within the stack. Thermocouples 1 and 7 were on the surface of the plank, and 2 and 6 were drilled into the corresponding plank centre. Thermocouples 3, 4 and 5 were in planks on the left, middle and centre of the middle row.

It can be seen that the rate for the 30 to 60°C interval increased from Day 1 (average 0.92°C/min for Run I) to 1.20°C/minute on Day 2 where the timber was drier. For the second interval (50 to 80°C), the effect was more varied across the stack, with planks near the bottom and the top showing faster rates, but those in the middle row (channels 3,4 and 5) being slower to increase in temperature. These data show the importance of treating the pack of timber as an entity, with a core which may heat at different rates to the upper or edge faces, due to different moisture dynamics and different thermal input due to distance travelled by the hot air.

It is known that after treatment the moisture content varied across the stack, with Run F having an average of 5.46%, but the planks in the higher temperature region of the oven had average moisture content of 4.17% while plank 1C had 6.95% and 3A had 7.91%. Plank 1C was the plank in which temperature on Day 1 and Day 2 was lowest (94°C and 151°C respectively). The temperature gradient was low in all segments for this plank, including the 110 to 140°C interval on Day 2, which was 0.14°C/min unlike the other planks which had temperature gains of 0.32°C/minute.

5.4 Continuous schedule process

The different temperature profiles experienced by planks in Runs F and G (as seen in Figure 5.7 and discussed in Section 5.3) are an artefact of the process of rapidly drying the timber to fit into a single working day, prior to a single working day treatment stage on Day 2. The set of experiments used in this section were agreed to investigate several factors:

- to avoid wasting energy heating then cooling then re-heating the timber;
- to see whether it is possible to reduce the internal timber stresses induced by these repeated heating and cooling steps; and
- to create a shorter profile capable of increasing timber throughput at a treatment plant.

A continuous kiln schedule was designed in which the drying stage was timed to happen in the afternoon and overnight, prior to the high temperature stage during the working day (ensuring staff are present and managing the oven) followed by a conditioning step overnight. This process was discussed to best fit the availability of personnel to check the ramp stages, and the high temperature hold stage, and may not be immediately transferrable to a kiln at a new location without serious consideration of site factors.

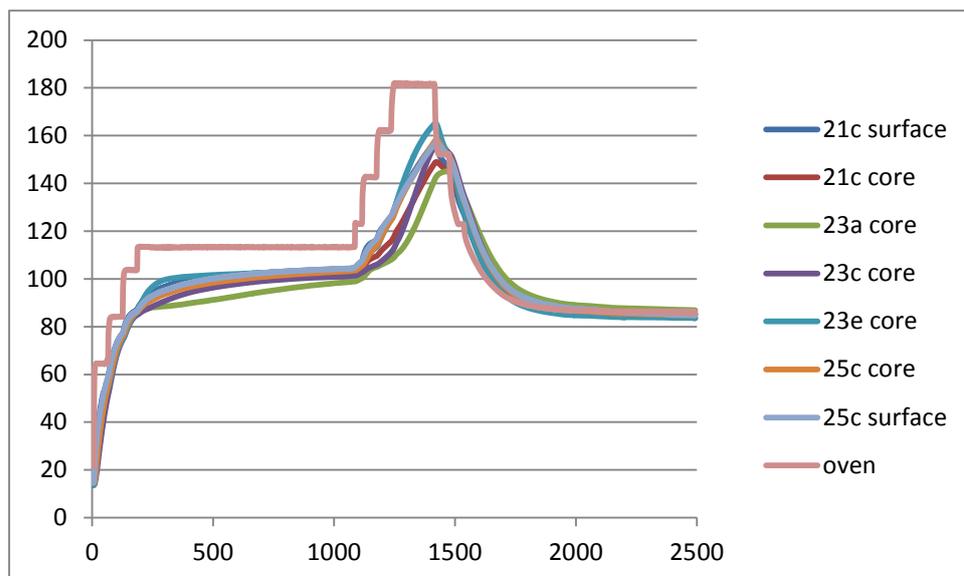


Figure 5.8. Continuous schedule used in Run H

Three treatments were performed using continuous schedule, as shown in the example Figure 5.8. The start of the treatment run was near midday, giving several hours of the working day to observe the stable operation of the kiln and humidifier unit prior to leaving the system operating overnight. This resulted in a 15 hour hold period at 110°C in Run H, and at 120°C in Run I. It was expected that the temperature of all planks would move above 100°C during this hold period, however plank 23c was slow to reach this temperature, and plank 23a only reached 100°C when the next temperature increment began. This implies that plank 23a was not sufficiently dry to be heated above 100°C due to the latent heat required for the evaporation of water within the wood. Slow heating above 100°C was also seen in planks 23c and the core of 21c and 25c. Thus the gradient of temperature and dryness across the kiln remained a consideration for this schedule.

The high temperature stage was also scheduled to occur during working hours, to allow monitoring of the kiln, and cooling of this step to begin before the end of the working day. A series of small temperature increments were selected for this stage, as had been used in the drying stage, in order to mimic the temperature ramp process. It can be seen that while these steps worked relatively well in the stage to 80°C, the lag between the oven temperature and the wood became very large above 100°C (Figure 5.8).

As the high temperature step had been programmed into the day, the conditioning stage was overnight. At the end of the schedule on Run H the kiln restarted to the manual set point of 190°C and timber temperatures reached approx 170°C before being quenched (this data not shown). As a result the observations of moisture content and chemistry may not only reflect the intended thermal process, but also this extra temperature and sudden soaking. For example, the moisture content of the timber at the end of the run was 3.20%, which is lower than expected for the three day schedule.

On the second continuous schedule treatment run some small adjustments were made to attempt to increase drying prior to the thermal treatment step, the overnight hold temperature was 120°C (Figure 5.9). Here the level of drying was much more effective, meaning that the temperature increments on the higher temperature stages were followed with a smaller lag than in Run H. The time that each plank spent within the treatment zone was greater (Table 5.4). Plank 33a still lagged behind the other timbers in approaching 100°C, but did cross this threshold seven and a half hours before the end of the drying stage (Figure 5.9). It was then able to spend 75 minutes above the threshold temperature during the treatment step.

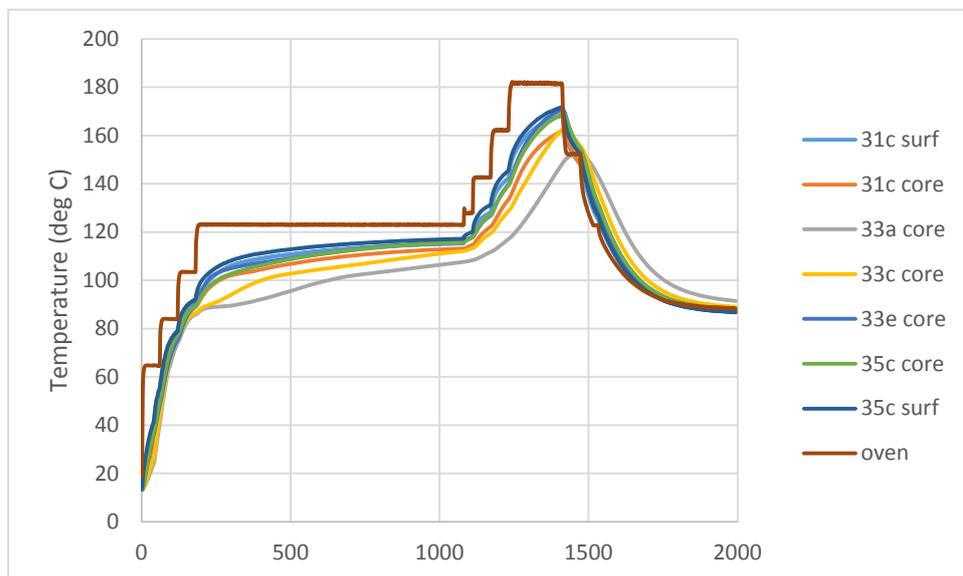


Figure 5.9. Temperature profile for Run I, demonstrating the benefit of additional drying prior to the treatment stage.

The timber from Run I was more uniform than had been seen in Run H. For example planks 33a to 33e showed relatively little change in colour from right to left (hot to cold) across the kiln (Figure 5.10). Limited iron staining (indicated by dark patches in plank 33b and 33d) had occurred in this batch (from condensed water dripping from overhead). In addition planks 33c and 33d show resin associated with the pith which has migrated to the surface and dried during the thermal treatment. The wide spreading of the resin on the surface was typical of the drying of these resin pockets.

The spread across a broad area assists in evaporation of the water and volatile terpenes within the resin to complete drying.

	Run H	Run I	Run J
x1c surface	83	218	195
x1c core	0	162	134
x3a core	0	75	0
x3c core	103	162	147
x3e core	160	220	201
x5c core	117	218	203
x5c surface	112	237	213
oven	300	300	330

Table 5.4. Dwell time in the treatment zone above 150°C for the three continuous treatment runs.



Figure 5.10. Surface of planks from middle layer of the kiln stack, showing generally uniform colouration (excluding iron stain and cured resin), which is indicative of uniform drying and treatment across the width of the stack.

During the final stages of Run I it was noticed that a considerable surplus of water condensed in the oven during the reduction of temperature toward the conditioning step. This was visible due to the iron stains which formed in affected regions of the stack (Figure 5.10), and is likely to correspond with the condensation and precipitation of water vapour as the air temperature drops from 180°C to 80°C. The saturated vapour pressure at 160°C is 3265g/m³ but this can only be achieved by applying pressure, even at a predicted relative humidity of 18%, the air would still hold 588g/m³ moisture. The value for saturated vapour pressure at 180°C is higher, but maximum relative humidity at one atmosphere will again impose a limit. By comparison, the saturated vapour pressure at 80°C is only 294 g/m³ and the

maximum possible r.h. is 100%, so all of this moisture can be contained as vapour. Simply using the 160°C figures, the drop in temperature from 160°C to 80°C would result in a balance of 294 g/m³ which must condense from the atmosphere.

The moisture which condensed inside the oven tended to drip preferentially from certain surfaces, such as the pan which collects condensate from the flue above the oven. This led to watermarks on the uppermost timbers, some of which contained ferric ions from the corroded metal surfaces where this was not stainless. Extra moisture content samples were cut and measured for this kiln run to observe the extent of this effect (Figure 5.11). A marked increase in moisture content was seen for planks from the top row (12-24% and 9-18%) compared to the central row (which was driest, 5-9% throughout). Each plank also showed a large difference in moisture content at the three sample locations, being more damp at the ends than the middle. In planks where high moisture measurements were observed, these tended to be consistently at one end of the planks, this being segment 6, the end nearest to the back of the oven.

	A	B	C	D	E
36		12-24%		9-18%	
35	9-11%		8-13%		9-11%
34					
33	5-9%		6-9%		6-9%
32					
31	8-10%		8-10%		9-11%

Figure 5.11 Schematic of the stack moisture contents at the end of Run I.

When the planks were cross-cut for moisture content samples, the interior of the planks was sound. There were no internal checks or splits relating to poor drying or other problems. The timber had a uniform colour internally when segments from the three sampling locations of each plank were compared. The longer segments planed to a good finish.

For the third continuous schedule, Run J, the temperature increase during the drying stages was altered to attempt to increase the temperature of the wood with greater control. The hold period for the small increments was increased by half an hour, but this time was subtracted from the duration of the 120°C hold, giving 12 hours rather than 15. The result was that the temperature of the timber tracked the oven closer than seen previously, but that the time spent above 100°C until the end of the overnight hold was actually shorter in all planks (Figure 5.12). The planks in hotter regions spent 11.5 hours above 100°C, and the colder locations only three hours, whereas previously the plank in the coldest spot spent 6.5 hours above 100°C.

The time spent above 150°C was reduced for all planks by between 15 and 30 minutes (Table 5.4), possibly relating to the slight reduction in the period above the drying threshold. The timber again appeared to contain few stress related checks, so it is possible that the slower ramp rate is beneficial. However, the difference in colour from plank 43e to 43a was slightly more pronounced (Figure 5.13) than had been seen in Run I (plank 33e to 33a). If using this slower ramp, the run should start three hours earlier to give the full benefit of the dwell time at 120°C to reduce the moisture content.

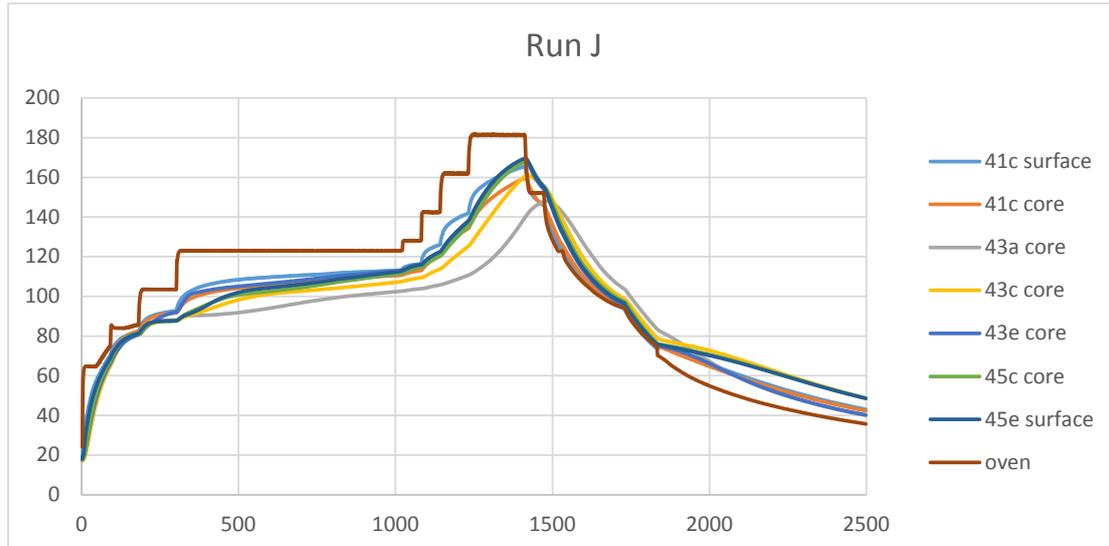


Figure 5.12. Thermocouple data from Run J, showing the effect of a slower sequence of temperature increments, and near 1850minutes, the effect of the oven air circulation being turned off.



Figure 5.13. Colour of surfaces and cross cut faces of planks from the middle row of Run J, showing variation from the hot side (right) to the cold side (left) of the oven.

In Run J it was also intended to reduce steam output during the final overnight conditioning period to reduce condensation within the kiln. The plan to reduce this by adjusting the rate of steam produced by the humidifier unit was unsuccessful, so instead the steam unit was turned off three hours after the sequence of temperature decreases. The oven itself was switched off an hour and a half later, by which time the temperature of the wood and the oven was down to near 75°C. The main effect of

turning the oven off is the end of forced air circulation, so any residual steam or warmth within the timber and oven chamber attains a balance under static conditions.

Less moisture was observed draining from the oven during this cooling phase than had been seen in Run I. On opening the oven, the staining due to metal ions in the condensation which forms during treatment was still apparent, indicating that this had occurred either during the treatment run, or during the sudden decrease in temperature while the air within the oven was still highly saturated with water vapour.

The timber appeared to be very dry, except certain locations near the top of the stack which felt wet as the planks were handled. The average moisture content for all planks sampled was 3.61%, and the few wetter planks in the top row (which were damper at one end due to the pattern of condensation drips) only showed moisture contents of up to 7.13% in these isolated samples, with the average for plank 46B being 5.72%. This is lower than had been seen in early runs (e.g. Run B-D) after the conditioning step, so the observed dampness to the touch indicates that this condensation is largely a surface phenomenon.

It appears that the short cooling stage with steam, and the decision to switch off the oven 7 hours after the 180°C hold for the treatment phase finished had been sufficient to allow the timber to cool, and additional humidity to recondition the timber. A large volume of moisture is known to condense from the hot air as the temperature drops, as calculated earlier. Note that in a kiln load with a greater volume of timber per cubic metre of air, the humidity may not have been sufficient, however for this experiment the balance was well matched, and all planks were ready to handle or process. Planks appeared evenly treated, and there was little evidence of splitting or defects due to kilning stresses in the timber. By stopping the cooling step at this time, the length of the continuous treatment schedule was reduced from 40 hours to 30½ hours. This saves energy, and reduces the number of overnight operations required for the operation of the kiln.

Timber from Runs I and J would be suitable as a mild thermal treatment for interior joinery purposes, in line with the categories (mild and moderate) developed in previous work. As this is larch timber, it may be suitable for exterior joinery if heartwood is used as the timber for treatment. This is on the assumption that larch heartwood has a moderate level of natural durability (Scheffer and Morell, 1998) which is unlikely to be reduced by the mild thermal modification, but would require durability testing to confirm.

6. Commercial scale oven

6.1 Introduction

The work at the pilot scale provided insights into the expected degree of thermal lag between oven temperature and the temperature achieved by the wood. It also demonstrated clearly that temperature distribution, even across a relatively small stack of timber can be significant. These principles were brought into the scale up process at a commercial thermal treatment plant located on Anglesey. The plan to also take the schedule to a plant in South Wales was hampered by changes in staff at the plant where the treatment plant was located. The same principles may be transferred to this or another thermal treatment oven:

- Run a simple three day schedule once, with thermocouples located in the middle layer of the oven, at least in the planks on both outer edges of the stack and the central plank of that row. Ensure that this timber is below FSP and uniformly dry to minimise extraneous effects while optimising kiln conditions.
- Record the temperature of the air within the stack as well as the temperature readings which are used by the oven control panel from the overhead thermocouple.
- Observe the time spent above 95°C, 100°C and 105°C by the plank thermocouples on Day 1. Observe the duration above the threshold temperature within the timber, and compare this for the different locations. Observe the magnitude of lag between the oven controller temperature and the timber temperature.
- Use this information to adjust the ramp rate and dwell time for the programme to be used in the second treatment run, bearing in mind that the drying process on Day 1 has the greatest influence on the treatment zone achieved on Day 2. Optimise Day 1 before making alterations to Day 2.

6.2 Treatment runs

Data are discussed here from a kiln run which used a simple 3 day schedule which was closely based on the pilot scale treatments seen in Runs B to E, and as shown in Figure 2.2. Day 1 was a drying day, reducing moisture content and generating a more uniform load for treatment. Day 2 was the treatment day and used a higher temperature than the other two days to effect the changes within the timber. Day 3 was the conditioning day, using a lower temperature and high humidity to restore some moisture content within the timber prior to unloading from the kiln.

The treatment runs were conducted on small (155 x 25 mm) cross section planks of 3m length, sourced from Esgair sawmill. The timber was predominantly heartwood, although a few pieces contained no more than 50% sapwood (Figure 6.1a). Some pieces were excessively resinous (associated with the pith), while others contained smaller resin pockets only. 1.2 cubic metres of timber were used in this treatment run.

The full scale treatment oven was built by RDM Engineering Ltd with small adaptations to balance two heating banks. Air flow within the oven was unidirectional, and air was forced through the stack of timber by a curtain as a baffle overhead which was lowered to the top of the stack prior to the treatment run (Figure 6.1b).

The oven was controlled using a Eurotherm control panel, and was equipped with a humidifier which generated steam through each day of the schedule until part way through the cooling stage. In this kiln it was possible to use a ramp to elevate the temperature of the kiln slowly to each set point on the drying day, the treatment day and the conditioning day. A four hour dwell time at 120°C was used on Day 1 to give maximum drying across the timber stack.



Figure 6.1a. Typical larch planks used in the study, showing one area of resin associated with pith in a plank with crooked grain (row 1 right) and several planks with 5 to 20% sapwood (row 2 and row 6). b. Timber stack in kiln after mild treatment, baffle curtain is retracted overhead.

The treatment phase at 190°C was relatively short (2 hours 30 minutes), however it was known that the kiln has a high energy output. This set point resulted in the thermocouple on the hot side of the stack reading temperature of 180°C or greater for 1¼ hours (Figure 6.2), i.e. the treatment zone for the timber was more intense than would be observed in the equivalent run on the pilot scale oven. Of more relevance to this study is the duration in the treatment zone above 150°C, which was over 2 hours for all planks. There was 20°C lag between the air temperature in the oven and the temperature of the plank on the hot side, but 35°C lag for the cold side. This indicated that the drying stage had not been completely effective prior to the treatment day.

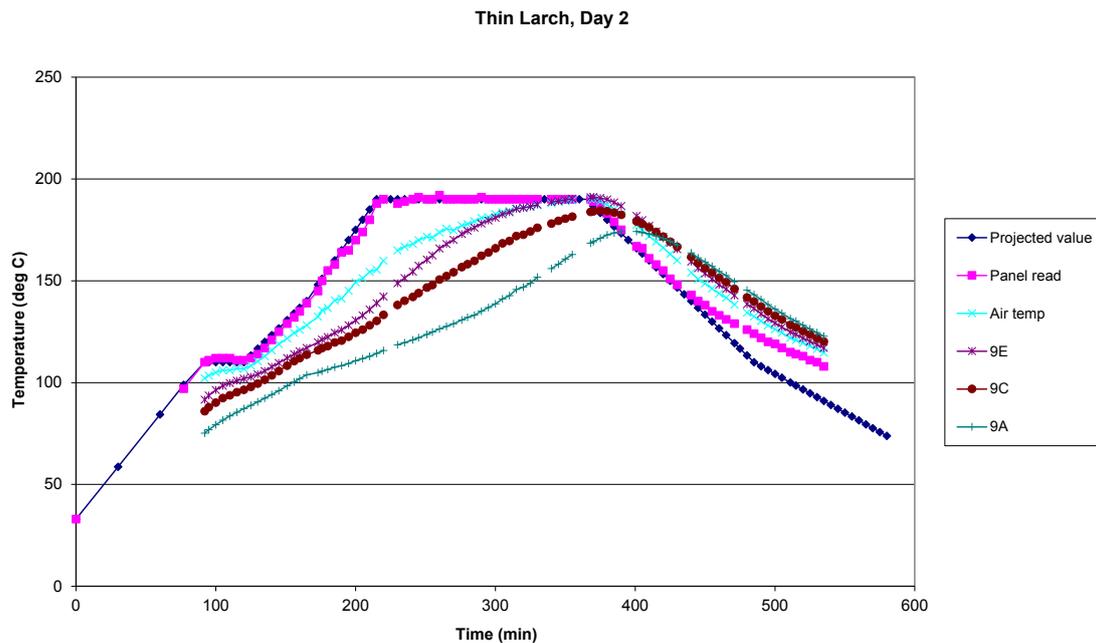


Figure 6.2. Thermocouple data and kiln controller temperature values during Day 2 of scale up treatment of larch timber.

The timber which had been loaded to the kiln in the run discussed above was supplied green, and despite a short period air drying was not below fibre saturation point. Its moisture content was calculated to be over 100%, and after treatment it was clear that some planks had dried more completely than others during treatment. The average moisture content of the treated conditioned timber was 4.0%, but plank moisture content changed across the stack, and more importantly with vertical location in the stack.

The same timber was to be used in the next run, so an additional drying stage was added prior to Day 1. This used a relatively long dwell time at 80°C before ramping to 110°C to hold for two hours, for clarity it will be referred to as Day 0 (Figure 6.3). The intention was to drive off a significant amount of moisture slowly, before approaching the boiling point of water. It is possible to see the slow heating rate of the timber, compared to the kiln set points, which relates to the drying of wood with a high moisture content. In addition, four days were allowed between Day 0 and the normal 'drying' Day 1 (Figure 6.2). This may have allowed slow air drying to continue at ambient conditions while the kiln was not operating.

In this run, the thermocouples read very close values during the treatment day (Figure 6.4), with all plank thermocouples showing a duration above 150°C of 4 hours. The thermocouple which was in the air spent 4 ½ hours above 150°C, which is very similar to the duration that the oven temperature was in this range. This is a strong indication that the drying during Day Zero and Day 1 had been successful in reducing lag across the kiln.

HEAT TREATMENT OF LARCH TIMBER

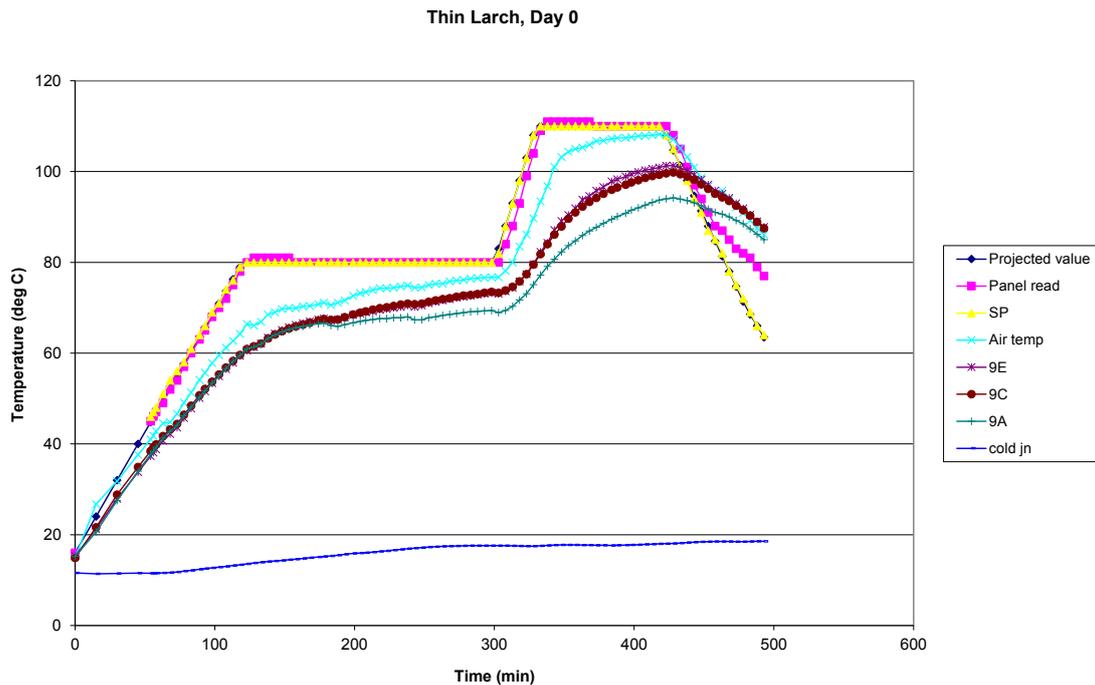


Figure 6.3. Programme for drying step (Day 0) prior to that standard drying/conditioning procedure on Day 1 in second run

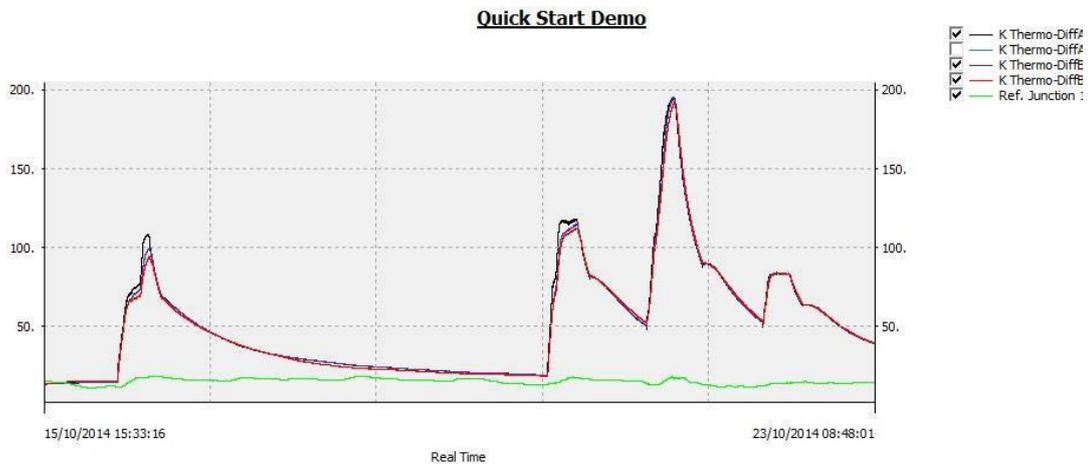


Figure 6.4. Thermocouple data for the full four day treatment after introduction of a drying stage on Day Zero before the established treatment schedule.

The timber from this run was more uniformly treated, and resin on the surface of the planks was cured. When cross cut to remove moisture content samples and observe internal structure, the colour development was uniform through the plank, and no cracks or splits were seen.

7. Conclusions

Thermal treatment, tailored to dry the naturally occurring oleoresin in larch, has been demonstrated at the laboratory, pilot and large scale. The natural resin was seen to have dried on the surface of planks treated in both ovens, and the processes behind this drying process have been investigated using chemical and physical techniques.

Let us therefore return to the initial questions to give context to the experimental results:

1. At what temperature does larch resin become cured or permanently hardened? And does it have to remain at this temperature for a specific length of time?
2. What is the minimum temperature larch planks need to be heated to in order to achieve this effect in practice? And, does the thickness and moisture content of the planks influence the length of time needed?

7.1 Question 1 – temperature and time

The DSC data (coupled with chemical analysis by GC-MS) has demonstrated that the process of larch oleoresin drying is one in which a combination of moisture and terpenes are driven off. This can occur slowly at room temperature – but is usually associated with slow resin bleed from deeper into the wood – so the balance of drying versus replenishment may take years to achieve. It may occur relatively fast at high temperatures, for example in one hour at 150, 170 or 190°C the small DSC samples gained a dry appearance. The 190°C sample also approached a stable mass in this time, which would indicate that all material which is volatile within this temperature range had been exhausted.

Using the rate of mass loss from the DSC isothermal samples, it is possible to note that 150°C gave a mass loss of approx. 0.545g/minute, while 170°C gave a mass loss of 1.846g/minute. Clearly the use of a higher temperature gives a more rapid drying process. In the studies, the samples which experienced 120°C isotherms approached a stable weight but with considerably lower mass loss – indicating that only moisture and some monoterpenes were being lost at this stage. 120°C as a treatment temperature can therefore be eliminated as a candidate, as resin 'cure' or hardening is likely to be only partial, and very slow.

However, the use of a temperature such as 170°C will be accompanied by thermal modification of the wood structural components – as described in the introduction. In some products this is desired, and in others it is not required. For joinery timber it may be preferred to use a threshold temperature of 150°C, and a longer time, while for external products, a moderate treatment, using a threshold temperature of 170°C may achieve a similar drying process but in addition, begin to modify the timber to enhance stability, alter colour and affect other properties.

It is also clear that the drying process is time dependent. The definition of a time period for the hardening process to occur in timber requires several parameters to be known. One is the **quantity of the resin present**, associated with this is the extent of its spread over the surface (or likely spread during thermal treatment). Another factor is the **thickness of the plank** and the depth within the plank that a resin pocket may

reside A further consideration is the **moisture content of the plank**, as the presence of large volumes of water in green timber will slow the progress of drying, as will be discussed in Question 2.

In practice the quantity of resin within a larch plank varies with several factors:

- Juvenile wood – the region closest to the pith may contain considerable quantities of resin, stored under pressure by the tree to be able to supply oleoresin in response to injury or other environmental factors.
- *Phytophthora* infection – one of the symptoms of infection by *P. ramorum* is heavy resin bleeding, and the infected trees amongst the sanitary fellings are likely to contain a higher resin content than the non-infected trees from the same stand.
- Other injury or damage – the primary purpose of the oleoresin as a protection mechanism for the tree, blocking ingress of pathogens means that frost damage, insect attack, machinery injuries from earlier forest operations or vandalism will heighten the likelihood of localised resin pockets within the trunk.



Figure 7.1a). Small resin canal (centre of picture), b). resin bleed from pocket in installed window. c). resin associated with pith in a stem which has distorted grain. d). ring shake in a plank with resin throughout the line of failure.

The quantity of larch can vary then between very small bleed from resin canals – barely visible to the naked eye; through 1-2cm width resin pockets, cut open during sawing, up to large shakes with accompanying resin throughout (Figure 7.1a-d). The more extreme cases are most effectively dealt with by removing these planks from further processing – the shake or splitting from the pith are likely to reduce timber quality even if the resin is successfully dried, as shown in Figure 7.1d. There is little economic merit in wasting kiln energy and space on such planks. However these

worst case planks are likely to be only in the region of 5% of the total, and this will vary with source of the timber.

The resin in the resin canals and the resin pockets can be successfully dried or hardened allowing use in joinery products. Resin within the thick planks used in Runs F to J was found to be dried in the majority of cases. The one case where liquid resin was found in a plank from Run F was from a plank which had been in the cold side of the stack prior to improvement in the Day 1 schedule. A target temperature of 150°C for resin cure appears to provide a good level of success.

7.2 Question 2 – plank temperature, thickness and moisture content

The pilot scale experiments have demonstrated that (depending on the oven properties) the set point for the treatment phase may need to be considerably higher than the target temperature for the planks. The concept of a threshold temperature – in this case 150°C to be sufficient to dry resin – and treatment zone (in which the core temperature of the planks exceeds the threshold temperature for a targeted period of time) has been introduced (Figure 7.2) in the discussion of pilot scale results.

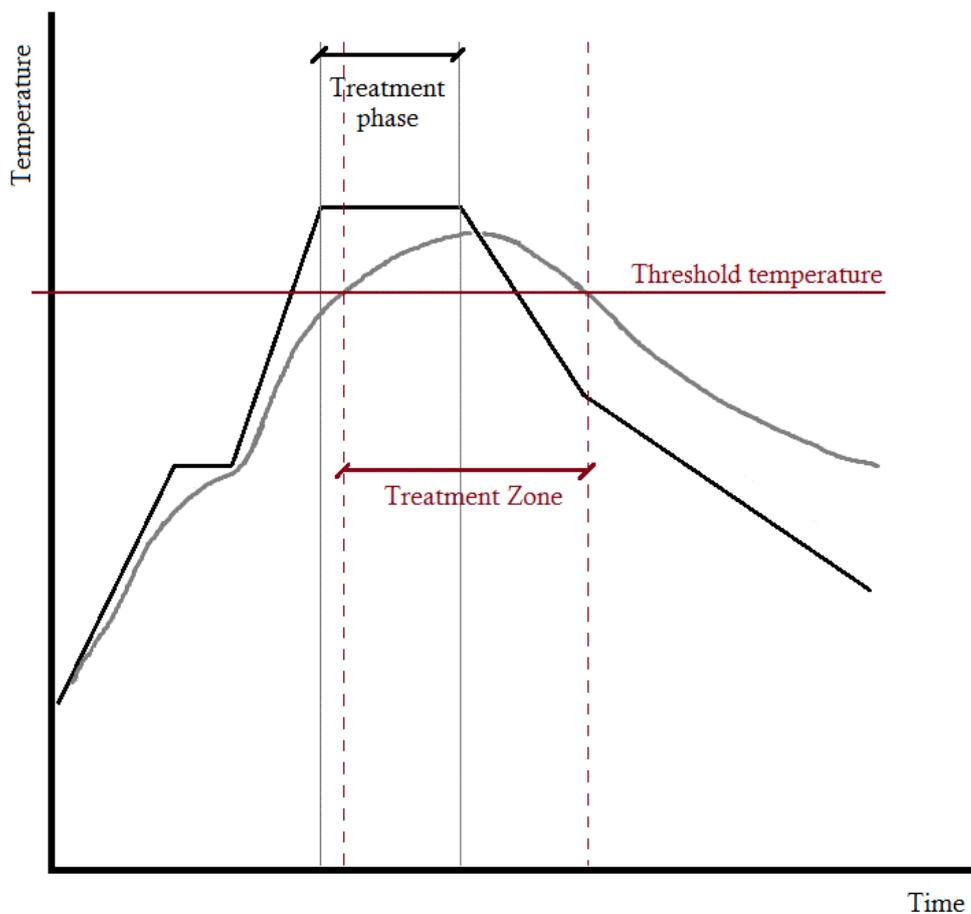


Figure 7.2. Schematic showing the treatment phase (controlled by the oven programme), and the resulting treatment zone (duration where timber temperature is above the threshold temperature).

The efficiency of the oven in putting the timber into the treatment zone is determined by the maximum thermal output of the oven, the level of insulation of the oven and the efficiency of the oven in creating full air circulation to avoid hot and cold spots. Good stacking of the timber also facilitates good results – stacking planks edge to edge to minimise diffuse air flow between layers, good stickering, and the avoidance of uneven lengths of timber (which then require end to end butt joints inside the stack, often resulting in uneven lengths at the stack ends). It is also best to avoid loads with uneven moisture contents (e.g. where the top of the stack has been exposed to weather while the side and base may be dry) or mixed species loads.

The moisture content of the timber which enters the oven has a very large effect on the efficiency of heating by the oven. Rough calculations performed in the early stages of this study demonstrated that to heat timber at a moisture content of 38% to 120°C required 662 MJ, while to heat the timber alone required 132MJ. This five fold increase was due to the larger thermal capacity of the water (4.168 kJ/kgK) compared to wood (2.5 kJ/kgK), but also the latent heat of evaporation of the water (2272 kJ/kg). For a stack of green timber of the same size 1816MJ would be required. This is nearly a further 200% increase. It makes good economic sense to do this drying process in advance of the thermal treatment step. The relatively slow approach of the timber to temperatures above 100°C which can be seen in the Day 1 thermocouple graphs (see Appendix) is entirely due to the moisture content of the timber, the majority of which must be driven off before the plank may reach higher temperatures.

It is not the intention of this study that thermal treatment ovens are used as a substitute for a fully controlled timber kiln for routine preparation of material. Good practice in kiln drying may be learnt from many textbooks (e.g. Pratt *et al.* 1997, Keey *et al.* 2000) and applied in conventional lumber drying kilns. A key feature of a drying kiln is the precise control of humidity within the kiln, to slow drying rate and avoid drying defects. The 'drying stage' referred to in this report is simply the preparation platform on which the thermal modification (Day 2) may happen most efficiently.

The drying schedule used here for Day 1 is most ideally suited to timber which is already below fibre saturation point (30% moisture content). For wetter timber it may be necessary to spend longer than one day drying the stack out before treatment. If receiving green timber for treatment it is therefore more efficient to facilitate air drying prior to loading the oven – e.g. storing the timber under cover, well stickered and with good ventilation.

The same considerations about kiln set point and threshold temperature discussed for Day 2 (Figure 7.2) can be used to understand the Day 1 schedule. Here the threshold can be considered to be approx. 105°C, the point where the timber has moved fully through the boiling point of water (100°C). The oven set point used in the three day experiments was therefore 120°C, as this had been demonstrated to get the timber up to 105°C for sufficient time (drying zone) within the approx. 3 or 5 hour drying phase (treatment phase). By adjusting the duration of this drying phase the duration in the drying zone can be altered. Similarly adjustment of the oven set point could have some effect on duration in the drying zone.

When approaching adjustment of the schedule to run on a different oven of higher or lower thermal output, the control of treatment phase duration can therefore be useful in ameliorating effects due to different heating rates. Likewise, when an oven is loaded with a greater volume of timber, or timber of a different species, both parameters will alter the rate of heating in the stack, so control of treatment phase to

alter treatment zone dwell time is useful. If the kiln is loaded with wetter timber, some control can be gained in this manner, but as demonstrated for the commercial scale kiln, it may be wise to focus the effort on the pre-drying to enable the treatment schedule to work as intended. By the same token, thicker planks will require a longer drying phase on Day 1, due to rate of thermal transfer the greater distance into the plank, in the same manner as they will require a longer treatment phase on Day 2.

Considering the plank thickness in greater detail, some caution is required here. There are several reasons for increasing drying time when handling thick planks. In thermal modification (where timber is dry) it is tempting to consider only the rate at which temperature passes to the core of the plank, which is a function of the thermal conductivity of wood (typically 0.12 to 0.15 W/mK for softwoods). In practice this is rarely the full story – the rate of moisture loss at the outside of the plank must be kept in balance with the rate of migration within the plank to avoid premature drying of the surface. This balance is increasingly difficult to control for thick sections, with a greater risk of developing the various drying defects (case hardening, honeycomb). When working with thicker sections of timber in the three stage model programmes discussed here it may be advisable not only to increase the dwell time of the treatment phase, but also to reduce the gradient of the ramp stages used. There is a practical limit to this, if length of working day is the motivation for the three step schedule. Depending on oven thermal output rate, and timber moisture content, plank thickness may be limited by the available time for ramping and then maintaining temperature, and initiating cooling. For example, the 38mm thick planks used in Runs F and G are close to this practical limit for the pilot kiln.

7.3 Recommended Basic Schedule: Mild Modification

The schedule below has been proposed as a method for achieving mild modification, that is, one sufficient to cure larch resin and induce only mild modification of the wood substance. The target products would be joinery for interior use, furniture and decorative purposes.

The timber should be below fibre saturation point (FSP, 30% moisture content) before starting Day 1. As discussed earlier, although Day 1 can be termed the 'drying day' this is not intended for drying green or very wet timber, simply preparing the timber for the high temperatures it will experience on Day 2.

The Schedule below assumes that all practical and safety considerations relating to use, maintenance and repair of the thermal treatment oven will be performed in line with manufacturer or designers guidelines. No liability for malfunction, incorrect programming, or unsupervised operation of the kiln is accepted by the authors.

The schedule has been written in the assumption that the thermal treatment oven will be capable of controlling a ramped temperature, such as 1°C per minute, for the temperature increments, not a stepped temperature increase. In the event that the oven requires a stepped temperature, the hold period following the step should be extended (for example by 30 minutes or one hour) depending on kiln performance. The decision regarding length of this increased hold duration can be made using thermocouple data from within the timber stack by an experienced operator.

The set temperature for the treatment phase of Day 2 of this schedule has been set as 180°C based on prior experience in the pilot scale oven. In transferring this schedule to an oven, the use of thermocouple data to confirm whether 180°C is correct for that oven is advised. If a large capacity oven is operating with high efficiency, it may be possible to reduce the set point of the treatment phase to for example 170°C or below and still achieve a treatment zone above 150°C for the desired period of time. The process of verification requires at the least two runs with thermocouple data and uniform conditions (plank dimensions and plank moisture content) and is the responsibility of the oven operator.

In the Day 2 schedule, duration X at the treatment phase may be 2 hours 30 in an efficient kiln, or 5 hours in a kiln which is showing a large lag in temperature between the kiln and the wood. It has therefore not been specified in this schedule, and must be confirmed in practice by the kiln operator using thermocouple data. It should also be re-confirmed for any batches which are using planks of a different thickness.

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Table 7.1. Day 1

Ramp	1°C/min	to 80°C	Steam	60°C in 60 mins
Hold	1 hour at	80°C	Steam	60 mins
Ramp	0.5°C/min	to 120°C	Steam	40°C in 80 mins
Hold	4 hours at	120°C	Steam	240 mins
Ramp	1°C/min	to 80°C	Steam	40°C in 40 mins
Ramp	0.5°C/min	to 40°C nominal	no steam	40°C in 80 mins
Total run time				9 hours 20

Table 7.2. Day 2

Ramp	1°C/min	to 80°C	Steam	60°C in 60 mins
Hold	30 mins at	80°C	Steam	30 mins
Ramp	0.5°C/min	to 140°C	Steam	60°C in 120 mins
Hold	30 mins at	140°C	Steam	30 mins
Ramp	0.5°C/min	to 180°C	Steam	40°C in 80 mins
Hold	X minutes*	180°C	Steam	X minutes
Ramp	1°C/minute	120°C	Steam	60°C in 60 mins
Ramp	0.5°C/min	to 60°C nominal	no steam	60°C in 120 mins
Total run time				8 hours 20 plus X minutes

* See text for explanation of Duration X

Table 7.3. Day 3

Ramp	0.75°C/min	80°C	Steam	60°C in 80 mins
Hold	4 hours	80°C	Steam	240 mins
Ramp	0.5°C/min	30°C nominal	Steam for first half hour	60°C in 120 mins
Total run time				7 hours

7.4 Shortened Continuous Schedule for Mild Modification

In case future work were to replicate the shortened schedule used in Runs H, I and J, the parameters for this are provided in Table 7.4 below. These have been adjusted to incorporate a ramp rather than step to each hold stage. Note that caution and professional advice is required if transferring this to a large scale kiln, as the performance of that kiln may differ from the pilot kiln used for demonstration.

If moving from the pilot scale kiln to a large treatment kiln in will be necessary to review the ramp rates and duration of hold periods below in the light of the thermal capacity of that kiln, and the peculiarities of air flow within that kiln when loaded with timber of the desired size. This would naturally draw not only on the data in the table, but also practical experience and observations made in operating that kiln with that timber on simple schedules as outlined in Section 7.3.

Table 7.4. Continuous schedule as used in pilot scale kiln

Ramp	2°C/min	to 60°C	Steam	40°C in 20 mins
Hold	40 mins at	60°C	Steam	40 mins
Ramp	1°C/min	to 80°C	Steam	20°C in 20 mins
Hold	40 mins at	80°C	Steam	40 mins
Ramp	1°C/min	to 100°C	Steam	20°C in 20 mins
Hold	40 mins at	100°C	Steam	40 mins
Ramp	1°C/min	to 120°C	Steam	20°C in 20 mins
Hold	14hrs 40mins at	120°C	Steam	880 mins
Ramp	1°C/min	to 125°C	Steam	5°C in 5 mins
Hold	25 mins at	125°C	Steam	25 mins
Ramp	1°C/min	to 140°C	Steam	15°C in 15 mins
Hold	45 mins at	140°C	Steam	45 mins
Ramp	1°C/min	to 160°C	Steam	20°C in 20 mins
Hold	40 mins at	160°C	Steam	40 mins
Ramp	1°C/min	to 180°C	Steam	20°C in 20 mins
Hold	X minutes*	180°C	Steam	X minutes*
Ramp	0.5°C/minute	to 90°C	Steam	90°C in 180 mins
Ramp	0.5°C/min	to 60°C nominal	no steam	30°C in 60 mins
Hold	14 hours	60°C nominal	no steam	840 mins
Total run time				1370 minutes plus X minutes
				22 hours 50 plus X minutes

* See text for explanation of Duration X. For the pilot scale treatment Run I the equivalent value of X would be 160 minutes.

7.5 Quality monitoring for mild modification

When running the pilot and the large scale kilns for this project, thermocouples were used at different locations within the stack of timber. It is recommended that this is standard practice for any thermal modification unit implementing the work reported here in future. It is clear from the thermocouple data that the temperature of the timber at any given time can be considerably lower or higher than that of the oven, and a simple reading from the oven's own thermocouple is insufficient to have confidence in the processes occurring inside it.

The use of thermocouples with a datalogger allows real time information about the temperature profiles developing across the stack of timber, but also stores data to interpret at a later date if unusual or unexpected results are achieved. This data itself may be used for quality control of the kilning procedure. For example, if it is decided that on a given programme (e.g. based on Tables 7.1 to 7.3) the duration above the threshold temperature of 150°C should be 2 hours or greater, it is possible to check after each batch that this has been the case. It would also be possible to generate a simple macro to confirm this duration has been seen (or a related parameter – based on the expected time above 150°C prior to the end of the high temperature hold step) before the kiln can begin the cooling stage of the schedule.

Where overheating is observed, giving timber which is too dark; or where rapid heating has resulted in case hardening, the data from the thermocouples may also be used to identify whether this is a localised problem or a pervasive problem across the whole stack. New stocks of timber which are significantly drier or thinner than those treated previously could require small adjustments of treatment parameters, or this observation may prompt the kiln manager to make such adjustments if no schedule has yet been developed for the product.

In the experiments conducted here it does seem that durations above 150°C of four hours or more show considerable resin cure, even to some extent within resin pockets which were on the interior of thicker planks. Surface resin was in fact cured within three hours. In a few cases resin was observed which was tacky but definitely not a liquid. If encountered when finishing a piece of timber these would continue to dry rather than ooze liquid resin.

The mild thermal treatment to prepare joinery quality timber shows considerable promise for the additional benefit of resin drying or curing, which increases its suitability for decorative joinery. In addition, the drying of the resin makes applications such as lamination more attainable, where a good surface is required to form a strong bond when adhesive is applied.

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9. Appendix: Kiln schedule schematics and thermocouple data

Run B, 15-16 July 2013

The steam generator was on for first two hours of 120°C hold and off for the remainder. Treatment phase 180°C for 3 hours, steam supplied for 2 hours, and off for the third.

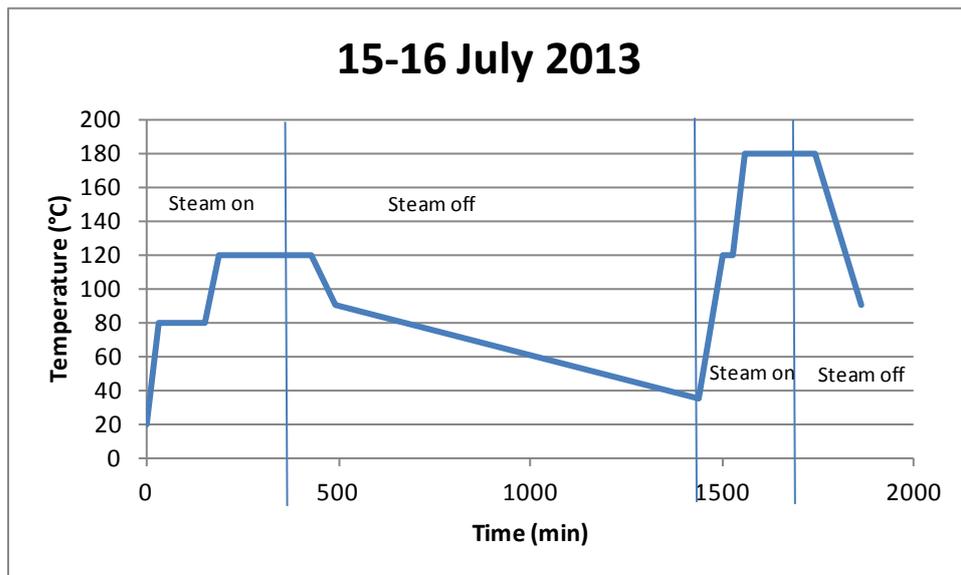


Figure A1. Schematic showing temperature profile selected for Run B

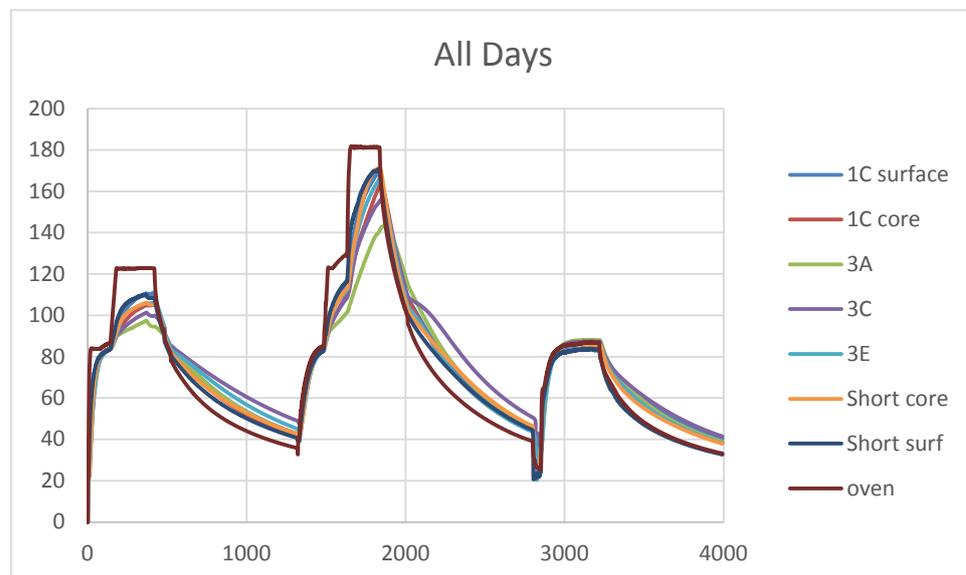


Figure A2. Datalogger output for Days 1 to 3 of Run B

Run C, 28-30th August 2013

Steam on for first two hours of 120°C hold and off for the remainder. Treatment phase 190°C for 4 hours, steam supplied for 3 hours, and off for the fourth.

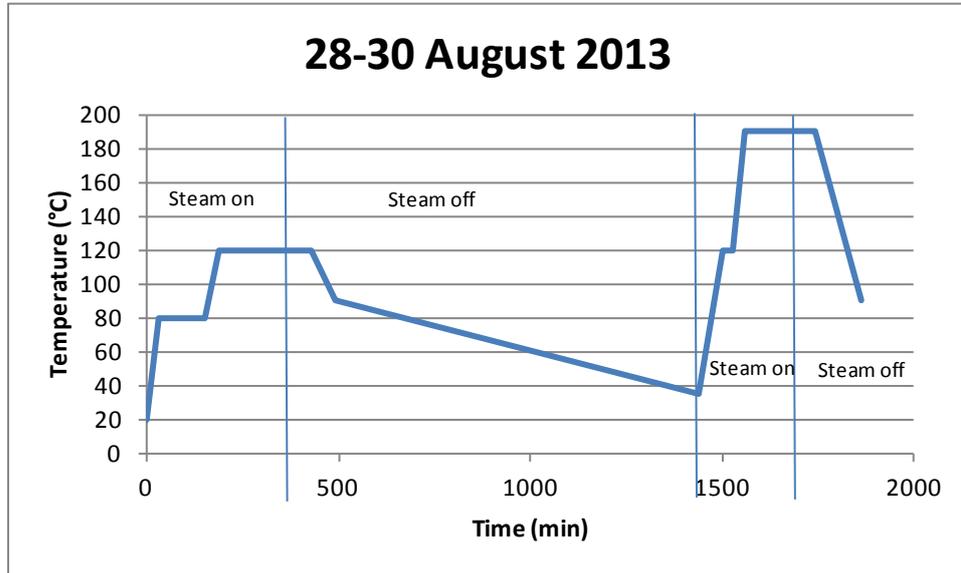


Figure A3. Schematic showing temperature profile for Run C.

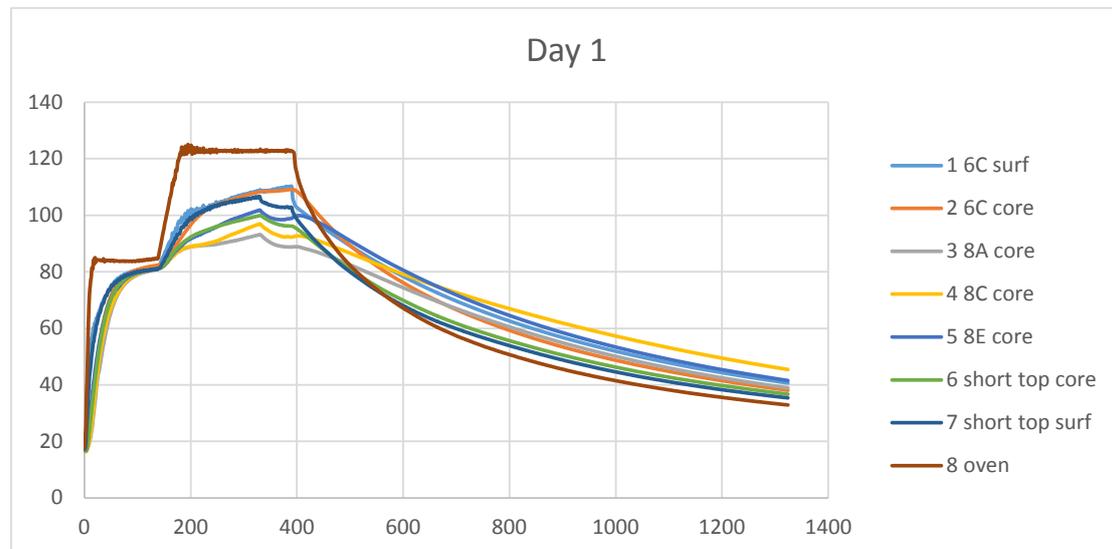


Figure A4. Temperature profile during Day 1 of Run C for all thermocouples. Showing the decrease in plank temperature when the steam generator was turned off after two hours at 120°C.

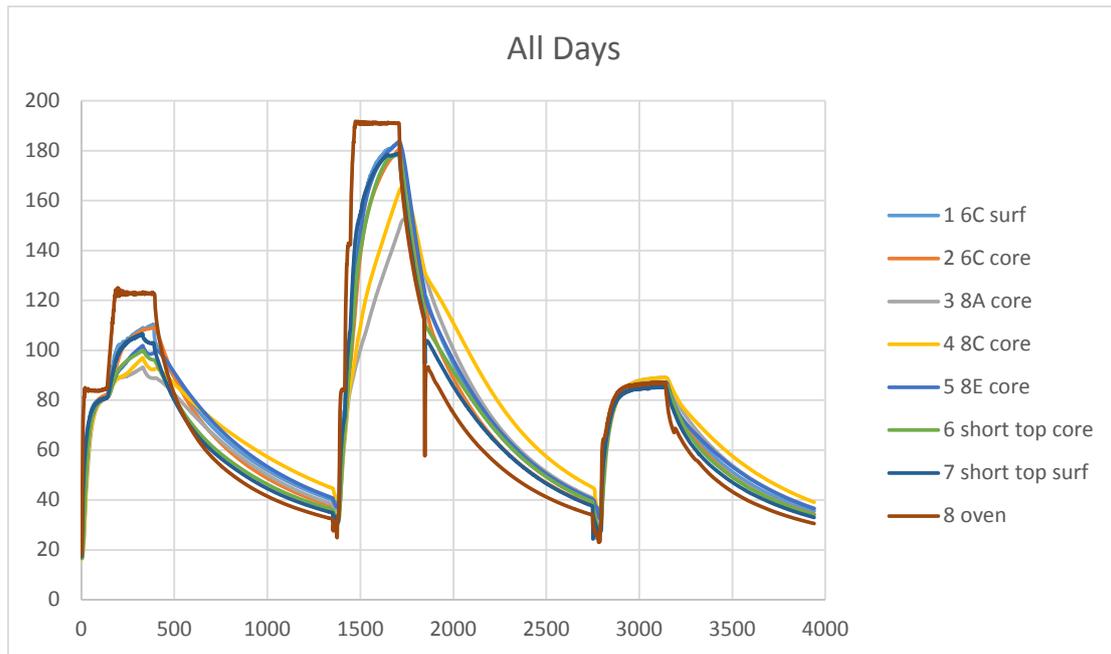


Figure A5. Datalogger output for Days 1 to 3 of Run C

Run D, 18-20th December 2013

The steam generator was on for the whole of Day 1 until the end of the 120°C hold period (3.7 hours). Treatment phase 190°C for 5 hours.

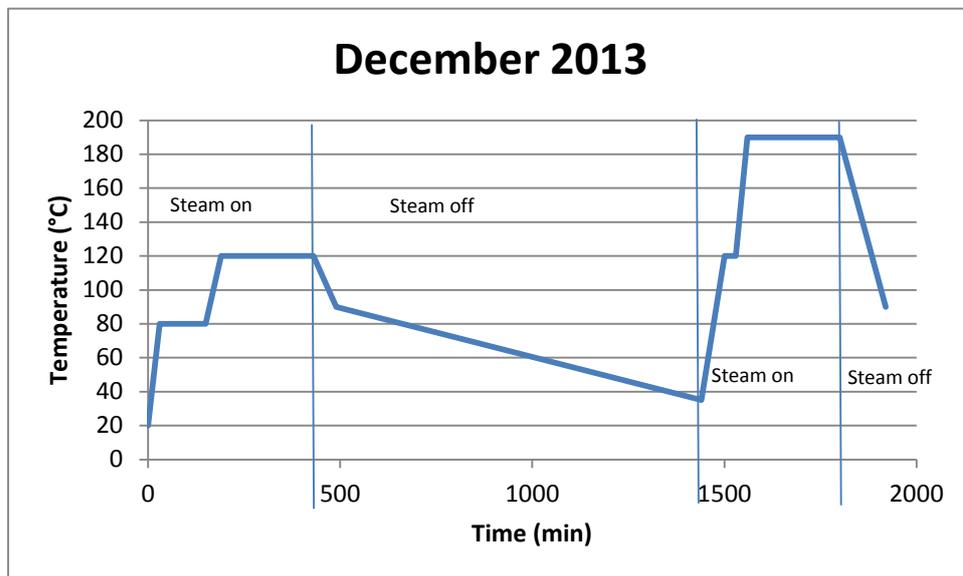


Figure A6. Schematic of treatment schedule for Run D

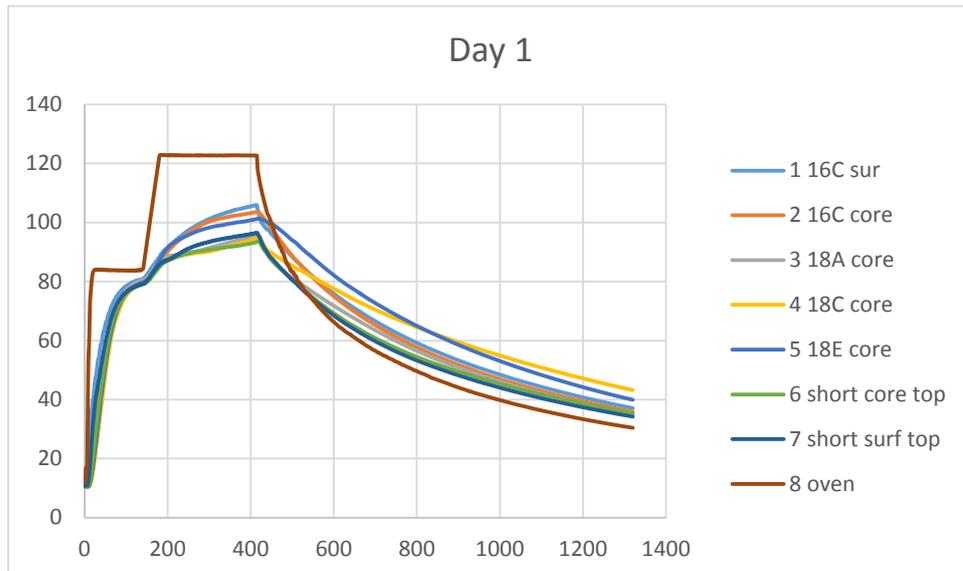


Figure A7. Day 1 temperature profile for Run D, steam was on continuously.

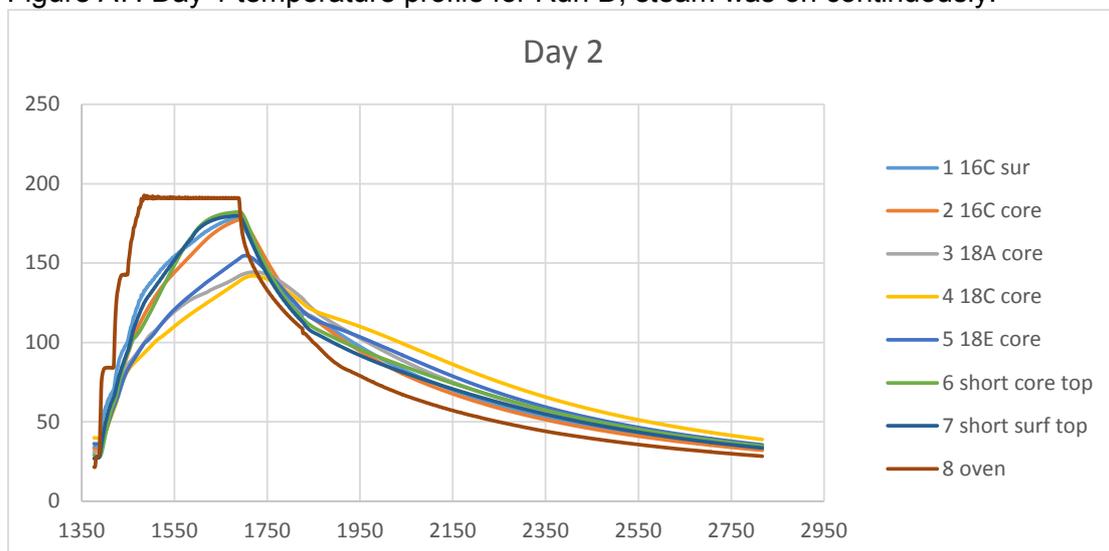


Figure A8. Day 2 temperature profile for Run D.

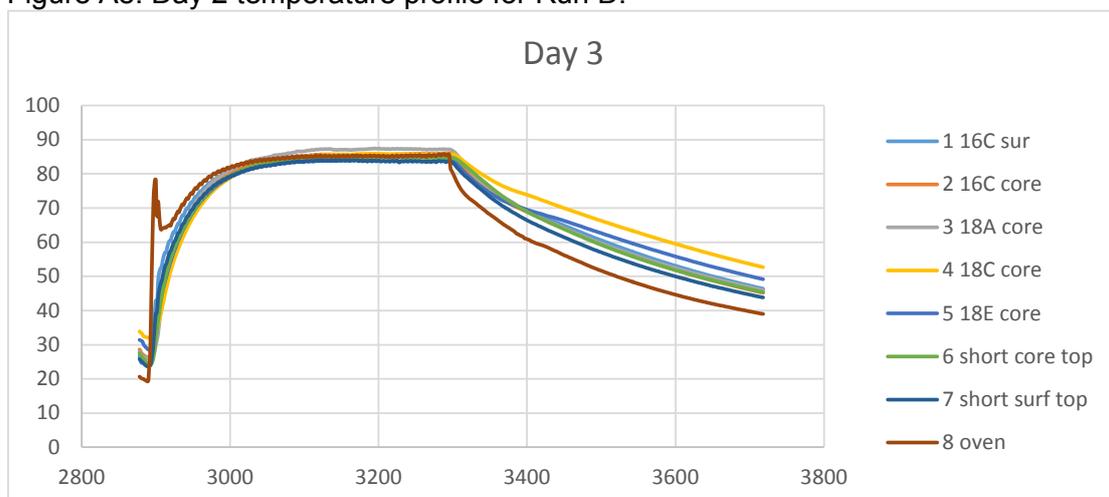


Figure A9. Day 3 temperature profile for Run D. The accidental short overheat of oven temperature at the start of the run (channel 8) had negligible effect on the rate at which the timber inside the oven heated.

Run E, 31st March – 2nd April 2014

The Day 1 schedule was altered to use a ramp rather than a step to 80°C to better track the timber temperature, steam was on throughout. The 120°C hold period was interrupted prematurely at 90 minutes. On Day 2 the 190°C treatment phase was extended to 4 ¾ hours.

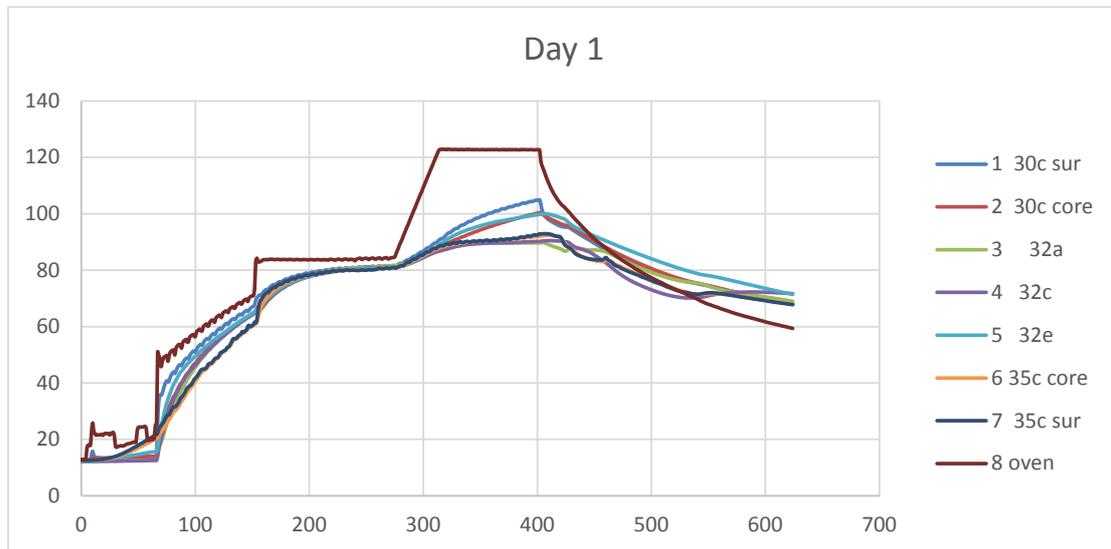


Figure A10. Day 1 of Run E, showing ramp stage, and delays in starting due to hold back.

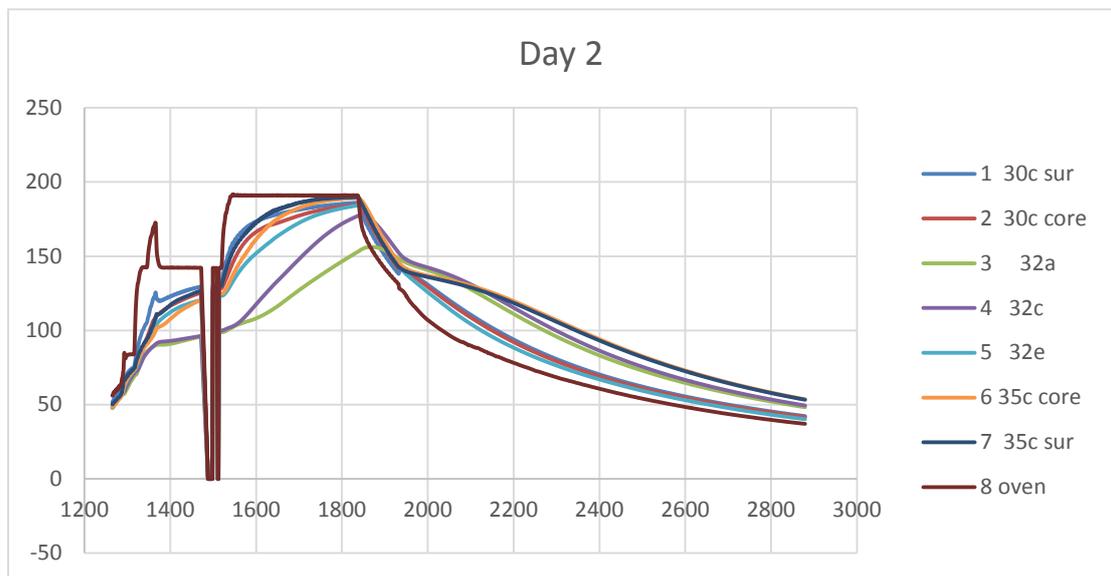


Figure A11. Day 2 of Run E showing small overshoot and correction, and several interruptions in the thermocouple data, oven temperature was not affected by this.

Run F, February 2015

Three day schedule with a 180°C treatment phase of 5 hours. Note that the spike in temperature at the end of the drying day (Day 1) was unintended. But the temperature of the wood increased by 10 to 30°C.

Large planks 1A-E to 6A-E

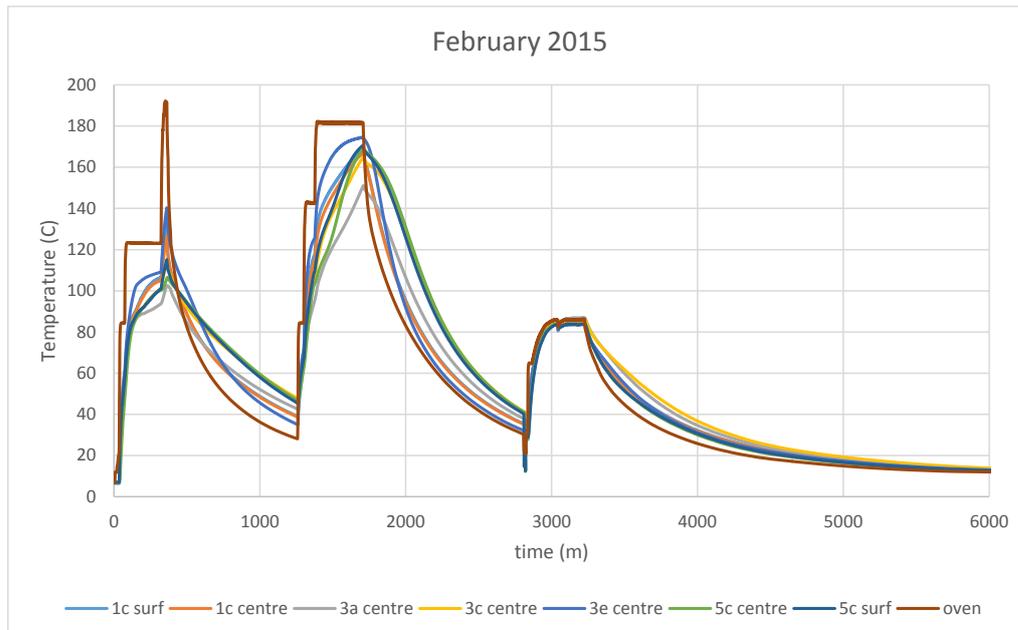


Figure A12. Showing thermocouple data from throughout the three treatment days.

Run G, March 2015

Three day schedule with a 190°C treatment phase of 6.4 hours. Large planks 11A-16E

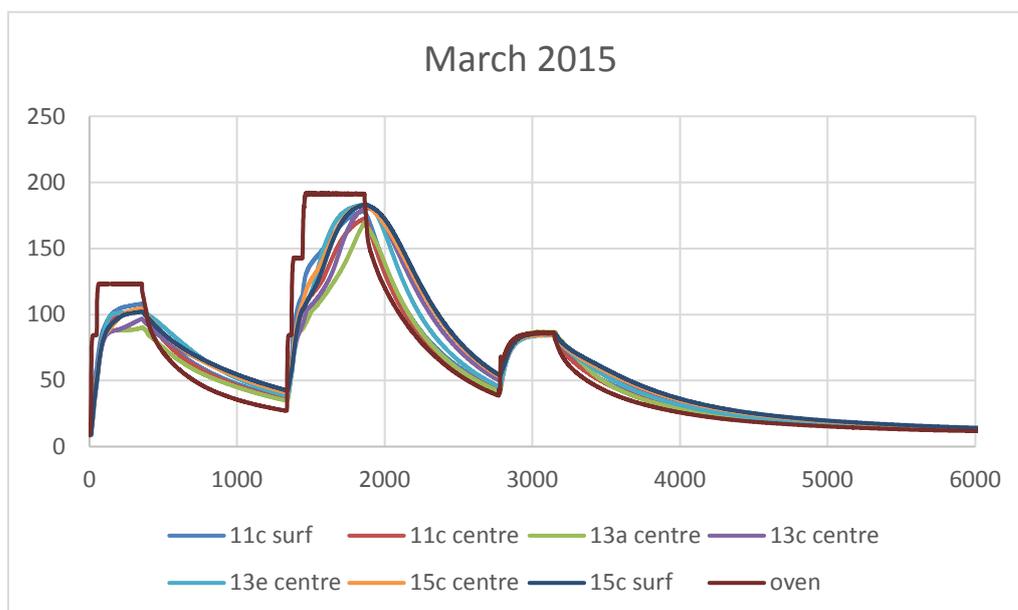


Figure A13. Thermocouple data from throughout the three day process.

Run H, April 2015

A continuous schedule using a three hour 180°C treatment phase. At the end of the run, the oven controller reverted to a previously set manual set point, and temperature increased to 190°C (not shown). Moisture content data for this timber was excluded from this study for this reason. Large planks 21A-E to 26A-E

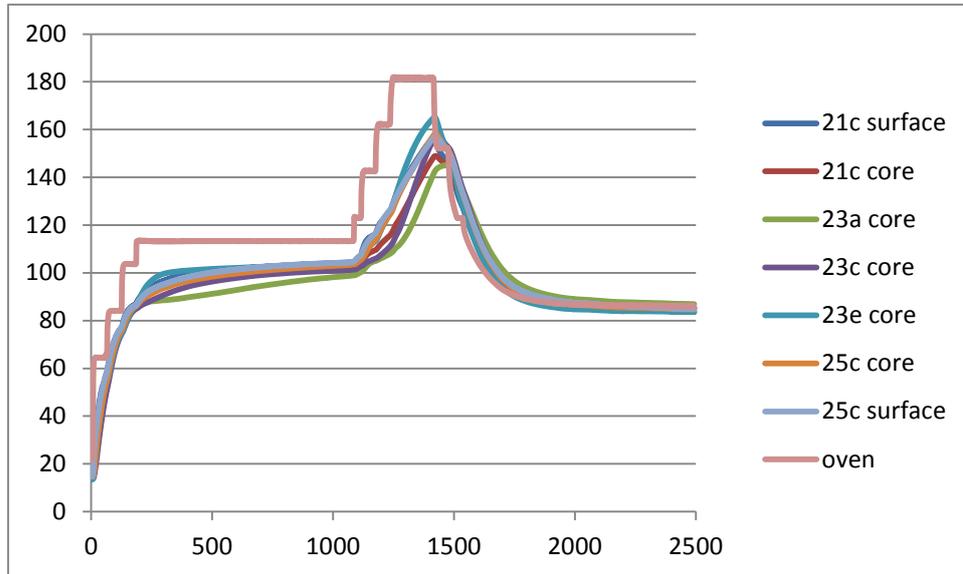


Figure A14. Thermocouple data for continuous schedule in Run H

Run I, May 2015

The same 180°C treatment phase as Run H, but using an altered drying profile with hold temperature at 120°C instead of 110°C. Large planks 31A-E to 36A-E

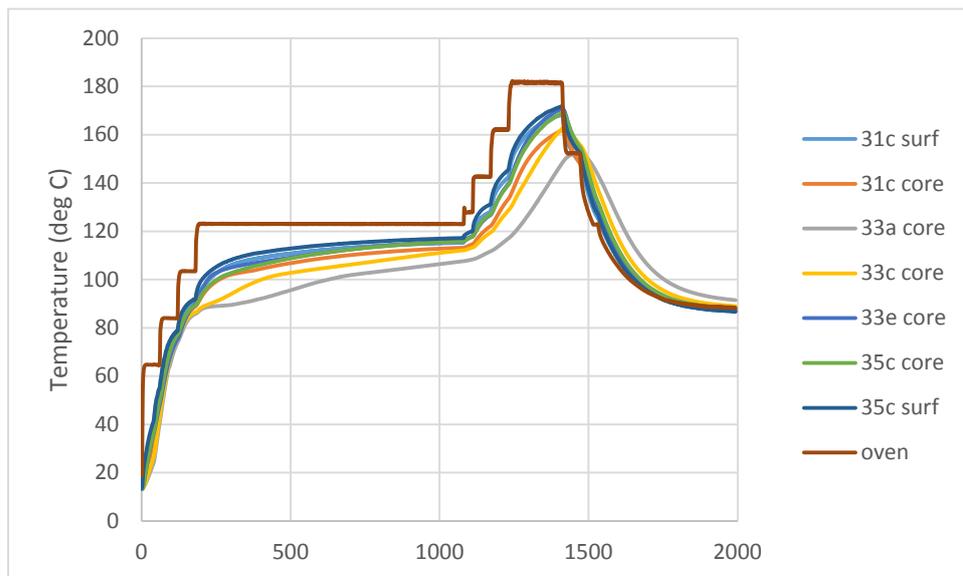


Figure A15. Thermocouple data for Run I

Run J, June 2015

The continuous process, altered to reduce the rate of temperature increase during the drying stage this shortened the drying period at 120°C. The steam was switched off 3 hours after the final step down in temperature, then the oven was switched off overnight, i.e. the conditioning step was a reduced duration. Large planks 41A-E to 46A-E.

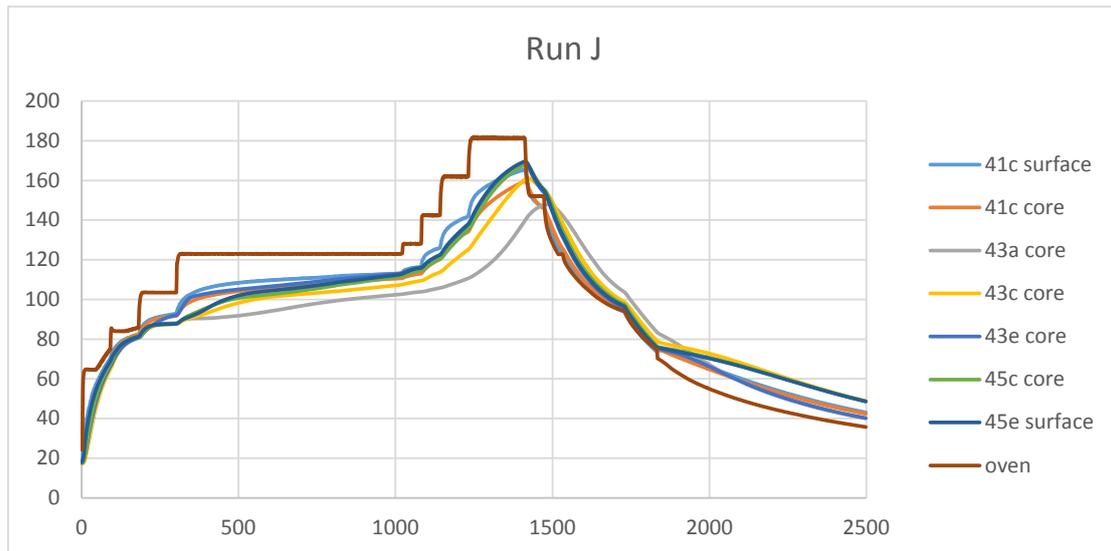


Figure A16. Thermocouple data for Run J.