MASTER'S THESIS

Impact of drying conditions, wood extractives and structure to uneven distribution of preservatives in Scots pine

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Abstract

An even distribution of preservatives is favoured as non-impregnated parts of wood will lead to a less durable material. Plenty of factors could be the reasons for the observed uneven distribution of preservatives, such as wood products dimension, moisture content, drying process, wood extractives and structure. In this study, the influence of drying conditions, extractives and wood structure to uneven distribution of preservatives was studied. 294 Scots pine (*Pinus Sylvestris*) boards were treatment with copper based preservatives. The boards were kiln dried under two different drying temperatures (dry temperature was 60 and 80 °C, respectively) to three different target MC (10-12, 18 and 24%). Before drying and impregnation, green and dried test samples (2×400 mm) from these boards were taken and stored in freezer at -24°C, respectively. The total failure ratio (boards which have failure/total boards) was 31%. The highest failure ratio occurred in group whose drying temperature was 80^{o}C and MC was 13.8%, and the minimum failure ratio occurred group whose drying temperature was 80^{o}C and MC was 20.2%. Quantitative analysis of extractives on matched impregnated and umimpregnated areas of dried and green samples were done by GC-FID. The microstructure of wood on the areas with impregnation failures was also studied by SEM. The results showed that fatty acids, resin acids and fats could play an important role in explaining uneven distribution of preservatives. The areas with impregnation failures contained more fatty acids, resin acids and fats than impregnated areas on dried samples. Those extractives could block resin canal (resin acids) as well as parenchyma cells (fats and fatty acids) which will hinder liquid penetration. Also, the drying process (drying temperature and MC) has an influence to presence of fatty acids, resin acids and fats, which could well explain the impregnation failure ratio of the whole batch. In addition, the influence of reconditioning to uneven distribution of preservatives was investigated with the help of CT-scanner. However, the results showed that the influence of reconditioning to impregnation results was not obvious.

Acknowledgement

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Content

1. Introduction

Wood product has its own merits compared with steel and concrete such as low cost, easy to manufacture, low weight and well established process, which have lead to a dominant place in the market. However, wood products expose to outdoor conditions could be easily degraded when left untreated (Ibach 1999). Applying treatment with preservatives could extend the life of wood products by 20 to 40 times than that of untreated wood (Morrell 2004). Accordingly, it is important to treat wood products in order to extend service life.

1.1 Impregnation

Impregnation and surface treatment are common ways to apply preservatives to wood. Impregnation under pressure is used for high absorption and deep penetration of wood preservatives into wood. Surface treatment aims primarily at giving the wood surface protection while the requirement of deeper penetration is not so high. When used in critical environments wood is usually impregnated with preservatives which are resistant to biodegradation and which inhibit decay. The common preservatives nowadays are copper-based salts, creosote oil, and pentachlorophenol. Following the North America action in forbidding CCA, similar actions were taken in EU, Australia and other parts of the world. While CCA wood is still widespread used in many countries due to the excellent antiseptic property. Pentachlorophenol was also not used in Europe, China and it was restricted to the treatment of utility poles and railroad ties in USA. Some copper based preservatives such as acid copper chromate (ACC), alkaline copper quat (ACQ) and CuHDO which could be used as alternatives to Chromated Copper Arsenate (CCA) as their primary biocide. (Lebow 2004).

Different impregnation methods have been developed in order to satisfy different requirement. One kind of impregnation method is diffusion impregnation which is commonly used to some extent in the industrial treatment as a precaution and the artisanal treatment to repair damage to such as utility poles and window (Jermer 1984). A prerequisite for diffusion impregnation is that the moisture content of wood is high. Another kind of method is impregnation with pressure and/or vacuum. One of popular impregnation method is full cell impregnation (Fig. 1.1) a process that was firstly developed by John Bethell in 1838 with oil as preservative. Nowadays, both oil and water solutions of preservatives salts are usually used in full-cell process. Full cell process starts with vacuum to remove air from the wood allowing

an easier penetration of preservative into the wood. The applied preservative solution starts to penetrate and is followed by a pressure increase (up to 15 bar) to ensure that full penetration of sapwood by the preservative occurs. After release of pressure and emptying the preservative solution from the impregnating vessel, a vacuum is applied to remove excess of preservative from the wood surface. It should be pointed out that one important merit of full-cell process is that it creates deep penetration and to a lesser extent the amount of liquid.

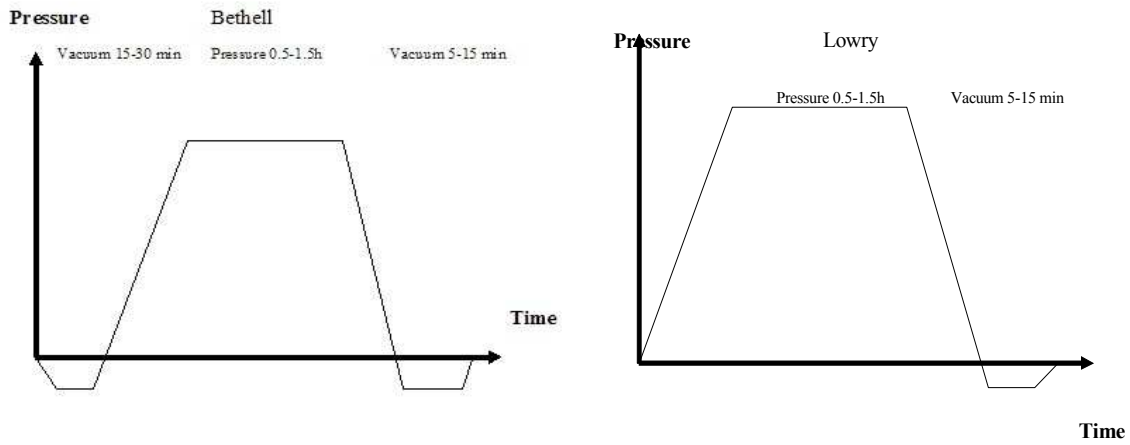


Figure 1.1 Bethell impregnation (left) and Lowry impregnation (right)

Another famous impregnation method is Lowry impregnation (Fig. 1.1), which requires no initial vacuum. However, the preservatives are forced deep into the wood with the help of high pressure. The air inside the wood expands when the pressure is released leading to any excess preservative to be forced out of the wood. The concentration of preservatives will be adjusted in accordance with the required preservative retention levels. In Nordic countries NTR control and certifies impregnated wood products where NTR-AB class contains lower amounts of preservatives than NTR-A and is used above ground while the latter one can be used in contact with soil. Furthermore, other impregnation processes like Rüping (empty cell) impregnation is usually used for creosote impregnation (Fig. 1.2). Before impregnation air is pushed into the cells under pressure (0.2-0.3 MPa). Then the intake of preservatives can be kept as low as 200 l/m^3 compared to 600 l/m^3 for the full cell process (Johansson and Lindgren 1990). OPM (Oscillating Pressure Method) is used for raw/green wood and low permeable species. “Pressure surges” are used so that the preservatives are more efficiently pumped into the wood materials (Fig. 1.2). Nowadays, OPM is popular in mid-Europe and USA. In Royal impregnation wood is pre-impregnated with a water-soluble preservative, after fixation hot oil is added and a vacuum is often created in the beginning in order to reduce the

boiling point of the water in the wood. Subsequently heated by oil, the water is given off which enabling the oil to penetrate deep inside the wood. The direct addition of pigment to the oil enables the wood to be dyed in various colour tones. The outstanding properties of royal impregnated wood are its effective protection, dimensional stability and lasting water-repellent finish.

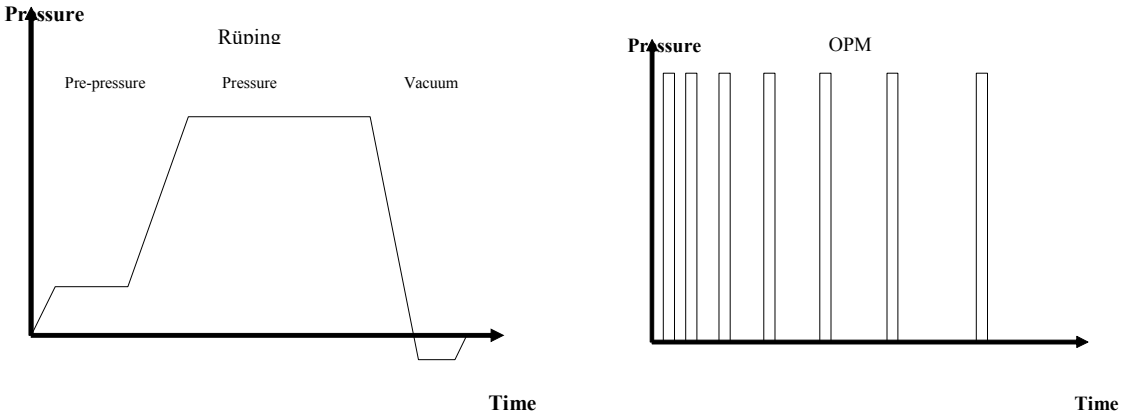


Figure 1.2 Rüping impregnation (left) and OPM impregnation (right)

1.2 Factors influencing impregnation

1.2.1 Fluids flow in softwood

It is well known that one of the most important properties of wood related to impregnation is how fluid flows in wood. There are two kinds of modes for the transport of fluids inside the wood: bulk flow through voids in the material like lumen in wood cells and diffusion into cell wall. The application of bulk flow is for example to treat wood with liquid preservatives under pressure for protection against biological decay, fire and moisture, that is, impregnation. However, diffusion of preservatives into cell wall also takes place during impregnation. Many investigations have been made for studying the flow in softwood. The bordered pit is generally regarded as the most important structure as far as permeability of softwood is concerned and the rays are also proved to be influential (Kevin 1995). The question is whether drying can influence permeability of wood. After air-drying, permeability to water was reduced with 1 to 3% (Erickson and Crawford 1959).

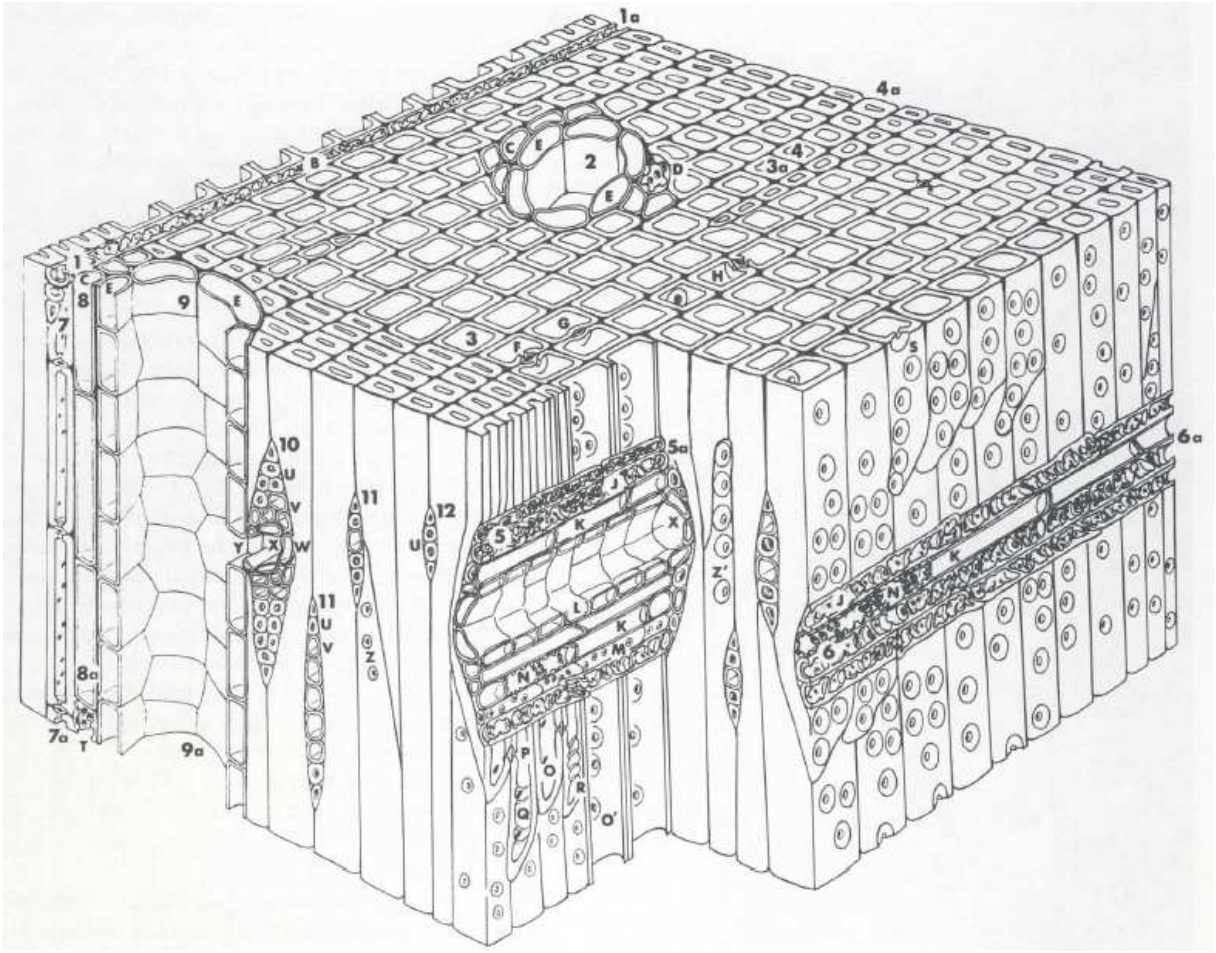


Figure 1.3

Gross structure of a typical southern pine softwood.
Transverse view.l-1a ray;B dentate ray tracheid;2 resin canal;C thin-walled longitudinal parenchyma;E epithelial cells;3-3a earlywood tracheids;F radial bordered pit pair cut through torus and pit apertures;G pit pair cut below pit apertures;H tangential pit pair; 4-4a latewood.
Radial view.5-5a sectioned fusiform ray; J dentate ray tracheid; K thin-walled parenchyma; L epithelial cells;M unsectioned ray tracheid;N thick-walled parenchyma;O latewood radial pit (inner aperture);O′ earlywood radial pit (inner aperture);P tangential bordered pit;O callitroid-like thickenings;R spiral thickening;S radial bordered pits (the middle lamella has been stripped away, removing crassulae and tori);6-6a sectioned uniseriate heterogeneous ray.
Tangential view.7-7a strand tracheids;8–8a longitudinal parenchyma (thin-walled);T thick-walled parenchyma;9-9a longitudinal resin canal;10 fusiform ray:U ray tracheids;V ray parenchyma;W horizontale pithelial cells;X horizontal resin canal;Y opening between horizontal and vertical resin canals;11 uniseriate heterogeneous rays; 12 uniseriate homogeneous ray:Z small tangential pits in latewood;Z′ larger tangential pits in earlywood. (Howard and Manwiller 1969).

Rays (Fig. 1.3 6-6a) are more important to act as flow path in softwood than hardwood and vertical (Fig. 1.3 2) and horizontal resin (Fig. 1.3 X) canals are generally penetrated (Siau 1995). Also, due to the aspiration of bordered pits and the blockage by extractives, flow in heartwood is lower compared with sapwood. Individual difference is also big among the softwood. For instance, Norway spruce is more difficult to be impregnated than Scots pine due to the smaller pits which connect longitudinal tracheids and the ray parenchyma cells.

Usually, more penetration takes place in latewood than earlywood in most of softwood species (Behr et al. 1969). Due to the smaller diameter of pit pair and thicker membranes in latewood, which would resist the forces causing aspiration, the latewood is more permeable than earlywood in dried softwood (Siau 1995). However, another study showed that latewood is more permeable than earlywood in kiln-dried timber while it is opposite in green one (Petty and Preston 1969). Furthermore, it is also more difficult to predict the flow for large timbers than clearwood. The radial flow path into the sapwood of long samples mainly depends on rays connecting to the longitudinal tracheids. However, the penetration could also start from radical direction and then continue in longitudinal direction. Also, aspiration of bordered pits has huge influence on radial flow since all the pitting is on the radial surfaces of the cells, and the blocking of longitudinal resin canal should be paid attention to as well. In addition, polar liquids can penetrate the cell wall while the penetration of non-polar liquids stops at lumens (Siau 1995). Thus, water-borne preservatives can penetrate cell wall and interact with cell wall components whereas oils seem not impregnate cell wall. It is reported that treatment of Scots pine and Norway spruce with ammonia-based solutions improved the ability to swell the wood leading to increase permeability and enhanced penetration (Rhatigan et al. 2004). Penetration was significantly higher in air dried logs compare to kiln-dried logs when using copper azole (CUAZ) alkaline solution in Japanese cedar logs (Ikuo et al. 2009). However, preservative penetration was found to not correlate with preservative absorption, density and moisture content (MC of 10% to 40%).

1.2.2 Wood extractives

The content of extractives can influence the utilization of wood products both positively and negatively. On one hand, the presence of extractives in the heartwood plays an important part in biological resistance. For instance, phenolics in Scots pine give effective biological resistance to heartwood but not for sapwood (Harju et al. 2003). On the other hand, some extractives in sapwood like triglycerides, long chain fatty acids, steryl esters and waxes could be degraded by fungi (Martínez-Iñigo et al. 1999). Hence, the distribution of extractives plays a significant role in wood utilization.

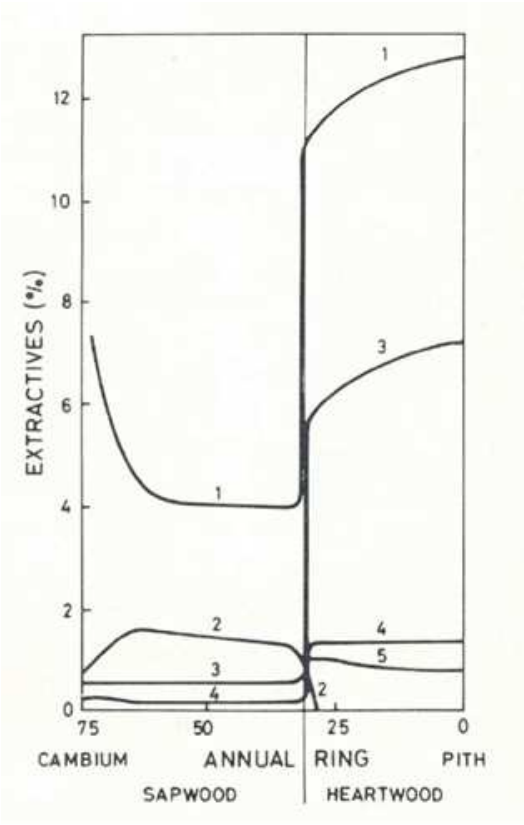


Fig 1.4 Differences in the amount and composition of extractives across the stem of a Scots pine (Pinus sylvestris) tree. 1. total extractives 2. triglycerides 3. resin acids 4. free fatty acids 5. pinosylvin plus mono methyl ether. (Sjöström 1992)

As can be seen in Fig. 1.4, the dominating extractive both in heartwood and sapwood of Scots pine is wood resin acids and the total amount of wood resin acids is higher in heartwood than sapwood. Also, the amount of fatty acids (also proportion of saturated fatty acid) is higher in heartwood while triglycerides are only found in sapwood and areas close to annual ring in heartwood.

Wood is commonly dried before impregnation in order to get rid of water and leave room for preservatives to penetrate the wood. However, extractives are affected during the drying process. Migration of extractives as well as removal of lower terpenes (alfa pinene) already occurs at lower temperature drying. Monoterpenes, waxes, fats will migrate to wood surface during the air and to a larger extent during artificial drying which may be a problem in end-products especially at high content of resin in wood. Around 100^{o}C wood starts to slowly degrade and reduce weight mostly related to degradation of saccharides (Karlsson et al. 2012) and evaporation of monoterpenes. Ethanol, methanol, acetic acid, formaldehyde and furfural have been found in vapours when drying of radiate pine at 100^{o}C (McDonald et al. 2002).

Decrease in phenolic compounds such as pinosylvin and its monomethyl ether in Jack pine has been observed at 160-200^{o}C (Poncsak et al. 2009). The total phenolics extractives was found to decrease continuously in saw dust from heartwood of Scots pine when heating in a closed chamber at a temperature that exceeded 70^{o}C (Sehlstedt-Persson and Karlsson 2010). One speculation was that migration of fats along axial parenchyma cells to the wood surface happen during the steam heat treatment of Scots pine (Nuopponen et al. 2003). Resin acids are still existing in the center of the wood with the heat treatments in the range of 100^{o}C to 180^{o}C, however, they lost more than 20% of their original weight in the whole wood after drying at 103^{o}C (Larnöy 2008) and disappeared when the temperature reaches above 200^{o}C (Hill 2006). Migration of extractives to the surface results in resin patches that need to be removed both for visual appearance (Hill 2006) and good impregnation.

Migration and redistribution of extractives could alter the properties of wood (Hse and Kuo 1988; Yeo at al. 2007). In consideration of relationship between extractives and permeability, one study showed that the lower penetrability of heartwood was due to blocking substances on the parenchymatous cell walls and within the actual cells in Scots pine (Olsson et al. 2001). Since redistribution of extractives during the drying, some penetration path may be blocked and others may be opened. One hypothesis is that some extractives like fats, fatty acids usually with long aliphatic tail may block the parenchyma cell. Resin, produced by epithelial cells which stay in resin canals, could also act as obstacles during the impregnation process (Ahmed et al. 2011).

1.2.3 Copper-based preservatives fixation

Copper-based preservatives enjoy popular support with their excellent properties such as fungicide, low mammalian toxicity, relatively easy to create water based formulations and so on. However, leaching of copper-based preservatives is dangerous to environment especially for aquatic animals. Therefore, before using of wood leaching of copper-containing preservatives must be avoided. A fixation mechanism for amine-copper preservatives has been reported: copper connects with wood via rapid ion exchange reaction followed by a slower complex formation reaction (Jin and Archer 1991). Adding carboxylic acids (octanoic, 2-ethylhexanoic, decanoic) could increase the fixation of copper significantly (Humar et al. 2005) while increased temperature during fixation increased copper leaching from Norway spruce using copper-ethanolamine-based wood preservatives, probably due to that ethanolamine did not evaporate from the wood (Humar and Zlindra 2007). However, when

using Cu-HDO-amine wood preservatives. the influence of temperature was not significant (Craciun et al. 2009). Studies at SP-Borås Sweden indicate that leaching from impregnated terrace is rather slow also for copper preservatives (Jermer 2011).

1.3 Previous study on uneven distribution of preservatives

Preservative penetration has been approved to be more critical in the performance of impregnated wood than preservative retention (Blew et al. 1970). An even distribution of preservatives should be favoured as non-impregnated parts of wood should lead to a less durable material (even if un-impregnated areas are found more deep in the sapwood due to cracking and penetration of water into those areas). However, impregnated lumber could pass testing even though certain percentage of wood may be not fully penetrated. This means that if less than 20% of the boards show sign of un-impregnated areas in sapwood the whole batch of impregnated wood is accepted (NTR Dokument nr 3 2011).

Plenty of factors could be the reasons of uneven distribution of preservatives, such as wood products dimension, moisture content, drying process, wood extractives and structure and so on. Studies on structural features of impregnated and un-impregnated areas in sapwood from Scots pine that had been pressure impregnated with copper based preservatives has been performed (Ahmed et al. 2011). Also, studies on the distribution of preservatives indicated a more even distribution when moisture content of board from Scots pine was 20-25% compared with other ranges between 7-20 and 25-70% (Sehlstedt-Persson et al. 2011). The numbers of axial resin canals per mm^2 in impregnated parts of wood from Scots pine were higher than those in unimpregnated parts. It was also indicated that extractive content was higher in un-impregnated than in impregnated areas (Sehlstedt-Persson et al. 2011). Furthermore, the percentages of axial resin canals filled with extractives were less in impregnated parts than those in unimpregnated parts (Ahmed et al. 2011). The ultrastructural difference in the texture and porosity of pit membranes between ray parenchyma cells and also between fibres and parenchyma cells may also be related to impregnability of wood materials (Adya et al.1999). Also, incrusting extractives can influence the permeability of such membranes. Thus, differences in the distribution of extractives in impregnated and non-impregnated parts of wood are of high interest.

1.4 Extraction and Chemical Analysis

A wide variety of solvents have been used for wood extractives isolation. Acetone enjoys popularity due to its high extraction power for phenolics, lignans and lipophilic wood resin and so on. Dichloromethane is specific for wood resin while it has recently been replaced by acetone due to its toxicity (Ekman and Holmbom 2000). In this study, pure acetone was used in order to isolate extractives without sugar. However, the wood contains some water especially green ones which can help wash out some sugars from wood. But as water content is low the solubility of sugars seems also to be low in case of green wood. Therefore they are not believed be the reason for uneven distribution of preservatives.

The analysis of extractives is mainly performed using gas chromatography (GC) analysis with internal standard. Gas chromatography can be used for separating and identifying compounds from a complex sample. The principle is that chemicals pass through a narrow tube which is a capillary glass column with help of a carrier gas stream at a certain flow rate. Typical carrier gases are nitrogen, helium, argon, hydrogen and air. The inner part of column is coated with stationary phases that plays an important part in separating different chemicals and make them leave the column at a different time. Some compounds are more strongly bonded to stationary phase than others which mean that they are eluted after those who bonds more loosely. Furthermore, the column is situated in an oven where the temperature could be controlled and thus differences in compounds boiling points could be used to increase the separation. When the chemicals get out of the end of the column, they are detected. The most common detector is FID (flame ionization detector) where the sample is burnt in a hydrogen/air gas flame resulting in formation of charged particles and changes in impedance is measured.

Direct analysis of fats of triglyceride type was not possible due to low volatility of fats as well as lack of temperature programmable injector for analysis with gas chromatography (Björklund-Jansson 2008). The method for analyzing fats in wood was successfully developed by means of transesterification (Fig. 1.5). In this study R´OH is methanol (R´ is CH_3) and when it reacts with triglycerides (R″OCOR), glycerol, $C_3H_5(OH)_3$ as well as the methyl ester, (CH_3OCOR), is formed. The formed methyl esters can be detected using gas chromatography – flame ionisation detector (GC-FID).

Figure 1.5 Transestification scheme

Another method was used for analyzing fatty acids and resin acids. It is based on trimethylsilylation of hydroxyl groups of alcohol, phenolic and carboxylic types in extractives. Figure 1.6 shows the reaction route for trimethylsilylation of carboxylic acids. Trimethylsilyl groups were transferred into fatty acids and resin acids to make them more volatile and amenable to analysis by gas chromatography or mass spectrometry.

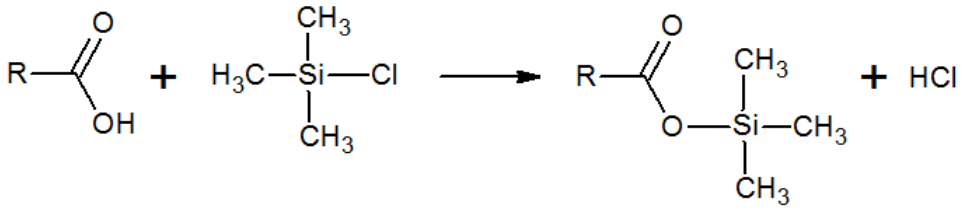


Figure 1.6 Trimethylsilylation scheme

A gas chromatograph could also be connected with a mass spectrometer as detector which is named GC-MS. Compared with other detectors such as FID, GC-MS could identify single compounds by finding molecule peak of the actual compound and characteristic fragments formed by ionisation in the detector. For example, it has been used to study pinosylvin in Scots pine heartwood (Bergström 2003). Different GC-MS temperature programme has been developed in order to have group determination of wood extractives such as fatty acid, resin acids and sterols (Fernandez et al. 2001 and Gutierrez et al. 1998).

1.5 Aim of the study

The aim of the study is to investigate how extractive distribution in wood after drying at various conditions influence the impregnation result after full cell impregnation of Scots pine boards. The influence of extractives in various parts of wood in terms of amount and types will be studied. Furthermore, the impact of drying process to extractives changes from green wood to dried wood will be studied. The potential relationship among drying, extractives and wood structure in explaining uneven distribution of preservatives are investigated. In addition, the influence of reconditioning to uneven distribution of preservatives will also be studied.

2. Methods and materials

2.1 Study on impact of extractives, structure and drying condition to uneven distribution of preservatives

2.1.1 Wood samples and drying

294 Scot pine (Pinus sylvestris) boards (30×125 mm in cross section and 4-5 m long) were divided into 6 groups (A, B, C, D, E and F), 49 boards for each group. Green test samples (400 mm in length) from top end of these boards were taken and stored in freezer at -24°C. Remaining boards from the 6 groups were industrial kiln-dried at two temperatures: 60°C (D, E and F) and 80°C (A, B, and C) (2 groups at each drying temperature). The drying schemes used are shown in figure 2.1 and figure 2.2. When the target MC was 22%, 2 groups (A and E) dried at the two temperatures (80 and 60°C) were taken out of kiln. Similar handlings were done for target MC of 18% (B and D) and 12% (C and F), respectively. Dried test samples (400 mm) from top end of these boards were taken and stored in freezer at -24°C. Moisture content of samples after drying was measured from each individual's top end.

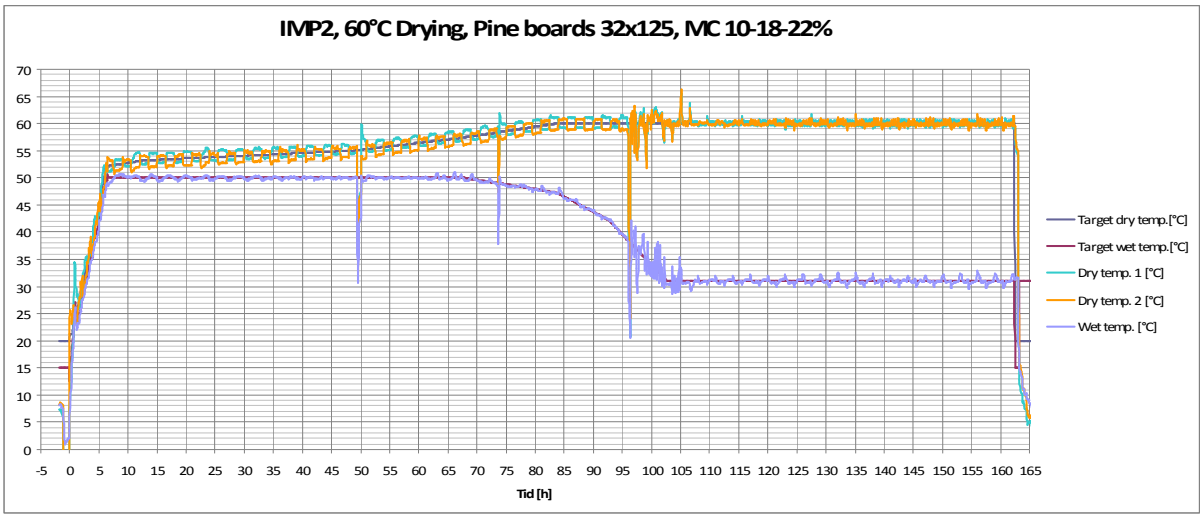


Figure 2.1 Drying scheme at 60°C

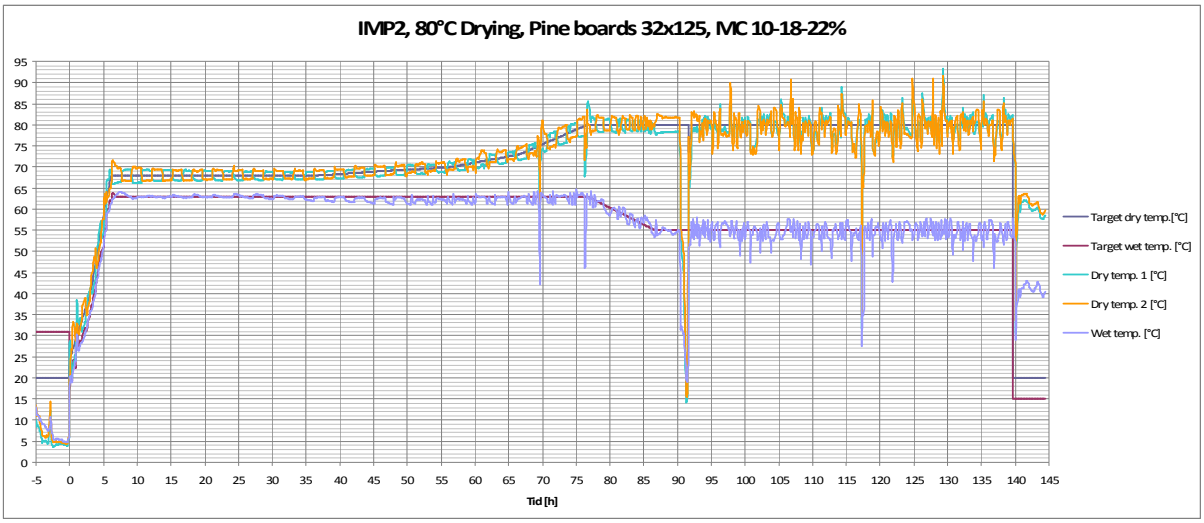


Figure 2.2 Drying scheme at 80°C

2.1.2 Impregnation

Before impregnation, the boards were planed to 28 x 120 mm^2. Impregnation was carried out for the impregnation class NTR-AB runs at 3.4% concentration Celcure AC800. The preservative was copper based preservatives. The impregnation process was performed as follows:

- 90% pre-vacuum for 20 minutes
- Approximately 40 minutes of pressure (1400 kPa)
- After-vacuum for 20 minutes
- Dripping of excess liquid

The liquid temperature was about 15°C during impregnation. After impregnation, the wood samples were placed in the dryer for three days for fixation and dry handling by drying at 40 °C.

2.1.3 Impregnation evaluation

Heartwood reagent (diazoniumsalt of sulfanilic acid) was prepared as described in NTR-AB (NWPC Document No. 3 2011). Two solutions, A and B, were prepared. In solution A 400g sodium nitrite ($NaNO_2$) was dissolved in 600 ml water and in solution B a saturated solution of sulphanilic acid ($C_6H_7NO_3S$) in water was prepared. Similar parts were mixed together and diluted 2.5 times with water.

The boards were cut every 50cm after impregnation (Fig. 2.3). One side of each cutting surface was evaluated with the help of application of heartwood reagent (Fig. 2.4). The number of both boards and surfaces which have failures for each group were counted.

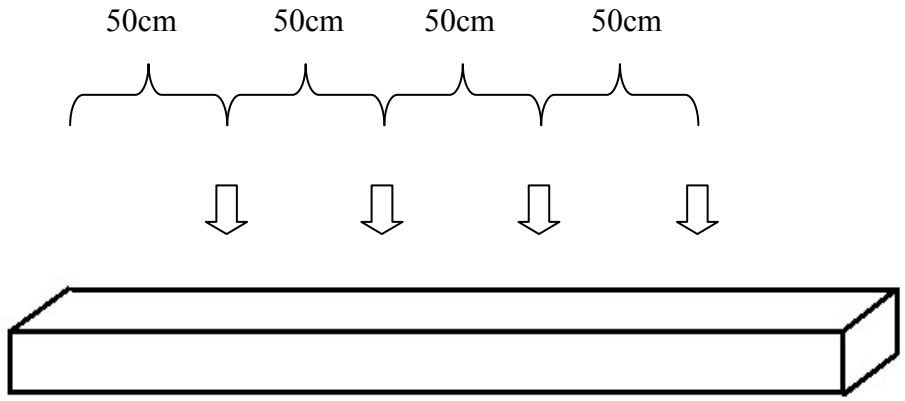


Figure 2.3 Cutting positions after impregnation

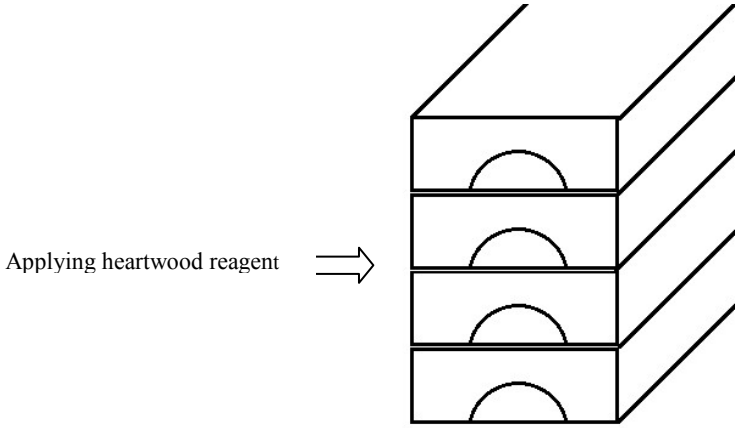


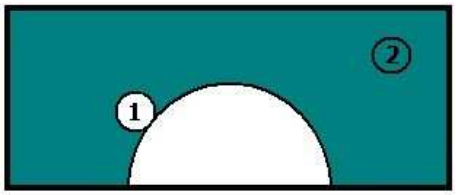
Figure 2.4 Evaluation surface for one board.

2.1.4 Chemical analyses

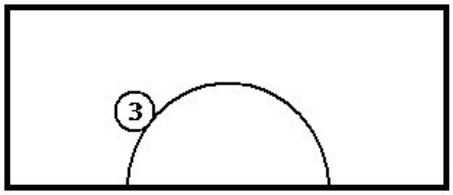
2.1.4.1 Extractives isolation

According to the result of impregnation, two areas for each sample were chosen which were impregnated (Fig. 2.3, position 2) and unimpregnated (Fig. 2.3, position 1). Sawdust (1.00 g dry weight) was made from the same areas on matched green samples (Fig. 2.3, position 3) and dried samples (Fig. 2.3, positions 4 and 5), respectively. Afterwards, the sawdust was extracted for 4 hours (6 cycles per hour) with pure acetone solution (40ml) using

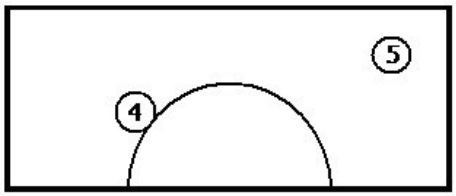
micro-Soxhlet extractor. The water bath temperature used for heating during extraction was 90^{o}C.



Impregnated sample



Green sample



Dried sample

Figure 2.3 Locations from which sawdust for extraction and GC-analysis was isolated (1 and 2 are reference points, 3, 4 and 5 were locations from which sawdust were made)

2.1.4.1 Analysis of extracts with Gas Chromatography - Flame Ionization Detector (GC-FID) and Gas Chromatography - Mass Spectrum (GC-MS)

1) Trimethylsilylation was used for determination of fatty acid and resin acids in wood. 5 ml of samples (equal to 0.125g dry wood) from extraction step were evaporated by a rotary evaporator. Trimethylsilylation of dried extract was performed by addition of 200µl naphthalene in pyridine (1.682 g/L). Then 200µl hexamethyldisliazane and 100µl chlorotrimethylsilan were added followed by waiting for 5 minutes. 1 µl was injected into the GC-FID and GC-MS (GC-MS was used only for the first time in order to determine the location of fatty acids and resin acids).

2) Transesterification was used for determination of fats in wood. 2 mol/L of sodium methanolate (CH_3ONa) solution was prepared by mixing 2 mmol Na (460mg) with 10ml anhydrous methanol. 5 ml of samples (equal to 0.125g dry wood) from extraction step were evaporated by a rotary evaporator. 1ml naphthalene in petroleum ether (1.01g/L) was added with an automatic pipette. Then another 0.9 ml petroleum ether and 100µl CH_3ONa were added (petroleum ether: CH_3ONa = 19:1) followed by waiting for 1 hour. 1 µl of upper lay was injected into the GC. For determination of the elution time in the chromatogram of fats in wood samples after transesterification, similar handling was done for glyceryl triheptadecanoate ($C_{54}H_{104}O_6$) in advance. Injection of known amounts of this fat at three different concentrations was used to make a calibration curve used to estimate the amount of fats in the extracts.

SHIMADZU GC-2014 was used. Injector temperature was 280°C, split mode. The column was produced by SUPELCO, SLB5MS 30m×0.25mm. The column inlet pressure was 100kPa, column flow was 1.00 ml/min, linear velocity was 27.4 cm/sec and total flow was 33.9 ml/min. Split ratio was 30.0. The program temperature was from 120^{o}C to 270^{o}C with 10°C/min. heating rate. Detector temperature was 300°C. The program time was 24 minutes for both trimethylsilylation and transesterification.

SHIMADZU GCMS-QP5050 was also used to study structure of analyzed extracts. The column is produced by SUPELCO, SLB5MS 30m×0.25µm, film is 0.25nm. The column inlet pressure is 88.9 kPa, column flow is 1.2 ml/min and linear velocity is 40.7cm/sec. The column is heated from 100°C to 270°C with 10 °C/min. heating rate. The program time is 18 minutes.

2.1.4.2 Determination of total extractives

20 ml of the extract was taken into a weighed beaker for evaporation (in air) in order to record the total amount of extractives.

2.1.5 Scanning electron microscopy (SEM)

The anatomy and histochemistry of one wood sample with typical impregnation failures were investigated. The failure area was separated into three 3×3×3mm (radial×tangential×

longitudinal) blocks followed by being finished with a microtome and sputter-coated with gold. Afterwards, radial, tangential, longitudinal sections were observed by SEM (JSM-5200, JEOL, Akishima, Japan) at 15 kV.

2.2 Study on impact of reconditioning to the impregnation

2.2.1Wood samples

Five Scots pine (Pinus sylvestris) planks (50×125×1500 mm^3) were used. 5 planks (groups 1 to 5) were dried in climate chamber (60^oC dry temperature, 91% RH) to moisture content of 17.6%. The rest were kiln-dried to moisture content of 7-8% and then reconditioned to 17.6%. Afterwards, all 10 planks were impregnated with the same procedure as mentioned above (see ***Impregnation*** section) without planning.

2.2.2 CT-scanning

The ten samples were scanned immediately after impregnation by a CT scanner, Siemens SOMATOM AR.T, at Luleå Technical University. The CT images have been obtained using the scan settings of 110 kV, 50 mA and scan width of 10 mm. Afterwards, the image were evaluated by ImageJ (National Institutes of Health, USA). The positions with impregnated failure were chosen according to the image. The wood samples were subsequently air dried for 2 weeks after CT-scanning followed by cutting cross sections from the positions which had been chosen based on the results from applying heartwood reagent on cross section area. The differences between the CT-scanning images and the images of samples after drying were investigated.

3. Results and discussion

3.1 Study on impact of extractives, structure and drying condition to uneven distribution of preservatives.

3.1.1 Statistics of failure impregnation

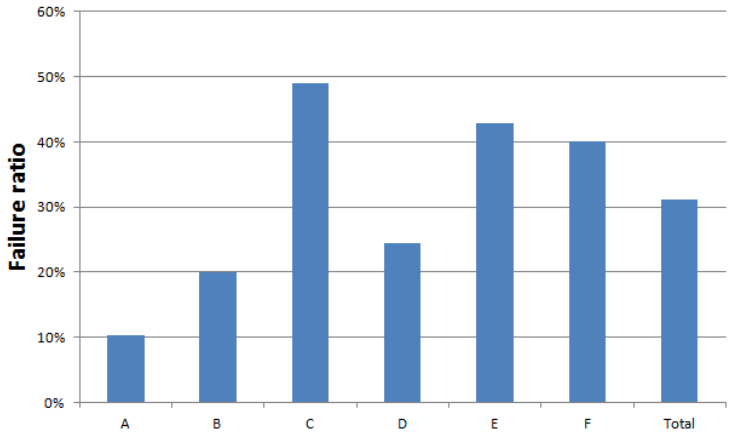


Figure 3.1 Failure ratios of boards at different drying temperatures and average MC: A (80°C, 20.2%), B (80°C, 13.8%), C (80°C, 8.4%), D (60°C, 22.8%), E (60°C, 16.3%), F (60°C, 8.7%).

The results obtained from impregnation evaluation is summarized at Fig. 3.1, the total failure ratio (boards which have failure/total boards) was 31%. The highest failure ratio occurred in C group (80°C, 13.8%) and the minimum failure ratio occurred in A group (80°C, 20.2%). Considering the influence of temperature, samples dried at 60°C appeared with more failures than those dried at 80°C except when average moisture content was around 8% (compared between A & D, B & E and C & F since they have similar average MC). Also, samples with low moisture content had more failures at 80°C (A<B<C) while samples whose average moisture content was 16.3% had more failures compared with other when drying temperature was 60°C (E>F>D). Probably due to the failure ratio was decided by drying temperature and average moisture content simultaneously, and further investigation are needed with large experimental samples. If the average moisture content was not very low (more than 13.8%), fewer failures happened at higher drying temperature (80°C).

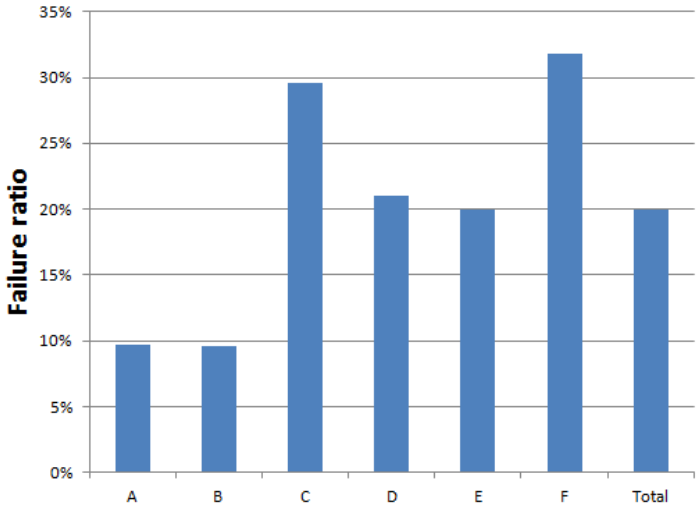


Figure 3.2 Failure ratios of cutting surfaces at different drying temperatures and average MC: A (80°C, 20.2%), B (80°C, 13.8%), C (80°C, 8.4%), D (60°C, 22.8%), E (60°C, 16.3%), F (60°C, 8.7%).

1527 cutting surfaces were evaluated and as can be seen in Fig. 3.2, the total failure ratio of cutting surfaces was 20%, which was lower than that of boards. It means that some failure occurred only on some parts rather than through the whole board. Unlike the results in Fig. 3.1, the maximum failure ratio occurred in group L (60°C, 16.3%). However, still both group A (80°C, 20.2%) and B (80°C, 13.8%) had a low failure ratio (around 10%). In addition, samples dried at 80°C had lower failure ratio than that dried at 60°C (compared between A & D, B & E and C & F since they have similar average MC) (Figure 3.2).

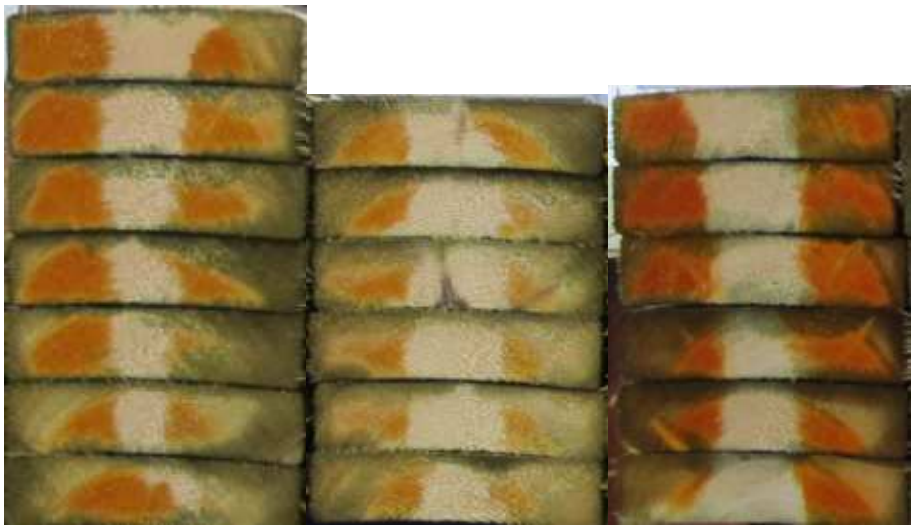
3.1.2 Photos of selected samples used for extractives analysis

In figures 3.3 to 3.8 selected samples from each group of treatments is presented after application of heartwood reagent. The impregnation failures occurred in most of cutting surfaces of the selected ones. Failures in the samples were organised as follows:

- Clear impregnation failure areas
- The type named “mickey mouse” was prioritized since it is speculated caused by extractives difference. Such failures were located on the left or/and right of the heartwood and just like two ears of the mouse. White arrowhead showed the typical “mickey mouse” type of impregnation failure.
- The samples with impregnation failures throughout the boards were prioritized since similar extractives distribution were wanted on green and dried test samples.

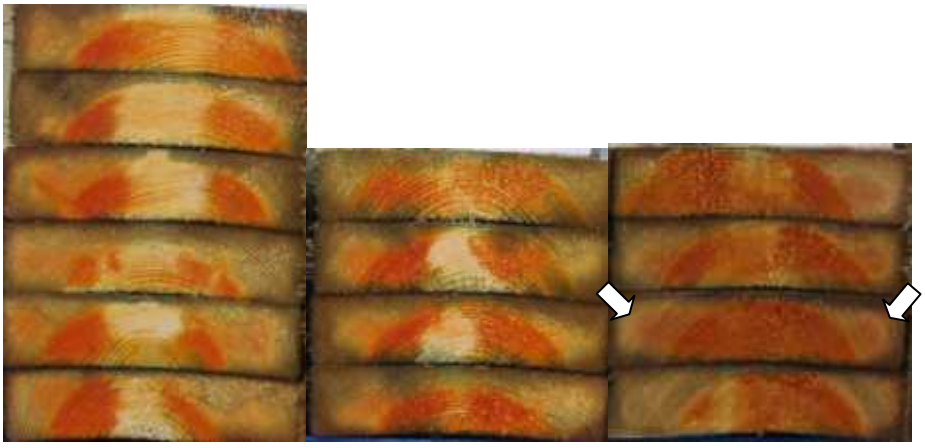
MC=19.4% **MC=20.5%** **MC=17.1%**

Figure 3.3 Cross-cut surfaces from selected boards from A group (drying temp. was 80^{o}C).



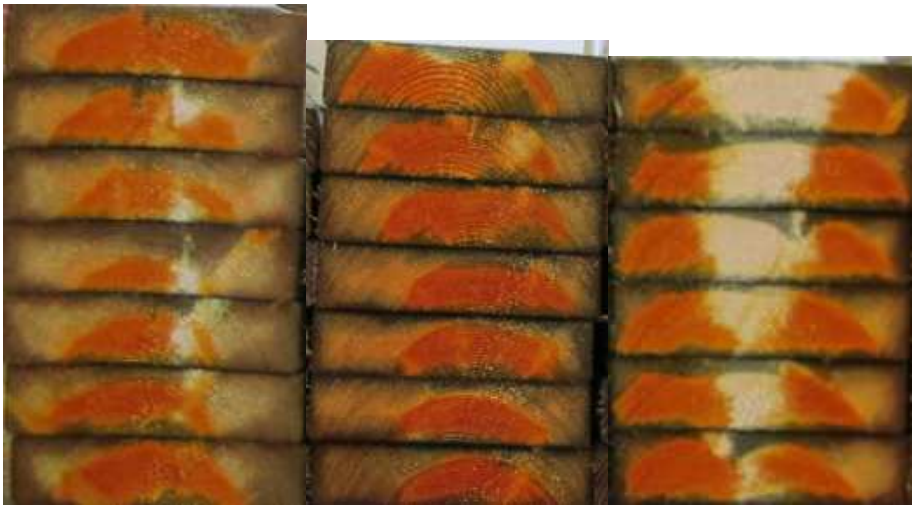
MC=12.9% **MC=13.2%** **MC=12.7%**

Figure 3.4 Cross-cut surfaces from selected boards from B group (drying temp. was 80^{o}C).



MC=12.9% **MC=13.2%** **MC=12.7%**

Figure 3.5 Cross-cut surfaces from selected boards from C group (drying temp. was 80^{o}C)



MC=17.6% **MC=14%** **MC=16.8%**

Figure 3.6 Cross-cut surfaces from selected boards from D group (drying temp. was 60^{o}C).

MC=24% **MC=22.9%** **MC=22%**

Figure 3.7 Cross-cut surfaces from selected boards from E group (drying temp. was 60^{o}C).

MC=9.2% **MC=9.2%** **MC=7.6%**

Figure 3.8 Cross-cut surfaces from selected boards from F group (drying temp. was 60^{o}C).

3.1.3 Scanning electronic microscope (SEM)

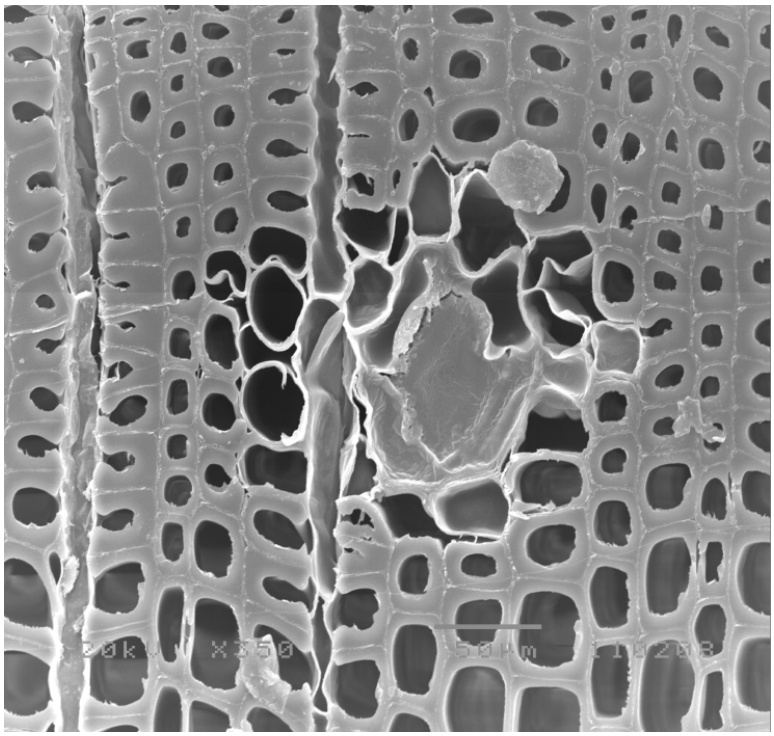


Figure 3.9 The SEM micrographs of areas with impregnation failures (cross-section). The resin canal was filled with resin.

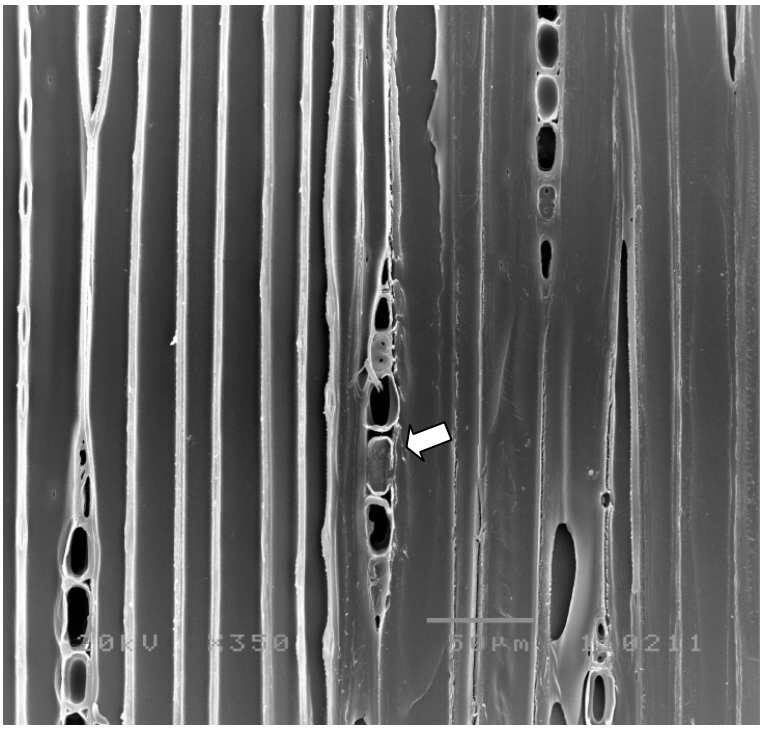


Figure 3.10 The SEM micrographs of areas with impregnation failures (tangential-section). The parenchyma cell was filled with resin (arrowhead).

As can be seen in Fig. 3.9 and Fig. 3.10, in the areas where impregnation failure happened, resin was found both in resin canal and parenchyma cell. The resin canal contains most of the free fatty and resin acids, together with some esters (Back 1960). Whilst the parenchyma resin is composed of fats, steryl esters and occasionally waxes. One hypothesis is that the resin could block the parenchyma cells and the resin canal and then hinder the liquid to penetrate, leading to impregnation failures. Therefore, the chemical analysis of fatty acids, resin acids and fats in these areas with control groups were investigated as follows.

3.1.4 Quantitative analysis of extracts with Gas Chromatography-Flame Ionization Detector (GC-FID).

3.1.4.1 Determination elution time of fatty acids and resin acids in wood samples after trimethylsilylation on chromatogram.

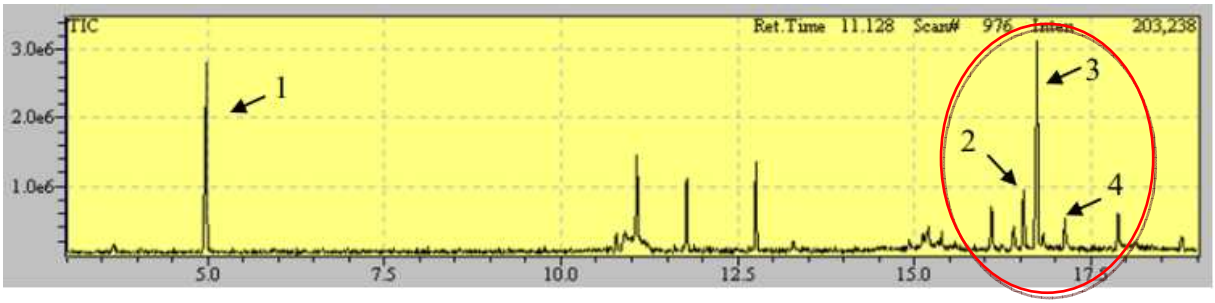


Figure 3.11 Chromatogram of green samples after trimethylsilylation from GC-MS. Peak 1 was naphthalene, peak 2 was fatty acids, peak 3 and 4 were resin acids.

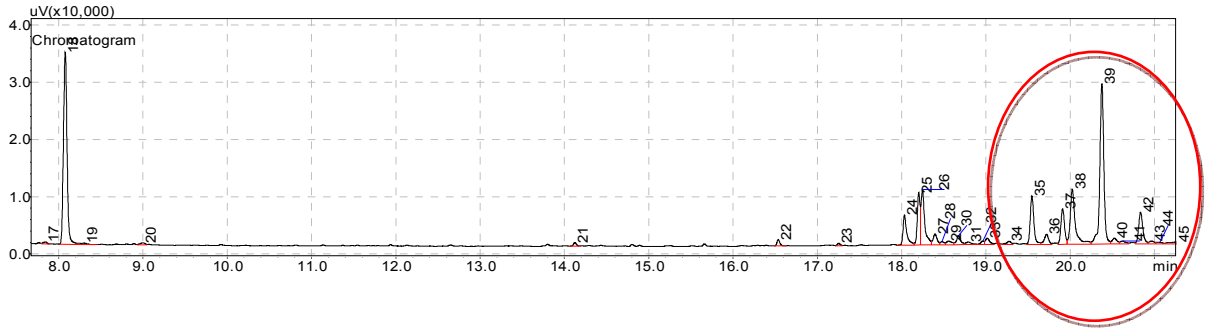


Figure 3.12 Chromatogram of green samples after trimethylsilylation from GC-FID. Peak 18 was naphthalene, peak 38 was fatty acids, peak 39 and 42 were resin acids.

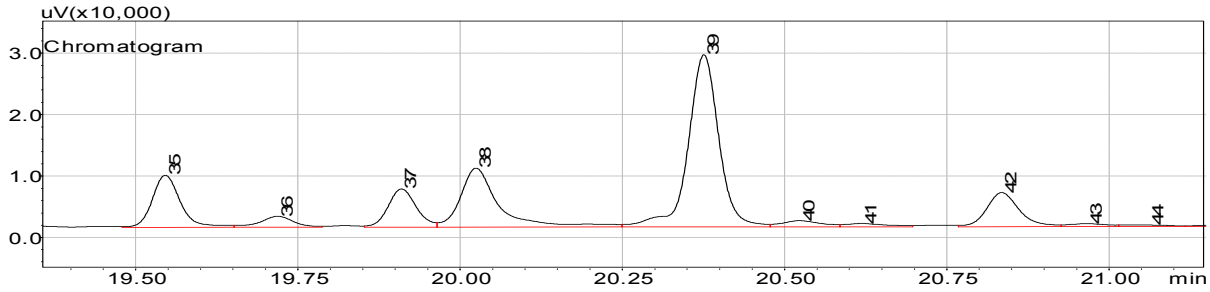


Figure 3.13 Magnifying chromatogram of samples after trimethylsilylation from GC-FID. Peak 38 (ret. time was 20.024 min) was fatty acids, peak 39 (ret. time was 20.375 min) and 42 (ret. time was 20.834 min) were resin acids.

Fig. 3.11 and Fig. 3.12 show the chromatogram of green samples after trimethylsilylation from GC-MS and GC-FID, respectively. As can be seen in Fig. 3.11, Peak 2 was proved as a fatty acid and peak 3 and 4 were resin acids with the help of GC-MS and comparison with NIST library software. Furthermore, the peaks were also found when analysing with GC-FID (inside the red circle in Fig. 3.12 and expansion view in Fig. 3.13). Therefore, peak 38 was regards as fatty acids and peak 39 and 42 were regarded as resin acids (Fig. 3.12 and Fig. 3.13).

3.1.4.2. Determination the elution time in chromatogram of fats in wood samples after transestrification.

The peak of methyl ester of fatty acid in the glyceryl triheptadecanoate ($C_{54}H_{104}O_6$) after transestrification could be detected by GC-FID (peak at about 16.5 min in Fig. 3.14). For wood samples, three peaks occurred (Fig. 3.15 and Fig. 3.16) and all of them increased greatly with treatment time during transesterification until one hour. Analysis with GC-MS and comparison with NIST software were used for structure elucidation of methyl ester of resulting fatty acids. Therefore, these three peaks were regarded as fats in wood samples.

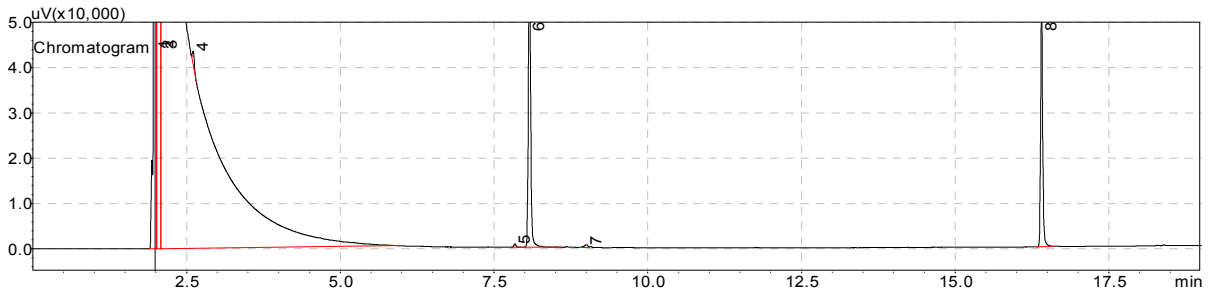


Figure 3.14 Chromatogram of pure fats after transesterification from GC-FID. Peak 6 was naphthalene, peak 8 was pure fats.

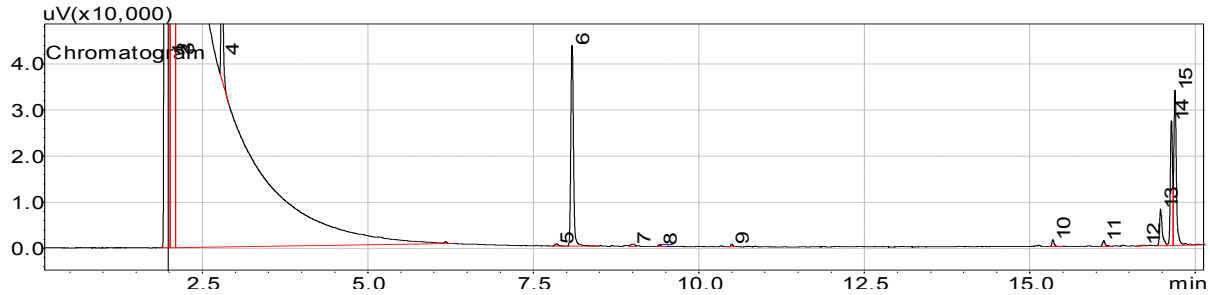


Figure 3.15 Chromatogram of samples after transesterification from GC-FID. Peak 6 was naphthalene, peak 13, 14 and 15 were fats.

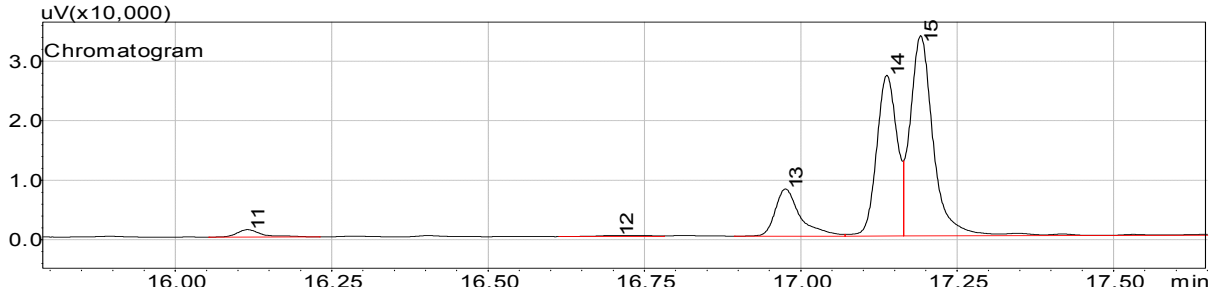


Figure 3.16 Magnifying chromatogram of samples after transesterification from GC-FID. Peak 13 (ret. time was 16.976 min), 14 (ret. time was 17.138 min) and 15 (ret. time was 17.192 min) were fats.

3.1.4.3 Overview of results from GC-FID

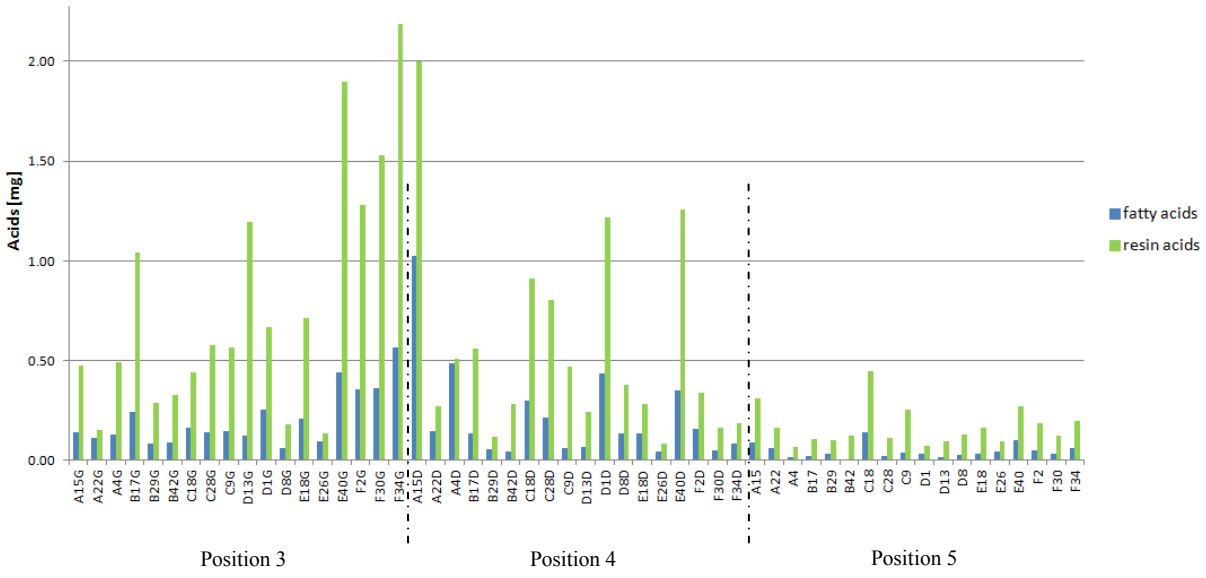


Figure 3.17 Quantitative analysis of fatty acid and resin acid for each sample (extracted from 0.125g dry wood). Position 3: from green samples areas with failures; Position 4: from dried samples areas with failure; Position 5: from dried samples areas without failure, details see material and method.

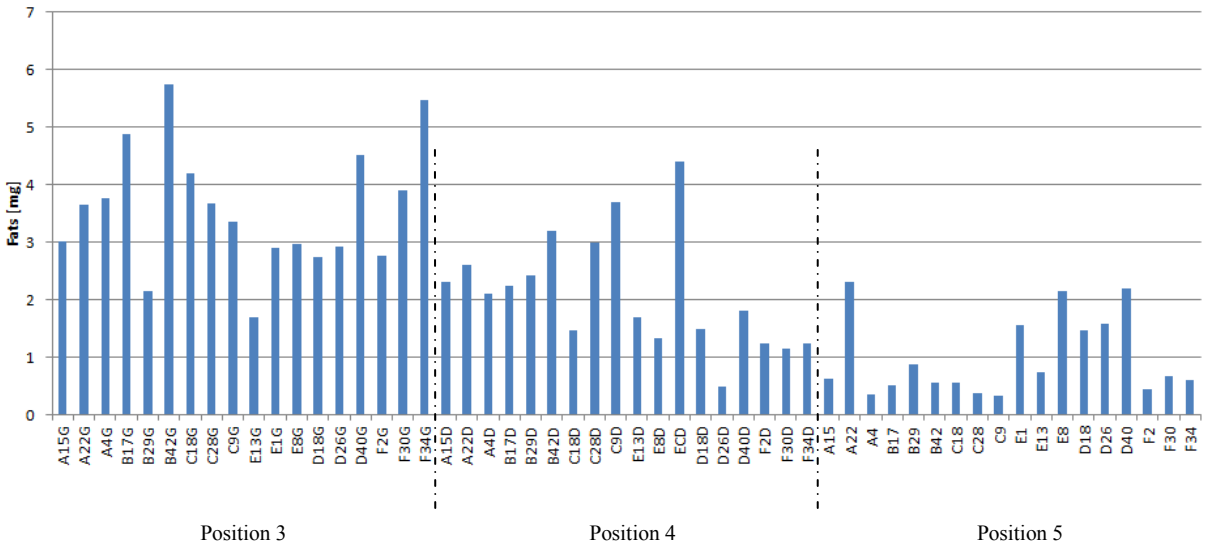


Figure 3.18 Quantitative analysis of fats for each sample (extracted from 0.125g dry wood). Position 3: from green samples areas with failures; Position 4: from dried samples areas with failure; Position 5: from dried samples areas without failure, details see material and method.

	Position 3		Position 4		Position 5		t-test(3-4)		t-test(4-5)	
Extractives	Mean(mg)	SD(mg)	Mean(mg)	SD(mg)	Mean(mg)	SD(mg)	t-value(df)	sig.	t-value(df)	sig.
Fatty acids	0,21	0,14	0,22	0,24	0,05	0,03	-0.198(17)	0.852	3.169(17)	0.006
Resin acids	0,79	0,61	0,56	0,51	0,16	0,99	1.216(17)	0.241	3.592(17)	0.002
Fats	3,58	1,08	2,11	1.00	1.00	0,69	4.385(17)	0.000	4(17)	0.001

Table 3.1 Mean and standard deviation (SD) of the quantitative analysis of extractives in different position (extracted from 0.125g dry wood). Significant at the 0.05 level (two-tailed), df: degree of freedom; sig.: significant

With the help of GC-FID, the result of quantitative analysis of fatty acids, resin acids and fats were showed in Fig. 3.17, Fig. 3.18 and Table 3.1. Data indicated that the amount of fats was much larger than resin acids in green wood and that fatty acids were fairly low as could be expected from literature data (Sjöström 1992). As a whole, it was found that the fatty acids were similar while fats and maybe also resin acids were lower in dried sample areas that gave impregnation failures (position 4) than in corresponding green samples areas (position 3). This suggests that drying process has an influence on presence fats was significant in various parts in wood (Table 3.1). Furthermore, dried sample areas with subsequent impregnation failure (position 4) contained more fatty acids, resin acids and fats than areas without failure (position 5) especially for fatty acids (Table 3.1). These results suggest that distribution of extractives within the position in sapwood of Scots pine boards could differ to a high extent and the distribution of these extractives could be the reason of impregnation failure. More details regarding those results will be discussed below (see 2.1.4.4 - 2.1.4.5). Also, it should

be pointed out that the individual difference existed and some samples such as C18D, C28D, D1D and E40D that had more fatty acids and resin acids than others in dried samples (Fig. 3.17, position 4); A similar phenomena (individual difference) applies to fats. It is difficult to substantiate that the impregnation failure occurred when fatty acids, resin acid and fats accumulate up to a certain amount by our results as impregnation failure still exist even the amount of extractives were low for individual samples (Fig. 3.17 and Fig. 3.18 position 3). Additionally, the amounts of resin acids appeared to be higher than fatty acids in each sample.

3.1.4.4 Comparison of changes of extractives between green samples (position 3) and dried samples (position 4)

Figure 3.19 Fatty acids and resin acids changes between green and dried samples (the amount of acids in position 4 minus those in position 3), extracted from 0.125g dry wood.

Fig. 3.19 shows the influence of drying to the amount of fatty acids and resin acids. Both fatty acids and resin acids decreased in group B, E and F while they increased in group A. In other groups, fatty acids and resin acids increased in some samples while decreased in others (Fig. 3.19). No trends or indications was found about how drying effected the change of both fatty acids and resin acids in this figure. However, one observation is that fatty acids and resin acids increased/decreased at the same time but to various extents (Figs. 3.19).

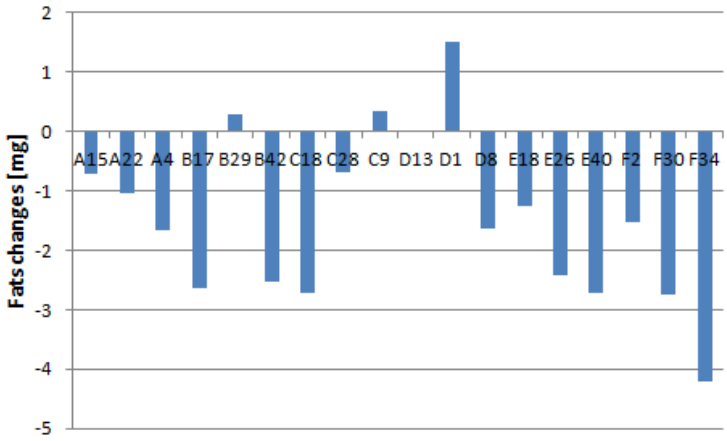


Figure 3.20 Fats changes between green and dried samples (the amount of fats in position 4 minus those in position 3), extracted from 0.125g dry wood.

Unlike fatty acids and resin acids, the amount of fats, in most of the samples, decreased from green wood to dried wood (Fig. 3.20). One reason could be that some fats degraded into other compounds during the drying process but probably not degrade into fatty acids since decrease of fatty acids for F2, F30 and F34 were also found. Therefore, the total amount of fats decreased. Some samples showed different behaviour such as B29, C9 and D1, in which the fats increased from green to dried wood. Since the green samples and dried samples were taken from different parts of one board, some potential factors could also influence the amount of fats like presence of knots, compression wood, resin pockets and so on.

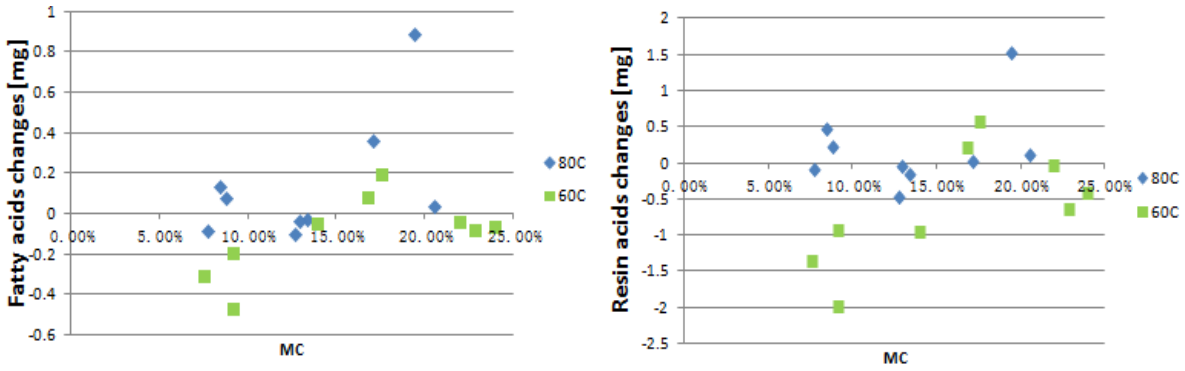


Figure 3.21 Fatty acids (left) and resin acids (right) changes (the amount of fatty acids and resin acids in position 4 – those in position 3) VS moisture content in extracts from 0.125g dry wood.

	fatty acids (mg)		resin acids (mg)	
MC	Mean	SD	Mean	SD
around 8%	-0.146	0.234	-0.618	0.974
around 14%	-0.058	0.033	-0.411	0.405
around 17%	0.374	0.359	-0.575	0.668
around 22%	-0.045	0.055	-0.252	0.346

Table 3.2 Mean and standard deviation (SD) of acids changes with different moisture content (MC) in extracts from 0.125g dry wood.

As can be seen in Fig. 3.21, the changes of fatty acids along with MC were different (left). They were rather small when the MC was around 14% and 22% while the points started to spread when the MC was around 8% and 18%. Also, Table 3.2 showed that the mean value of the fatty acid changes increased from around 8% to 17% and then decreased (around 22%) while resin acids changes increased (from around 8% to 14%) and then decreased (from around 14% to 17%) and increased (from 17% to 22%) again. Samples which had MC around 14% and 22% gave smaller standard deviation for fatty acids and resin acids compared with other MC, which means the changes at those conditions were stable. Additionally, samples dried at 60^{o}C had less fatty acids and resin acids than those dried at 80^{o}C when MC was around 8%. The same trend happened in the changes of resin acids (right). However, it was less significant than for fatty acids since the standard deviation (SD) of resin acids were more than fatty acids in each MC (Table 3.2). One interesting thing is that the direction of points spread was different (Fig. 3.21). For instance, when MC was around 8% the changes were below zero while they spread upward when MC was around 18% (figure 3.21). This is probably due to the large individual variation of wood tissue and a larger sample experiment set-up seems to be needed to find relations between the changes in extractives and MC.

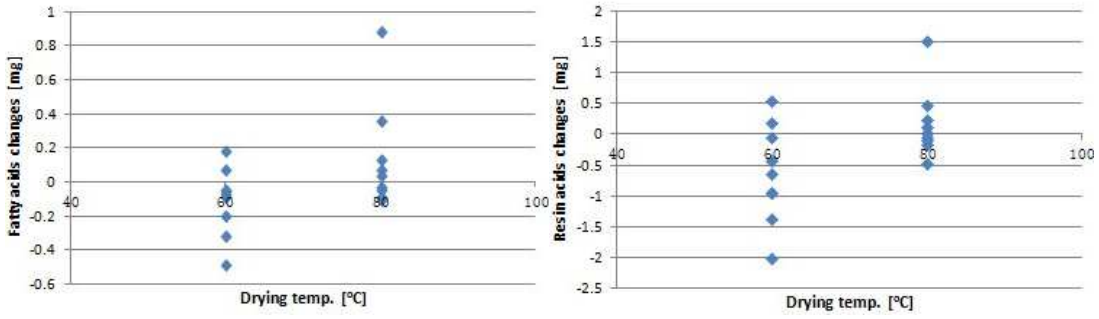


Figure 3.22 Fatty acids (left) and resin acids (right) changes (the amount of fatty acids and resin acids in position 4 – those in position 3) VS drying temperature in extracts from 0.125g dry wood.

	fatty acids		resin acids	
Temp. [°C]	Mean	SD	Mean	SD
80	0.042	0.151	0.006	0.281
60	-0.112	0.199	-0.625	0.797

Table 3.3 Mean and Standard deviation (SD) of acids changes with different drying temperature (exclude one outlier) in extracts from 0.125g dry wood.

As considering the relationship between the changes of extractives and drying temperature, the mean values of acids changes were increased from negative to positive when drying temperature increased from 60°C to 80°C (Table 3.3). This indicated that increasing drying temperature could increase the amount of fatty acids and resin acids in dried samples. Also, Content of resin acids and fatty acids for samples dried at 80°C were more stable (standard deviation was lower than samples dried at 60°C expect one outlier) than at 60°C (Fig. 3.22 and Table 3.3).

Figure 3.23 Fats changes (the amount of fats in position 4 – those in position 3) VS moisture content as well as drying temperature in extracts from 0.125g dry wood.

MC	Mean	SD	Temp. [°C]	Mean	SD
around 8%	-1.922	1.634	80	-1.264	1.197
around 14%	-1.224	1.585	60	-1.665	1.672
around 18%	-0.626	1.488			
around 22%	-1.858	0.837			

Table 3.4 Mean and standard deviation of fats changes with different drying conditions in extracts from 0.125g dry wood.

As can be seen in Fig. 3.23, compared to fatty acids and resin acids, large variation in data could be seen for changes of fats due to both MC and drying temperature. Samples with MC were around 18% had the lowest changes of fats but the standard deviations were high (Table 3.4). On the other hand, samples dried at 80°C had high mean value and low standard deviation. Compared with fatty acids and resin acids, the standard deviation of changes fats with different drying condition was high and the correlation was therefore less significant.

3.1.4.5 Comparison between dried samples with impregnation failure (position 4) and without impregnation failure (position 5)

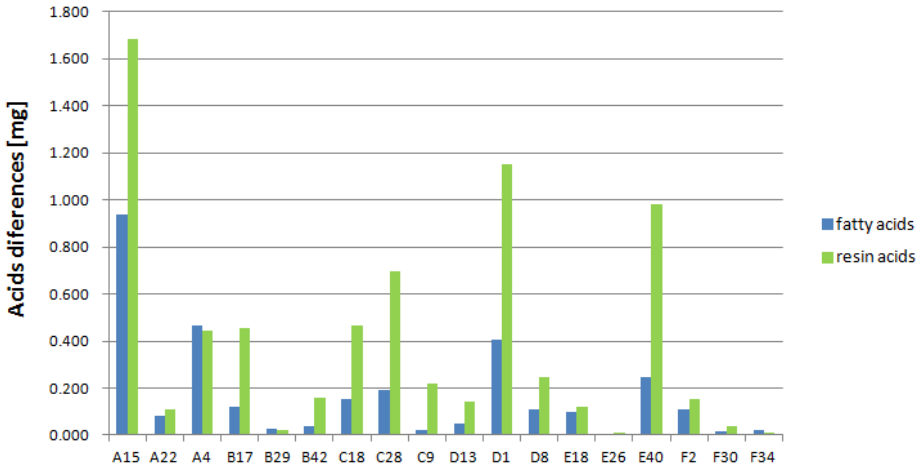


Figure 3.24 Fatty acids and resin acids difference between areas with and without impregnation failures on dried samples (the value is the amount of fatty acids and resin acids in position 4 minus those in position 5, extracted from 0.125g dry wood).

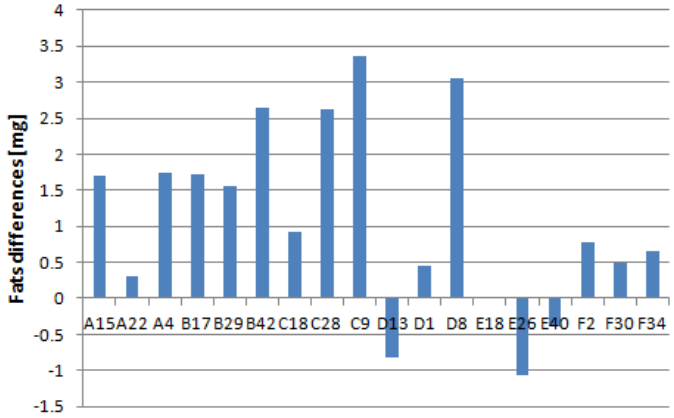


Figure 3.25 Fats difference between areas with and without impregnation failures on dried samples (the value is the amount of fats in position 4 minus that in position 5, extracted from 0.125g dry wood).

As showed in Fig. 3.24, the areas with impregnation failure (position 4) contained more fatty acids and resin acids than those without impregnation failure (position 5) based on dried samples. Likewise, by comparing the amount of fats differences in dried samples, the areas which were impregnated contained more fats than unimpregnated areas in most cases. (Fig. 3.25) Therefore, fatty acids, resin acids and fats difference could be one reason of uneven distribution of preservatives, although it is uncertain how big the difference should be. One hypothesis is that the higher amount of fatty acids and resin acids could block the resin canal to a higher extent and fats could block parenchymous cells which then could hinder the impregnating liquid to penetrate into those areas. Also, the difference was probably caused by drying rather than impregnation process since the difference existed before the impregnation, which indicated drying process plays a significant role in dealing with uneven distribution problems.

3.1.5 Quantification of total extracts in wood by evaporation of solvent

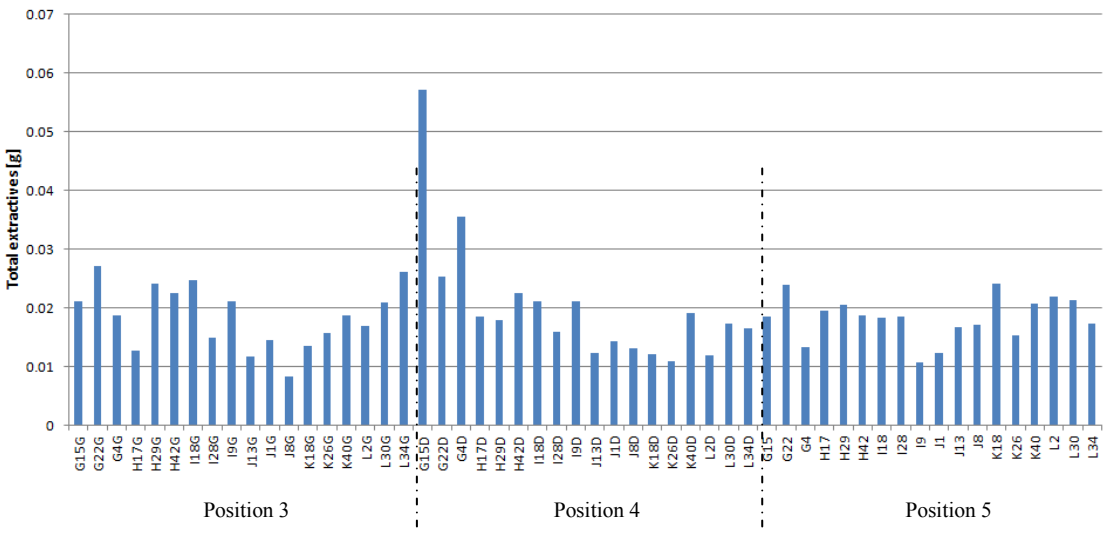


Figure 3.26 Total extractives in 0.5g dry wood. Position 3: from green samples areas with failures; Position 4: from dried samples areas with failure; Position 5: from dried samples areas without failure, details see material and method.

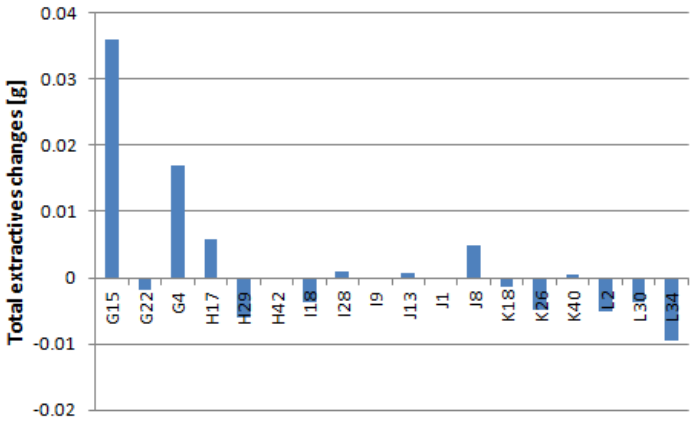


Figure 3.27 Total extractives changes (in 0.5g dry wood) from green to dried samples (the amount of fats in position 4 minus those in position 3)

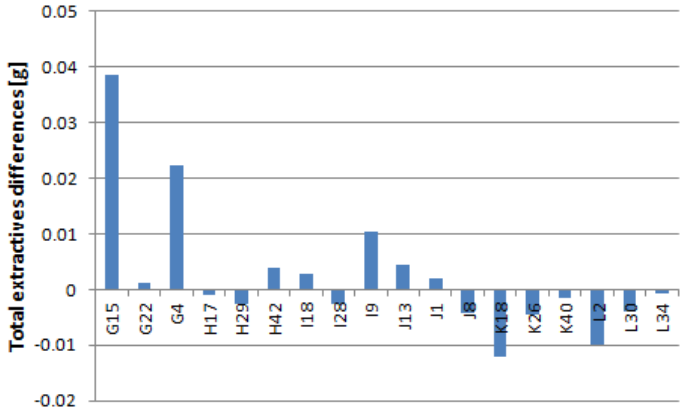


Figure 3.28 Total extractives differences (in 0.5g dry wood) between areas with and without impregnation failures on dried samples (the amount of total extractives in position 4 minus those in position 5).

Fig. 3.26 showed the amount of total extractives in each samples. The total content in green sapwood sample was ca 4% which could be expected from the literature (Sehlstedt-Persson 2001). As a whole, the differences of total extractives in different position (3, 4 and 5) were not big. The details were shown in Fig. 3.27 and Fig. 3.28. Both the changes of total extractives from green to dried samples and the differences between areas with and without impregnation failures have no significant correlation, which means:

1. The relationship between drying and total extractives was not obvious. Several factors could be the reason for the difference between evaporated extractives and those determined by gas chromatography. This could be different composition of other extractives than those determined by analysis with gas chromatography (many peaks were found in GC chromatogram while they were not fats acids or resin acids) but also

differences in composition of the fats, fatty acids and resin acids within the tree that sometimes makes evaluation of results from GC difficult.

2. Degradation/migration of different extractives, different drying conditions (temperature, MC…).
3. The amount of total extractives could not be the reason to explain the impregnation failures. A reason for this might be that extractives have different volatility. Especially if monoterpenes are evaporated which means that during drying a higher content of extractives such as fats may be enriched in areas that later becomes unimpregnated.
4. Fatty acids, resin acids and fats are more important compared to other extractives which could block the penetration path in wood.

3.2 Study on impact of reconditioning to the impregnation

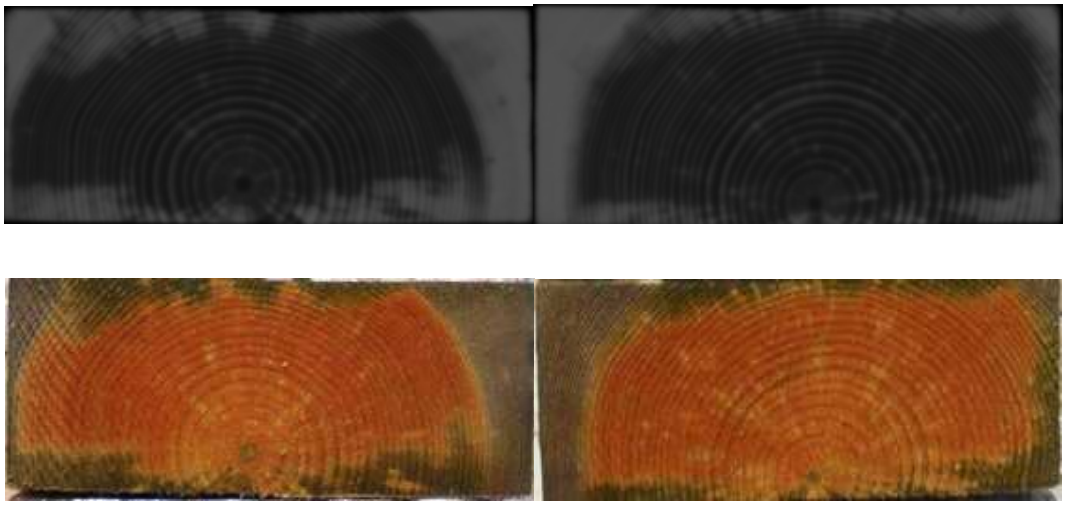


Figure 3.29 CT-scanning image (upper) and photos taken on matched position (down) of group 1. To the left were the reconditioning samples (final MC was 17.6%) and to the right were samples dried directly to 17.6% MC after application of heartwood reagent.

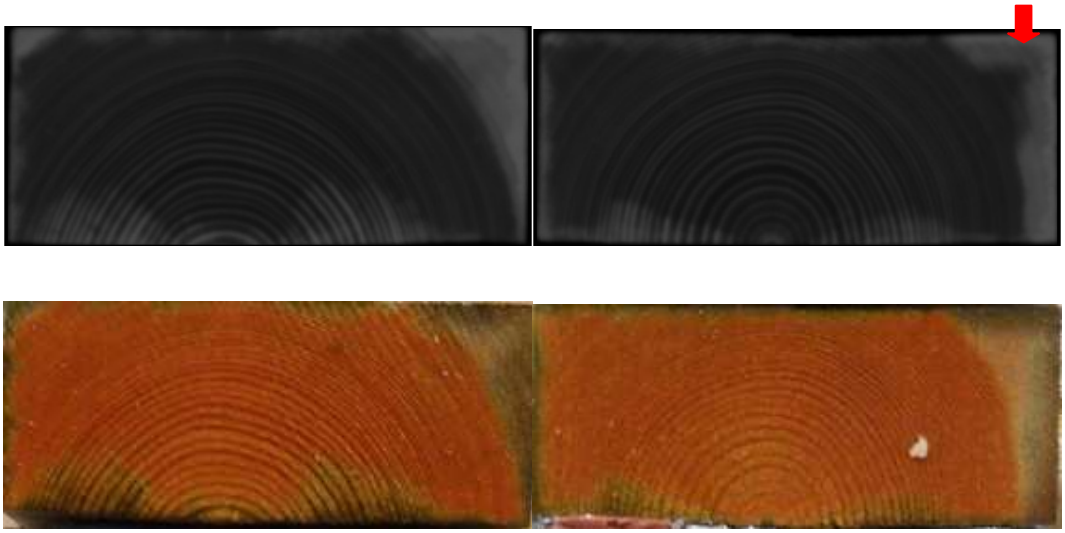


Figure 3.30 CT-scanning image (upper) and photos taken on matched position (down) of group 2. To the left were the reconditioning samples (final MC was 17.6%) and to the right were samples dried directly to 17.6% MC after application of heartwood reagent.

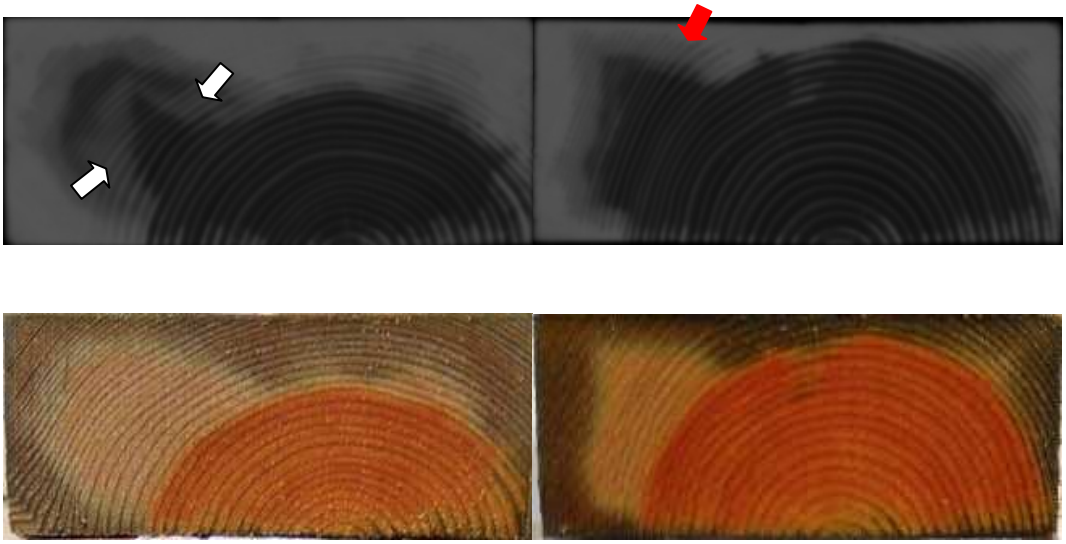


Figure 3.31 CT-scanning image (upper) and photos taken on matched position (down) of group 3. To the left were the reconditioning samples (final MC was 17.6%) and to the right were samples dried directly to 17.6% MC after application of heartwood reagent.

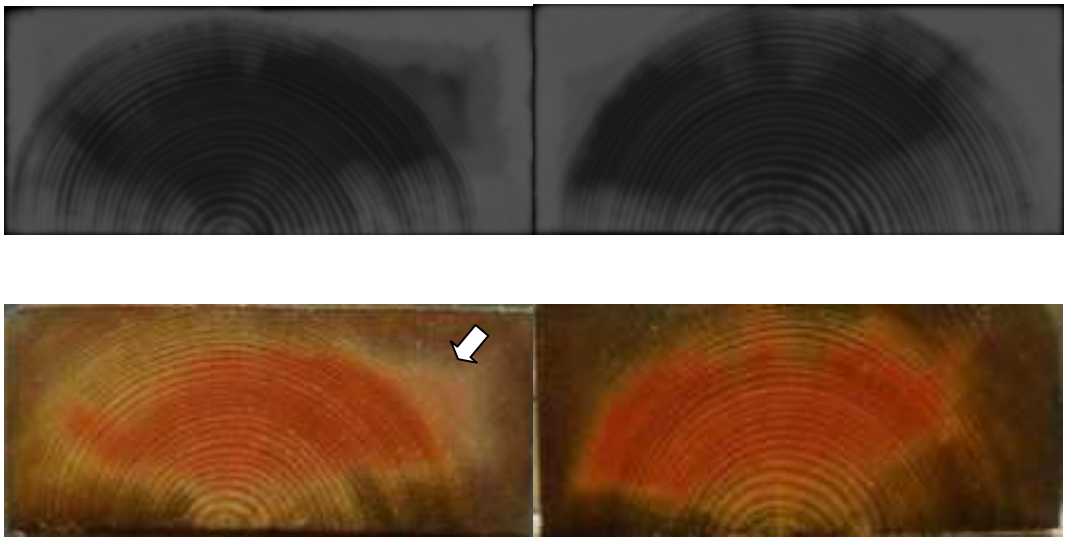


Figure 3.32 CT-scanning image (upper) and photos taken on matched position (down) of group 4. To the left were the reconditioning samples (final MC was 17.6%) and to the right were samples dried directly to 17.6% MC after application of heartwood reagent.

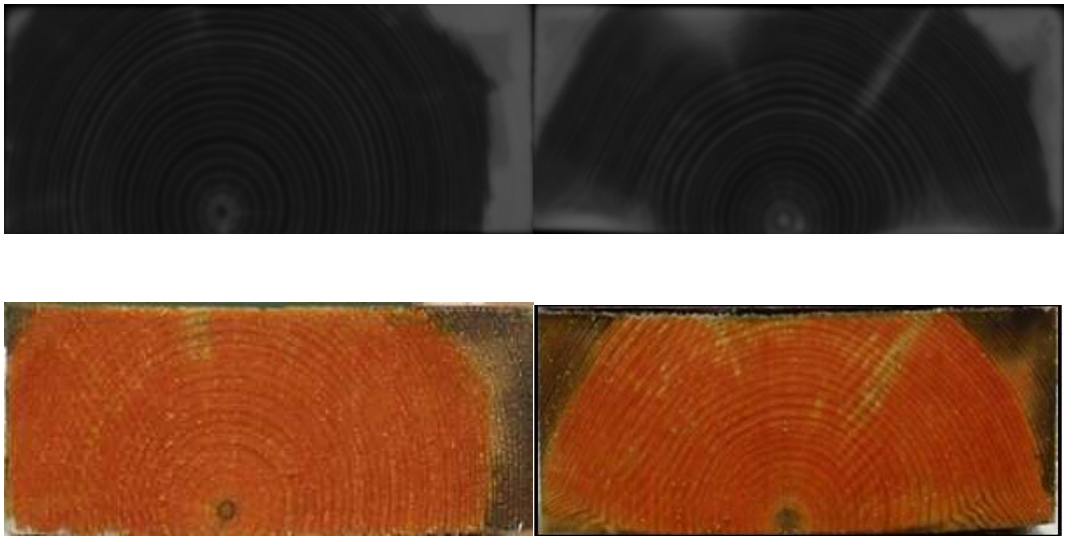


Figure 3.33 CT-scanning image (upper) and photos taken on matched position (down) of group 5. To the left were the reconditioning samples (final MC was 17.6%) and to the right were samples dried directly to 17.6% MC after application of heartwood reagent.

Results from drying and reconditioning of wood are shown in figures 3.29 to 3.33. One hypothesis is that bordered pits between tracheid fibres may start to break especially when dried to low MC during the reconditioning process making wood easier to penetrate. However, as can be seen from Fig. 3.29 to Fig. 3.33, group 1 had no impregnation failures on

both samples; group 2, group 3 and group 5 had impregnation failures on both samples. In group 4, the samples dried directly had no impregnation failure while the reconditioning samples had (Fig. 3.32 arrowhead). That is, only one out of five samples showed worse impregnation in reconditioned sample. Therefore, the influence of reconditioning to impregnation results was not significant but may exist to some extent.

In the upper part of figures 3.29 to 3.33 CT-images are shown. A higher density (more or less related to higher MC) is indicated as a darker contrast. One interesting observation is that the scanning image was different compared with the photo with heartwood reagent when sample was dry (MC was 17.6%) in group 3 (Fig. 3.31). Some parts in impregnation failure area still had high density (white arrowhead) which means the water had penetrated into this area while the copper based preservatives did not (Fig. 3.31). In addition, the gradient of preservatives penetration were found in group 2 (Fig. 2.30 red arrowhead) and group 3 (Fig. 2.31 red arrowhead). A probable reason for those two results is that the molecular size of copper based preservatives were bigger than that of water. Further investigations are needed for study in detail.

4. Conclusions

The impact of the total extractives to impregnation failure was weak. However, some extractives such as fatty acids, resin acids and fats could play an important role in explaining uneven distribution of preservatives. The areas with impregnation failures contained more fatty acids, resin acids and fats than impregnated areas in dried samples. It is speculated that those extractives could block resin canal, parenchyma cells leading to a lower liquid penetration.

The influence of drying process on the amount of fats was significant, that is, the amount of fats decreased during the drying process. The changes of both fatty acids and resin acids from green to dried samples were smaller when drying temperature was performed at 80^{o}C compared with 60^{o}C. Those changes were small when moisture content was around 13% and around 22%, and, thus, in order to reduce impregnation failures and considering a lower energy consuming, drying conditions at 80^{o}C and moisture content around 22% is a good choice.

In addition, the influence of reconditioning to impregnation failure was not significant. Probably due to the target MC (7% - 8%) in reconditioning process was still high, in which bordered pits were not broken. Further investigations are needed in this area.

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