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IMPACT OF WOOD SURFACE PRE-TREATMENTS ON THE BEHAVIOUR OF PHOSPHOROUS ADDITIVES

Master of Science thesis

Examiner: professor Minnamari Vippola
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ABSTRACT

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Wood is a versatile and widely used material in construction and furniture industries. However, easy flammability of plane wood prevents it from meeting the fire safety standards of buildings. To overcome this problem, the fire performance of wood can be enhanced by the use of fire retardant chemicals.

Fire retardant solution can be pressure impregnated or applied on the surface of wood. Pressure impregnation enables deep penetration of a fire retardant inside the wood, but it is an expensive method which requires special equipment and also affects the strength of wood. Surface applying of fire retardant is an easy and cheap method, but penetration depth is quite shallow, and typically, non-film forming chemicals are susceptible to leaching in moist environment.

In order to improve the durability and the penetration depth of fire retardant applied on the surface, different re-activating methods were tested on the wood surface. Planing, sanding, plasma treatment, microwave treatment or steam treatment was performed on the wood surface before the fire retardant application. The impact of treatments was evaluated first by the contact angle measurements and then by analysing the penetration depth of a fire retardant. Two fire retardants, a reactive and a two-component, were applied and compared with different burning methods; the small flame test, the in-house UL 94, the blow torch burning, the cone calorimeter test and the radiant panel test. All the available methods were evaluated in order to find an easy and fast in-house testing method before performing an official classification testing at an official test facility. Leaching of the fire retardants was tested by immersing the samples into distilled water for different times. The fire performance of samples after leaching was tested with the blow torch burning.

In all the burning tests, the reactive fire retardant presented more efficient fire retardancy than the two-component fire retardant, but no durable bond was formed between wood and fire retardants. After one hour in water immersion, half of the fire retardant was leached out and the fire performance was decreased.

TIIVISTELMÄ

MALLA JÄRVINEN: Puun pintakäsittelyiden vaikutus fosforipitoisten lisäaineiden käyttäytymiseen
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Puu on monipuolinen ja laajasti käytetty materiaali rakentamisessa ja huonekaluteollisuudessa. Mutta käsittelemättömän puun helppo syttyvyys estää paloturvallisuusstandardien täyttymisen. Puun palokäyttäytymistä voidaan kuitenkin parantaa palosuojakäsittelyllä.

Palosuoja-aine saadaan puuhun painekyllästyksellä tai levittämällä se puun pintaan. Painekyllästyksellä saavutetaan palosuoja-aineen tunkeutuminen syvälle puuhun, mutta se on kallis menetelmä, joka vaatii erityislaitteiston ja palosuoja-aineen kulutus on korkea. Palosuoja-aineen pintalevitys on helppo ja halpa menetelmä, mutta tunkeumasyvvys jää melko pinnalliseksi ja kemikaalit, jotka eivät muodosta kalvoa, huuhtoutuvat yleensä pois joutuessaan alttiiksi kosteudelle.

Erilaisia pintakäsittelymenetelmiä puun pinnan aktivoimiseksi testattiin, jotta palosuoja-aineen kestävyyttä ja tunkeumasyvyyttä pintalevityksessä saataisiin parannettua. Puu höylätiin, hiottiin tai käsiteltiin plasmalla, mikroaalloilla tai höyryllä ennen palosuoja-aineen levitystä. Käsittelyjen vaikutusta arvoitiin mittaamalla käsiteltyjen pintojen kontaktikulmat ja analysoimalla palosuoja-aineen tunkeumasyvyyttä. Kahta palosuoja-ainetta, reaktiivista ja kaksikomponenttista, levitettiin ja verrattiin erilaisin polttomenetelmin; pienen liekin testillä, sisäisellä UL 94 testillä, puhallusliekillä, kartiokalorimetrillä ja säteilypaneelitestillä. Myös näitä testimenetelmiä vertailtiin keskenään, jotta löydettäisiin helppo ja nopea, sisäiseen käyttöön sopiva testi ennen virallisia testejä ulkoisissa testauslaitoksissa. Palosuoja-aineiden poishuuhtoutumista testattiin upottamalla testikappaleet tislattuun veteen eripituisiksi ajoiksi. Tämän jälkeen kappaleiden palokäyttäytymistä testattiin puhallusliekillä.

Reaktiivinen palosuoja-aine suoriutui kaksikomponenttista paremmin kaikista palotesteistä. Kuitenkaan kestävää sidosta ei saavutettu puun ja palosuoja-aineiden välille. Jo yksi tunti vesiupotuksessa riitti huuhtomaan puolet palosuoja-aineesta pois ja palokäyttäytymisen heikkenemiseen.

PREFACE

Firstly, I would like to thank Kiilto Oy and Raija Polvinen, without support from work my studying would not have been possible. I am thankful to my supervisor, Tooran Khazraie, for guidance, support and kind words during this thesis project. All my colleagues in Kiilto Oy are earned their thanks for their emotional support and entertaining coffee breaks.

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Akaa, 14.05.2018

Malla Järvinen

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LIST OF SYMBOLS AND ABBREVIATIONS

DRF	durability of reaction to fire
FIGRA	fire growth rate
FR	fire retardant
HRR	heat release rate
ICP	inductively coupled plasma
LFS	lateral flame spread
SBI-test	single burning item test
SEM	scanning electron microscope
THR_{600}	total heat release rate during first 10 minutes
TSR	total smoke release
XRF	X-ray fluorescene
θ	contact angle
γ^D	disperse part of surface energy
γ^P	polar part of surface energy
γ_{lv}	liquid-vapor interfacial tension
γ_{sl}	solid-liquid interfacial tension
γ_{sv}	solid-vapor interfacial tension

1. INTRODUCTION

1.1 Background

Wood is one of our most widely used building material. It is lightweight but still mechanically strong, which makes it suitable for various applications. Wood is suitable for demanding structures like bridges and large halls, and at the same time it is used in doors, furnitures and in even small decorations. It can meet the growing demands of sustainability in climate-, environmental and natural resources issues [1][2][3]. However, when exposed to fire, wood burns vigorously endangering human lives and property. With fire-retardant treatment of wood, the ignition and the flame spread can be prevented or delayed and thus the fire safety of buildings increases.

First approaches to modern fire retardants was made by Gay-Lussac in 1821. He presented a number of fire retardant recipes for cellulosic materials based on ammonium phosphates and borax [4]. Similar systems are still in use today. Phosphorus, nitrogen and halogens are used as fire retardants, and among them halogens has been the largest group up until recent years. Use of halogens has raised concern; they accumulate in the food chain causing human health concerns, and reacting of halogens in the gas phase cause environmental pollution. This has led to prohibiting halogenated compounds and search for new eco-friendly, halogen-free, efficient and durable fire retardants [5]. Good fire retardants made of water-soluble inorganic salts do exist, but problems arise with their strength reduction and leaching in humid conditions.

Fire retardant can be pressure impregnated to wood or applied on the surface. Fire retardant applied on the surface can be film forming or non-film forming. These all have their advantages and disadvantages. With pressure impregnation, deep penetration of fire retardant is achieved. However, impregnation at high pressure needs special equipment, it might reduce the strength of wood, it consumes large amount of fire retardant and still fire retardant might leach out in humid conditions. Film forming fire retardants are paints or varnishes and thus change the appearance of wood, which is not preferable in many applications. Non-film forming fire retardants do not form a visible film on wood surface and the original appearance of wood is maintained. The penetration of a fire retardant applied on the surface is very shallow and thus it is hard to achieve an efficient fire retardancy. In case of destruction of the surface, also the fire retardant is removed. And because non-film forming chemicals are similar as in pressure impregnation, leaching occurs even faster with a shallow surface treatment than with a deep pressure impregnation [4][6].

1.2 Objectives

The theoretical part of this thesis describes the burning behaviour of wood and the mechanisms which reduce the burning; additionally, the Euroclass system is presented. The main focus is on the modification of wood surface and how different surface treatment methods can enhance wettability, penetration and durability of chemicals applied on the surface of wood. These methods include planing, sanding, microwave treatment, plasma treatment and steam treatment.

The aim of the experimental part of this master´s thesis was to study how these different surface treatments affect on the penetration of fire retardants in wood. With a higher loading of a fire retardant, a better fire-retardant property should be achieved. The best scenario was that a deep penetration leads to a chemical reaction between the wood and the fire retardant, and an end product is a leach resistant fire retardant inside the wood, so that rain and humid conditions do not affect to the fire-retardant properties.

To achieve this goal, the surface pre-treatment methods with two differently acting fire retardants were tested. One was a reactive fire retardant that should react with active sites of the wood. Other was a two-component fire retardant which should form a water insoluble compound inside the wood. The fire retardants were new, in a development phase at Kiilto Oy and not commercially available. Part of this study was to test the properties of these two fire retardants and to find good testing methods for in-house use at Kiilto Oy before more extensive tests at an official test facility.

The wood surface without any pre-treatment was used as a starting point. The impact of planing, sanding, plasma treatment, microwave treatment and steam treatment were compared to this starting point. In addition to the previously mentioned treatment methods, steam treatment was also combined with roasting (thermal treatment), which was done after fire retardant application to inactivate the wood surface. Also soaking without any pre-treatment was used to evaluate the penetration of fire retardant solution when enough time and fire retardant is available. Impact of the surface treatments were evaluated by measuring contact angle, liquid uptake, penetration depth and burning performance of the samples after the different treatments.

The durability of fire retardant in rain and humid conditions was tested by performing a leaching test on the selected surface pre-treatment methods. The leaching of fire retardants was evaluated by performing a burning test for the leached samples and measuring the fire retardant content from the selected leaching waters.

2. WOOD AS A MATERIAL

The evolution of wood structure has happened over the course of millions of years to serve three main functions of a living plant; mechanical support for the body of the plant, storage and synthesis of biochemicals and conduction of water from the roots to the leaves. To accomplish these functions, wood needs cells that are designed and interconnected in ways that these are performed. Even though, these three functions have had influence on the evolution of approximately 20 000 different wood species of woody plants, still every species have their unique properties, capabilities and uses. Reviewing, the functions of the living tree, will give us better understanding of its strengths and limitations as a material [7].

2.1 Wood structure

In a trunk of wood there are - from surface to center - outer bark, inner bark, vascular cambium, sapwood, heartwood, and pith (Figure 1). The function of the outer bark is to provide mechanical protection to the softer inner bark and to limit water evaporation. Sugars, produced by photosynthesis, are translocated in the inner bark. The vascular cambium, between the bark and the sapwood, produces both of these tissues. The sapwood is the actual active, living wood. It has newer growth rings and it has important part in the life processes of a wood by conducting water from roots up to leaves. When a tree grows, the diameter of the tree increases, and the inner, older layers no longer participate in the storing and transporting of water and nutrients and these layers become heartwood. After a certain age, the non-conductive heartwood is found in all species, and in most species, it has darker colour. At the centre of the trunk there is pith which is only a remnant of early growth before the wood was formed [7][8].

Botanically, woods can be divided to softwoods and hardwoods. Softwoods are usually coniferous, and hardwoods are flowering plants. In the temperatures of northern hemisphere, softwoods are generally evergreen trees with needle-leaves such as pine and spruce. Typical hardwoods are broadleaf, deciduous trees such as oak and birch. Softwoods and hardwoods differ also in terms of their cell structure [7].

Softwoods have quite simple cell structure. The majority of softwood trunk is comprised of long and thin cells called tracheids, generally known also as fibers. Because these tracheids form over 90 % of the cells in the softwood, they influence on the overall texture and feel of the tree and give it the most of its strength [7][9]. The tracheids have hollow cross section called lumen that works as a sap conductor in softwoods. Parenchyma cells are brick-shaped cells, which function in storage, synthesis, and transport of biochemicals, and small amounts of water. Parenchyma cells running in horizontal direction are called rays and in vertical direction running cells are called axial parenchyma [7].

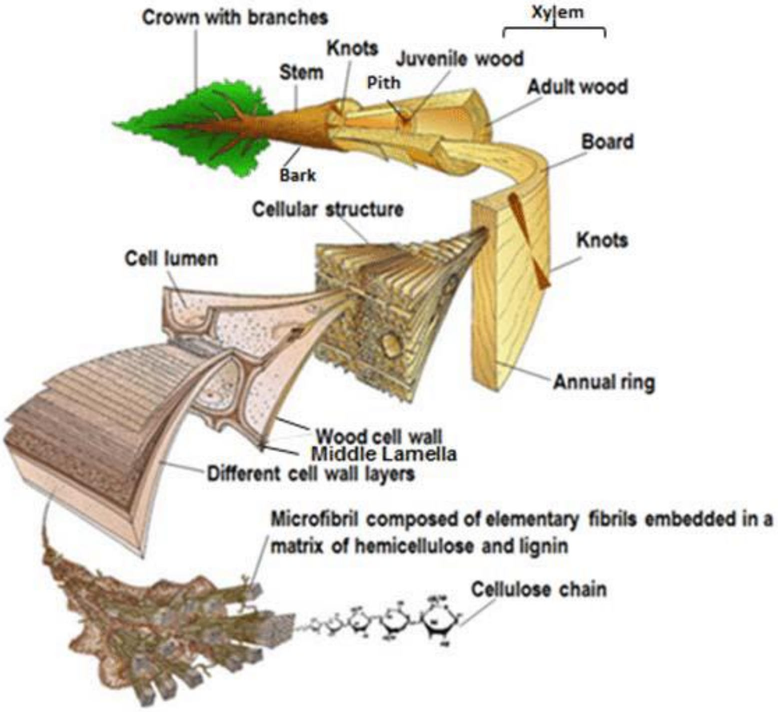


Figure 1. *Hierarchical structure of softwood [10].*

Hardwoods have more complexity in their structure because they have more cell types and greater variation in the cell types than softwoods have [7]. Fibers and vessel elements are always found in hardwood and they are axially oriented. Fibers provide the mechanical support in hardwoods and vessel elements are specialized to water-conducting. The vessel elements are contacted to each other by a perforation plate, a hole with no membrane. On transverse section, these vessels appear as large openings and are called pores. Vessels are the largest cell type, and they can be observed individually – sometimes even without any magnification, unlike any other hardwood cell type [7][11]. Also ray and axial parenchyma cells are often found in hardwoods [8].

Both, softwood and hardwood fibers, have closed ends, but have thin areas in the cell walls located between two cells, called pits. These allow transport of the sap from one fiber to another and from fiber to vessel element [1][12]. Pits and lumens of tracheids together provide good pathway for liquid-phase chemical flow [13].

2.2 Chemical composition of wood

Wood is practically a three-dimensional biopolymer composite. It has a hierarchical network of cellulose, hemicellulose and lignin as building blocks of multi-layered cell walls as was shown in Figure 1. It also contains small amounts of extractives and inorganic compounds [10][14]. Cellulose is a chainlike linear sugar molecule and provides a skeleton of wood [8][12]. Hemicelluloses serve as a matrix substance for cellulose. Hemicelluloses are lower molecular weight polysaccharides with short side chains. The third main component, lignin, has a high molecular weight, a complex structure and is highly branched. Its purpose is to bind all wood cell walls together and make wood a hard, rigid material, which is able to bear substantial mechanical stresses. Cellulose and hemicellulose are hydrophilic, where lignin is nearly water repellent [12].

Extractives are non-structural cell wall chemicals consisting fats, phenols, steroids, terpenes, resin acids, waxes and many others organic and in-organic compounds. Even though extractives are minor constituents in cell walls and cell cavities, they have great impact in many of the characteristic properties of wood, such as its odor, color, density, flammability, hygroscopicity, light stability, strength properties and permeability. Extractives often change the surface properties of wood, and therefore they have great impact on finishing characteristics and adhesion properties. Extractives can be soluble in water or in different organic solvents. And they can be reactive towards different chemical agents, which makes wood treatment more complicated. Softwoods usually have higher content of extractives than hardwoods, but in both wood types most of the extractives are located in the heartwood. All extractive types have high relevance in wood processing and utilisation [14][15][16].

2.3 Burning behaviour of wood

Wood, lignocellulosic and other natural polymers ignite when they are subjected to a heat release by some chemical, physical or microbiological stimulus. In addition to heat, natural polymers need direct contact with oxygen for combustion to begin and wood to decompose into volatiles and a char residue [4][17].

Thermal degradation of wood can be divided into three stages. At the first, preliminary (flameless) stage, happens removal of moisture when wood is heated to 105 °C (Table 1). Above this temperature, at 160-200 °C, slow thermal decomposition of cellulose, hemicellulose and lignin begins; gas products start to release, and char will form eventually. At this stage the gaseous products are mostly non-combustible. At about 200-275 °C pyrolysis takes place. The outside temperature increases the temperature of wood and leads to the breaking of chemical bonds. This thermal degradation leads to volatile gases to be produced and diffused into a surrounding air [4][17][18][19][20].

At the second, main (flame) stage, the physical structure starts to break down at temperatures above 300°C, char is forming rapidly and combustible gases are released. When surface reaches the temperatures of about 350-360 °C, ignition will occur in a presence of a pilot flame. The ignition of gases happens outside of the char layer, because wood, like many of other materials in our environment, burns “indirectly”. This means that the material itself does not actually burn, but combustion happens when volatiles, released from the wood, blend with the air and go through flaming combustion with the oxygen. The fast-growing char layer acts as an insulator for a virgin wood within. The char will retard the further degradation of wood by lowering the heat exposure to the uncharred wood and decreasing the heat release. After a while the heat release reaches constant value when thickness of the char layer remains almost constant [6][17][19][21]. When wood is burning at the constant rate of heat release per unit area, the pyrolysis front (the boundary between the intact wood and the pyrolysed material) proceeds the inside direction to wood. The charring rate of wood is typically 0,5-1mm/min. The charring is very essential for the fire resistance of wooden product, because original properties of wood are preserved under the char layer [6].

The final (flameless) stage takes place at temperatures above 500°C, where the formation of volatiles is small, but the formation of the char continues. Further mass loss is caused by smouldering and oxidizing of the char. Smouldering is a solid-phase combustion where the char produced by the pyrolysis combusts with oxygen to produce CO, CO_2 and water vapor [19][20][21].

Table 1. *Thermal degradation of wood (adapted from [18]).*

>100 ° C	Dehydaration
160 – 200 °C	Cellulose, hemicellulose and lignin begin to decompose. Formed gases are non-combustible (mainly H_2O).
200 – 275 °C	Breaking of chemical bonds. Volatile gases are produced.
275 – 500 °C	Second stage of thermal degradation. The physical structure begins to break down and char is forming rapidly. Ignition occurs around 350 – 360°C
>500 °C	The final stage. Formation of volatiles is small. Char is oxidized to CO, CO_2 and water.

The pyrolysis of wood can happen by two pathways (Figure 2). The way depends on environmental conditions such as moisture, pH, temperature, oxygen concentration and fire retardants. “Normal” burning of wood takes place by a tar forming pathway at temperature approximately 300°C. In this tar pathway, lot of tar including levoglucosan is produced. Under the influence of heat, levoglucosan decomposes easily to burning gases [6].

The other possible way for thermal decomposition is a char forming pathway, where cellulose transforms first to unstable, “active” cellulose. This “active” cellulose decomposes further to carbon dioxide and water, and to “backbone” of cellulose containing a lot of carbon. This char and water forming pathway is very unfavourable for burning. Char is protecting the wood and moist wood is harder to ignite because heating of water and especially vaporization of water consumes heat energy. Moisture also increases the thermal inertia of material [6].

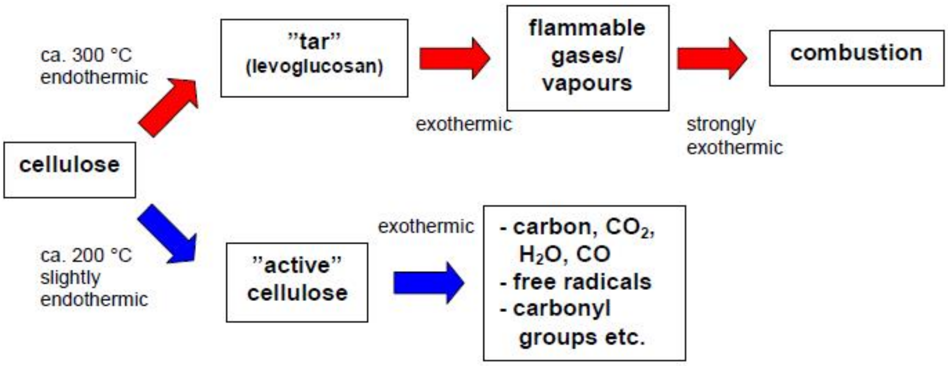


Figure 2. *Thermal composition of wood by the two main reaction pathways [6].*

3. FIRE RETARDANCY OF WOOD

Building material can be classified as fire resistant or fire retardant. Fire resistant refers to a non-combustible material which prevents penetration of fire. Fire retardant property can be a natural property of material or achieved through a treatment. Fire-retardant treatment improves the fire performance of material by limiting and delaying fire spread by altering ignition and heat release characteristics, but generally it does not totally prevent material from burning. It gives more time for rescuing people from burning houses and decreases property damages. Wood is not naturally fire resistant or even fire retardant material, it burns when exposed to elevated temperatures and air. Fire performance of wood can be improved by fire-retardant treatment to meet building regulations [17][22][23][24].

3.1 Inhibition of combustion and pyrolysis of wood

Browne [25] has made a literature survey about inhibition of combustion and pyrolysis of wood. These inhibition mechanisms can be divided into different classes:

- changing the pathway of pyrolysis
- coating the surface by protective layer
- changing the thermal properties of the material
- diluting the combustible gases of pyrolysis
- inhibiting the chain reactions of burning

Usually, the working method of a fire retardant is a combination of these systems to make the treatment more efficient.

Changing the pathway of pyrolysis is a common and best-known method for fire retardancy. In this method a fire retardant alters the production of the pyrolysis products by increasing the char formation, reducing the amount of volatiles and decreasing the temperature where pyrolysis begins. The amount of non-condensable gases increases at the expense of the flammable tar (levoglucosan) fraction leading to decease in flammability. Ideally this reaction pathway would lead cellulose to decompose only to water and char ($C_6H_{10}O_5 \rightarrow n\ (6C + 5\ H_2O)$. In practice, fire retardants that work through this pathway, reduce the volume of burning pyrolysis products and thus decrease the heat released by the product [6][20][26].

A material can be protected from fire by coating the surface by a physical barrier that retard both smouldering and flaming combustion. This layer prevents flammable gases from evaporating, oxygen from reaching the surface and also delays the temperature rise by insulating the combustible substrate. This effect is commonly reached by using coatings that intumesce (puff and form cellular structure on the surface when temperature rises). Intumescent coating forms a porous, carbonaceous foam. This layer delays burning and works as a good thermal insulator [6][20][25][26].

Changing the thermal properties of material can be made by fire retardants containing chemicals with a lot of water of crystallization. The fire retardants cause chemical and physical changes so that the chemicals absorb the heat and thus prevent the wood from igniting. A good example of making wood very poorly burnable, is to make it wet. Heating up and evaporating water consumes heat, because water has a higher specific heat value than dry wood. The combustibility of the pyrolysis gases is also reduced by water evaporating from a surface [6][20][25][26].

The flammable gases released during pyrolysis can be diluted by gases released from fire retardants. The gases that are considered working as effective diluents are water, ammonia, carbon dioxide, sulfur dioxide, and hydrogen chloride. Fire retardant should not decompose at ordinary temperature where wood is used, but it should release diluting gases just below the temperature where pyrolysis begins. It is beneficial to get any reduction in the percentage of flammable gases, because it increases the total volume of flammable gases that are needed for ignition. The gases also dilute the amount of oxygen when they move away from wood surface. Reduction in the oxygen amount near boundary layer leads to flame extinction [6][20][25].

Some fire retardants work as free radicals by inhibiting the chain reactions in the gas phase. Halogens, for example bromine and chlorine, are good inhibitors of free radicals. Usually, high quantities of halogens are required (15-30% by weight) to achieve practical degree of fire retardancy. However, this theory should be treated with reservations. Halogens, that are best known fire-retardants working in this way, should be avoided nowadays due to environmental aspects [6][20][25].

3.2 Suitable fire-retardants for wood

Fire-retardants for natural polymers and wood have been in use for thousands of years. Already 3000 years ago, Egyptians soaked grass in sea-water before using it for roofing purposes. Mineral salts, formed during drying, operated as fire retardants. The Chinese and Romans soaked wood in alum and vinegar and then covered it with clay layer which delayed fire spread. In 1821 Gay-Lussac made the first scientific approach to principles of fire retardancy. For cellulosic fabrics he recommended a mixture of ammonium chloride and ammonium phosphate or a mixture of borax and ammonium phosphate [4][25]. Examples of fire retardants used nowadays, classified based on their working mechanisms, are shown in Figure 3.

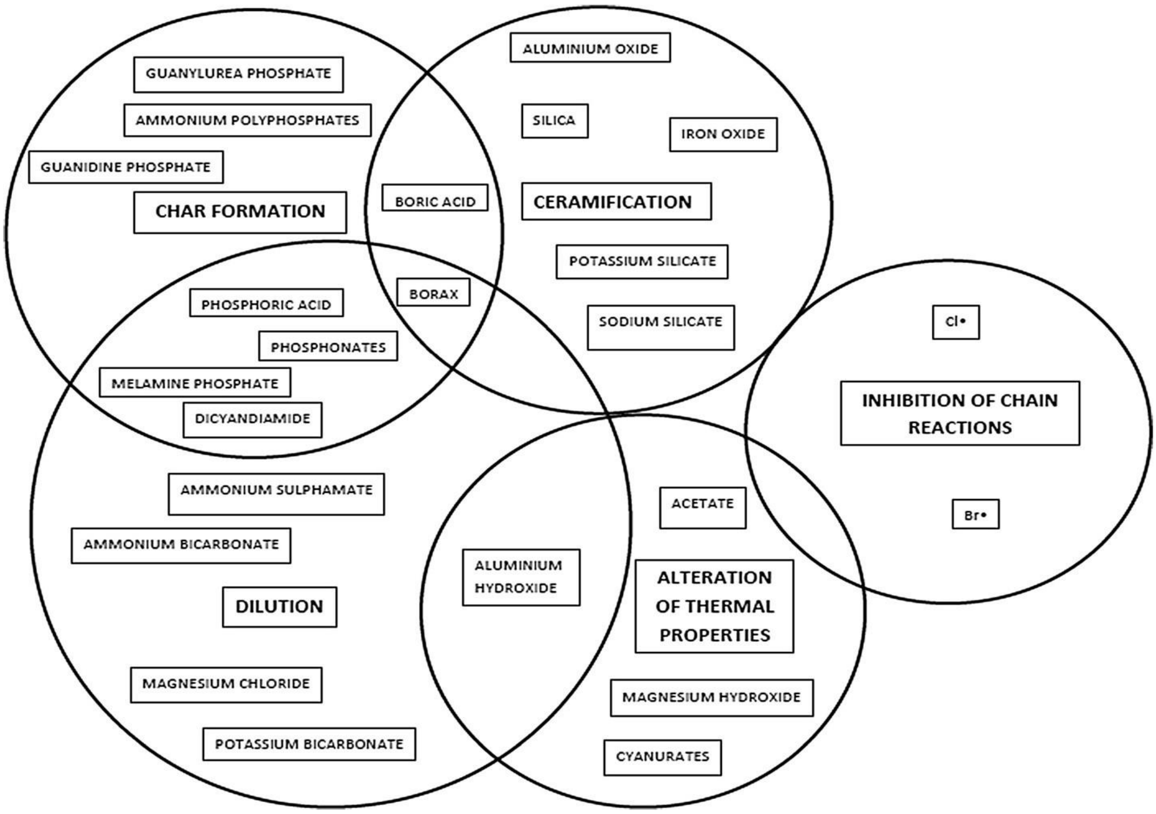


Figure 3*. Examples of fire retardants grouped by acting mechanisms [18].*

There are close to 200 different types of fire retardants. Usually they are divided into classes that include the phosphorous-containing, nitrogen-containing, halogenated organic (usually chlorinated or brominated) and inorganic flame retardants. Brominated flame retardants have high-performance efficiency and low cost. They have been the largest market group with more than 75 commercially recognized fire retardants [27]; however, nowadays many of them are restricted [28].

For timber, phosphorous based compounds are some of the best-known fire retardants [4]. Phosphorous containing fire retardants are quite versatile due to the several oxidation states of phosphorus such as phosphate, phosphonates, phosphines, phosphine oxides and phosphonium salts [5]. They work mainly in the condensed phase by enhancing char formation, through glass formation, or by yielding intumescent, and in the gas phase, through flame inhibition [29].

Nitrogen based compounds are mainly used in combination with phosphorus or sulphur [18]. But they can be very effective alone and thus should be considered as a separate class of fire retardants. The largest group of nitrogen-based flame retardants are derivates from ammonia or melamine, also some derivates of guanidine and urea are known [30]. Their main action mode is endothermic decomposition with release of non-flammable gases such as ammonia and nitrogen. This leaves condensation products such as melam and melem, which can form an insulating char layer. When released, nitrogen containing compounds also dilute the flammable gases. Nitrogen can also form cross-linked molecular structures in the wood and prevent the formation of volatile gases [18][30].

Typically, phosphorus and nitrogen are not used alone as a fire retardant for wood. Their individual fire retardancy performance is enhanced by their synergistic effect. The combination of phosphorus and nitrogen leads to an increase in char formation and released ammonia dilutes combustible gases. This potentially delays ignition and resists the flame spread [18][31][32].

Also new approaches to fire retardancy of wood have been made. Silicon based compounds form a layer that is resistant to heat and fire when applied as coatings. Inorganic metal hydrates absorb some of the heat and lower the temperature of material. However, they require unachievable amounts of chemical, so that their use is not practical in timber products. Use of metal salts, such as magnesium chloride and nickel chloride, is restricted due to their corrosivity and the possibility of forming hydrogen chloride on decomposition [18].

3.3 Treatment methods

Typical fire-retardant treatments used for wood can be divided into two classes. Fire retardant can be pressure impregnated in wood by using vacuum and overpressure or applied with a brush or a roller on the surface which needs the protection [4][6].

3.3.1 Pressure impregnation

In pressure impregnation, wood is regarded as a porous material like a sponge, with cell walls and cell cavities. The intention is to coat these cell walls with fire retardant [18]. In the pressure impregnation process, fire-retardant solution is impregnated to wood by using vacuum and pressure. The process can be divided to different phases. Firstly, air is removed from the cells of the wood by vacuum. The vacuum is maintained to keep the wood cavities free of air while fire retardant is inserted to the impregnating chamber. When the chamber is full of fire retardant, an overpressure is applied to force the fire retardant into the wood. After releasing the pressure, the fire-retardant solution is removed from the chamber. Finally, the end vacuum is applied to reduce the outlet of the fire retardant from the wood. To avoid deformations, drying after impregnation have to be performed in a controlled environment [6].

The pressure impregnation method is typically more effective and more durable than the surface applying method. The penetration depth is affected by wood specie, moisture content and structure of wood. Still typically, as a result of the pressure impregnation, the fire retardant is located deep inside of wood and thus even destruction of the surface cannot remove it. However, the pressure impregnation cannot be performed to existing constructions. It requires special equipment which endure both vacuum and overpressure, it consumes large amounts of energy, time and fire-retardant chemical. It also requires considerable skill and careful supervision to ensure acceptable product, because of different properties of woods [4][6][17]. For the best result, the lumber should not be cut after treatment if complete impregnation through whole cross-section is not achieved [23]. Moreover, the pressure impregnation of phosphorous based fire retardant decreases mechanical strength of wood [33][34].

3.3.2 Surface treatment

Surface treatment of a fire retardant can be performed by brushing, rolling, spraying or dipping the product into a fire retardant solution. Superficial treatment has many attractive properties: application is easy, only moderate equipment is required, application defects can be corrected, renewing can be performed as often as required and only comparatively small amount of solution is required for fire protection [18][23]. Even though pressure impregnation gives long term durability, can surface treatment be sometimes more practical and economical. For some applications, pressure impregnation is expensive, impractical or even impossible. Such applications are for example temporary constructions and ready-made or previously constructed objects (doors, walls etc.). For these application surface application is a suitable solution [6].

The main difference between surface treatment and pressure impregnation is the penetration depth of the fire retardant. The penetration depth of surface treatment method is usually approximately 1 mm or even less, when in pressure impregnation, the whole sapwood can be thoroughly impregnated. Still surface treatment can prevent ignition and burning just as well as the deeper treatment, since ignition and burning are surface processes [6][23]. The drawbacks of using surface treatment is their vulnerability to abrasion, wear and other damages resulting in decrease in fire performance [4][18].

When impregnating, fire-retardant comes automatically to all the surfaces, but when using surface treatment, it is important to coat all the surfaces. Even though surface treatment prevents spreading of fire on the exposed surface, heat transmitted to the opposite, untreated surface can result in ignition and proceeding of fire. If sufficient penetration is achieved to all the surfaces, there is no objections to use surface treatment method [23].

Fire retardants for surface application can be categorized to two groups depending on their action mode: intumescent and non-intumescent fire retardants. When intumescent fire retardants are exposed to high temperatures, the coating films swell and increase their volume by 50 to 200-fold and form insulating, heat resistant carbonaceous or silicate layer on the surface of the coated material (Figure 4) and thus the intumescent layer physically protects material from oxygen access and flame spread and simultaneously releases non-flammable gases. Non-intumescent coatings work mainly through different chemical means discussed earlier. However, they also have slight swelling abilities and thus they work partly through the same physical phenomena as intumescent coatings [6][35].

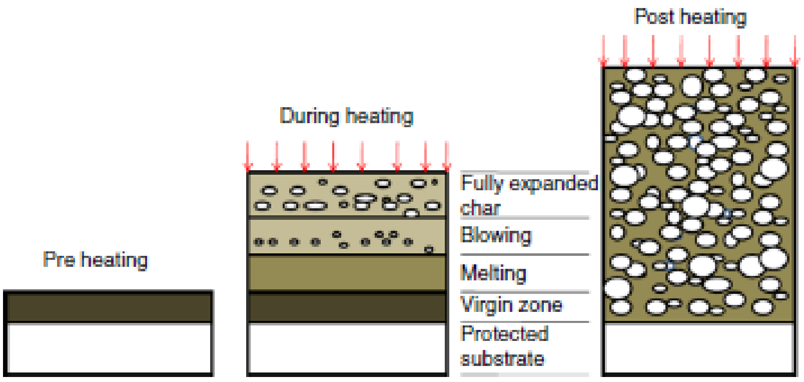


Figure 4. *Schematic representation of intumescent process [36].*

Surface applied fire retardants can be coatings, like varnishes and paints which form a clearly visible film on the surface altering the appearance of wood. This is not preferable property in many applications. Non-film forming fire retardants are similar as used in pressure impregnation process. They penetrate the surface layer and do not change the appearance of wood. There are not a lot of fire retardants that are transparent and meant for the surface treatment of wood. The main reason is that it is very difficult to achieve sufficient fire performance using only surface treatment [6]. Fire is more capable to continue into the untreated wood beneath the surface treatment layer than in thoroughly impregnated wood [23]. Therefore, it is essential to achieve the deepest possible penetration into the wood when applying a surface fire retardant.

3.4 Leaching of fire-retardants

As discussed earlier, suitable fire retardants for wood are mainly phosphorous and nitrogen based compounds. Drawback of these, and other salt based inorganic solutions, is their hygroscopicity. This is not an issue in indoor applications, but in outdoor use, it presents problems. In exterior applications wood is exposed to fluctuating humidity and rainfall. This causes water-soluble salts to migrate slowly towards surface and leach out, resulting in lose of fire retardant properties [4][17][37][38][39][40]. Wood, which is pressure impregnated with fire retardant, can maintain its effectiveness slightly longer than surface treated but will also lose its fire performance eventually [23].

To enable the use of fire retardants in exterior applications, the reaction between water and fire retardant must be prevented. This can happen by applying a coating or through chemical reaction between fire retardant and wood [20][37][38]. Coating wood with a paint is not preferable method in all cases, because it covers the appearance of wood. Fire retardant can also affect the performance of the paint. Colour of the paint can be changed, and water-repellency is decreased, which finally leads to detachment of the coating and leaching of fire retardant. Any cracks or wear on coating will allow water to penetrate in wood and result in leaching of fire retardant [37]. And in the worst case, if the paint is flammable, it can enhance the combustibility of wood [41].

Water-insoluble fire retardant can be achieved thorough two different approach. One is to make fire retardant react and form a complex and insoluble substance inside the wood, other is to make fire retardant attach directly to cellulose in the wood [20][22][38]. Complex forming can happen with the aid of additive, which forms insoluble agglomerates with fire-retardant. For example, forming insoluble, metallic salt complex by reacting soluble salt with metallic salt [20]. Many of these complexes forming fire retardants are based on halogens, like bromine, and are not therefore viable options anymore [4][28]. New approaches are also performed on this field; nano-SiO_2 sol, obtained by sol-gel method and combined with a phosphate fire retardant forms agglomerates in the vessels and pits of wood and reduces leaching of fire retardant [39].

Self-bonding directly between cellulose and fire retardant can be achieved through functional groups. Functional groups in fire retardants form covalent bonds with functional groups of wood, which in wood are mainly hydroxyl groups. With activation of wood surface, the number of functional groups can be increased and thus achieve better bonding and increased resistance against weathering [4][42].

Wood surface itself can be affected after fire retardant treatment to decrease leaching. Heat treatment of wood makes wood surface more hydrophobic and complicates water penetration to wood and thus decrease the leaching of fire retardant. It is worth noting that the hydrophobic surface does not completely prevent leaching, but only decelerates it [43][44].

4. WETTING AND MODIFICATION OF WOOD SURFACE

Considering fire-retardant treatment of wood, good result in treatment is achieved through two synergistic effects. Firstly, wetting, penetrating and anchoring of the fire-retardant solution into the void spaces of the wood surface. Secondly, achieving a strong interaction or chemical reaction between the solution and the major elements of wood [45][46].

The term wetting expresses the process of adhesion (drop of water encounters a solid surface), penetration of water into the pores and spreading of water over the surface [47]. The wetting behaviour of material can be evaluated by its surface energy. If it is higher than the surface energy of the used liquid, good wetting will occur. The easiest method to evaluate the surface energy is to measure the contact angle [48].

4.1 Contact angle and wetting properties of wood surface

A contact angle is defined as an angle between the liquid-vapor and liquid-solid interfaces of liquid-solid-vapor system (Figure 5). When a drop of water is placed on a solid surface it might spread on the surface. This will result in a small contact angle. But if liquid stays as a bead on the surface, it forms a large contact angle. More specifically, a contact angle greater than 90 degrees means hydrophobic surface (low wettability), a contact angle less than 90 degrees means hydrophilic surface (high wettability) and when a contact angle is 0°, complete wetting occurs on the surface. On superhydrophobic surfaces water shows almost no contact between the surface and the liquid drop resulting in a contact angle greater than 150° [48][49].

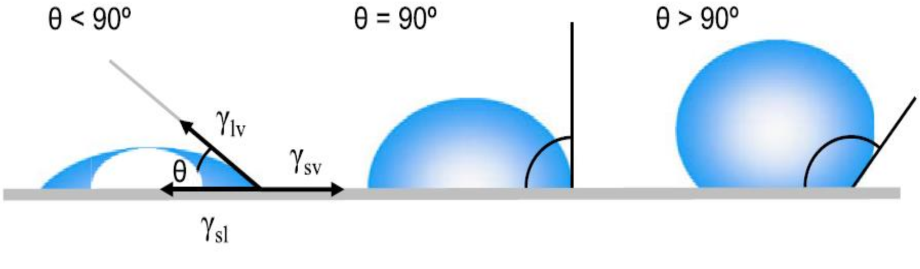


Figure 5. *Illustration of contact angles on a smooth homogenous surface [48].*

Contact angle measurement can be used to calculate the surface energies to predict the wetting phenomena of different liquids on various surfaces. If the surface energy of solid surface is greater than the energy of wetting liquid, then the liquid will spread on the surface and wetting will occur. And if liquid has higher surface energy it will form a bead on the solid surface [50]. The correlation between surface energy and contact angle was first described by Thomas Young in 1805:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{1}$$

where γ_{sv}, γ_{sl} and γ_{lv} represent solid-vapor, solid-liquid and liquid-vapor interfacial tensions respectively, and θ is the contact angle [48]. Young´s equation assumes that there is thermodynamic equilibrium in the entire system and that the solid surface is ideally smooth, chemically homogenous and not affected by chemical interaction or penetration of the liquid into the surface. Measurement of solid surface tension was later divided to measurements of polar γ^P and disperse γ^D or nonpolar components [51]. Polar part increases surface energy and wettability, because only polar-polar and dispersive-dispersive interactions occur [52].

The contact angle measurement has high value in industrial processes. Contact angles can be measured in a laboratory situation and the collected data can be used to predict the wetting behaviour of the same material in a technological process [53]. The average wettability of material affects, for example, on spreading and bonding characteristics of adhesives, coatings and preservatives; and thus, it influences on the durability and life time expectancy of an end product.

Various methods exist for measuring contact angle, but two most common methods are the sessile drop method and the Wilhelmy plate method (Figure 6). In the sessile drop method, a small drop of liquid is placed on the surface with a syringe. The contact angle is observed through a camera lens. All this is made automatic nowadays and proceeding of the contact angle can be recorded and calculated with a computer program [48][54]. In the Wilhelmy plate method, a rod or plate is partly or entirely immersed in a probe liquid and the force F, which acts on the sample, is measured. This technique does not measure the contact angle directly, the contact angle is determined from the measured force. This method also enables detecting the weight change of the sample due to sorption during the test cycle [55].

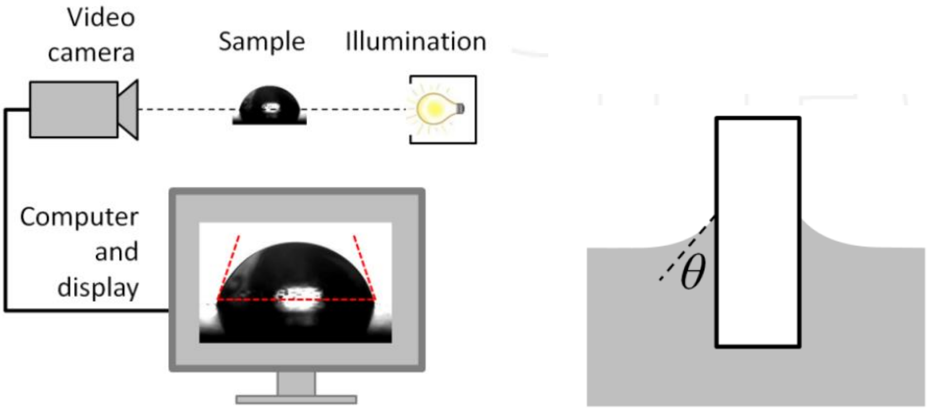


Figure 6. *On the left: schematic representation of the sessile drop method. On the right: a rod is immersed in a wetting liquid in the Wilhelmy plate method [56].*

Predicting wetting properties of wood surfaces is widely performed by measuring contact angles of liquids on the wooden surfaces [47]. However, measuring the contact angle of wood has many problematic issues due to the composition of wood. Wood is very porous, heterogeneous, a composite type material, which is consisted of cellulose, hemicellulose, extractives and lignin. This uneven distribution of cell wall components means that a liquid on the surface will encounter different chemical compositions depending whether liquid is outside, inside or in cross section of cell wall. On the cell walls, adsorbed water will always be present, but the amount varies depending on the relative humidity of the environment and the wood species. This heterogenous structure and porous surface of wood cause differentiation and continuous change in the contact angle due to varying penetration of the sessile drop into the wood structure. This causes major problems when trying to determine the equilibrium contact angle of wood [51][57][58]. Some authors determine contact angle between wood and liquid at the first moments of the wetting process [59], some authors use some other constant moment [60] and others calculate an average contact angle during a certain measurement interval [58].

The contact angle is affected by a surface roughness as shown in Figure 7. The cellular, anisotropic structure of wood causes surface roughness on a microscopic scale and already roughness as small as 0,5 µm can affect on the contact angle. The roughness and hygroscopic properties also differs in radial, tangential and longitudinal direction within the wood. Thus, measuring the contact angle of wood is also affected by direction of the measurement; measuring perpendicular to grain results in different spreading of drop and contact angle than parallel to grain [58][60][61].

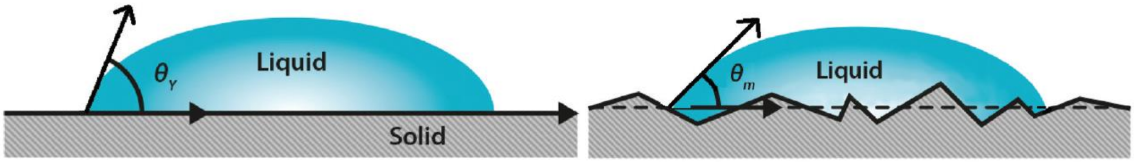


Figure 7. *Contact angle on an ideally smooth surface (left) and on a rough surface (right) [62].*

Wood wettability is affected by its chemical composition, and especially by its O/C-ratio. For cellulose and hemicellulose, the theoretical O/C-ratio is 0,83, for lignin much lower 0,33 and for extractives very low 0,10. Low O/C-ratio represents high concentration of lignin and extractives on the surface, both of them being very hydrophobic. Whereas high O/C-ratio makes wood surface polar and increases wettability by water [63].

As a porous material, wood wetting is affected by the penetration of solution. Penetration happens through tracheids of softwoods and through fibers and vessel elements of hardwoods. These cells have lumens large enough to provide good pathways to liquid flow, and interconnecting pits usually offer adequate flow between cells. Thus, the penetration is largely affected by the surface preparation and open pathways to cell lumens [13][64].

Additionally, the wettability of wood is also affected by pH value [65], location of wood (sapwood or heartwood, earlywood or latewood) [66][67], machining conditions [68], aging time of exposed surface [69], extractive amount [70] and treatment and drying methods [71]. Thus, it is clear that many conditions assumed in Young´s equations do not come fulfilled, especially on wood but rarely on any real surface. Still, the sessile drop method is considered the preferable method for wood, because no sealing or perimeter measurements are not needed on the contrary to Wilhelmy plate method [51].

4.2 Inactivation of wood surface

A basic requirement for optimum contact between a substrate and a solution is a clean, solid surface. This is true for wood surfaces too, but in addition to air born contaminants, such as dust, wood is subjected to self-contamination called inactivation. Surface inactivation changes the natural hydrophilic property of wood by causing physical and chemical modifications on the surface. Inactivation results in lower ability of water-based solutions to wet, flow and penetrate to the surface of wood. The inactivation of wood surface can be evaluated with contact angle measurement [63][69].

The inactivation of wood surface has many sources: air, heat, wood, light, machines and chemical treatments. Some degree of the wood surface inactivation is caused by typical processes like wood ageing, wood seasoning, wood weathering and wood heating or drying. The most prevalent reason for inactivation is drying at high temperatures (Figure 8). At the beginning of drying, evaporating water provides cooling on the surface. After evaporation of free water, strongly bound water diffuses to the surface as a vapour and does not provide the cooling effect anymore. This leads to increased surface temperature, overdrying and development of inactivation [63][72]. Inactivation can occur also in low temperature, but it requires longer time (i.e. ageing) and is not as severe as inactivation at high temperature [60][63]. Drying of wood can be accelerated with fans, which allows faster heat and water transport across the wood surface, but it also increases the changes for inactivation before wood is completely dry [60][72].

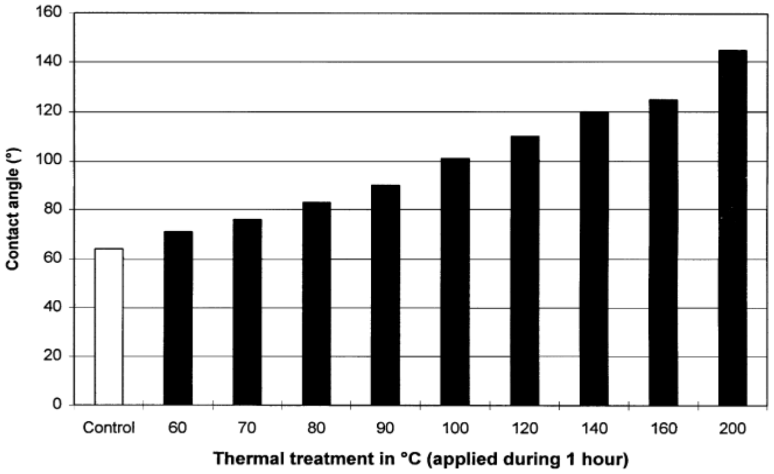


Figure 8. *Influence of thermal treatment on wettability of fir wood [73].*

Drying of wood is important part of converting timber to appropriate for construction and other wood working purposes. Drying of wood reduces its dimensional changes and increases strength, electrical and insulation properties. Properly dried lumber is cut easier to precise dimensions and machined more efficiently. There are several drying methods for lumber including, air drying, kiln drying, shaft drying, dry air drying, vacuum kiln and dehumidification kiln. Air drying does not require increased temperature, but it is very slow and uncontrollable. Usually it is used prior to kiln-drying reducing the energy consumption. Air drying can be accelerated by using fans that force air through lumber piles. Kiln-drying is the most common method in Finland. Kiln-drying is a batch process where lumber remains in place during the drying cycle. The drying temperature is usually 50 – 70 °C and it is observed along with humidity. These drying parameters are changed based on a schedule, which takes into account the drying rate or the moisture content or both. All other mentioned methods - regardless of differences in process systems - use increased temperature to accelerate drying. Drying of wood is usually performed as fast as thickness, specie and end-product allows. At the same time, damaging the wood is tried to avoid. Uncontrolled drying leads to drying defects and limits the use of the wood [74][75]. It is not easy to control inactivation of wood surface during drying. Softwood species are more prone to surface inactivation than hardwoods. Also, heartwood is more easily overdried than sapwood, because it has readily lower moisture content than sapwood [72].

Christiansen [72][76] has reviewed mechanisms that are proposed for inactivation. They can be categorized to physical and chemical phenomena. Physical mechanisms are self-contamination of the surface, molecular reorientation and micropore closure. Self-contamination is caused by extractives migration on the surface. In molecular reorientation natural polymers, cellulose, hemicellulose and lignin, reorient themselves to reach a low energy surface (hydrophobic) with fewer reactive groups. This is accelerated at high temperatures. In micropore closure, many micropores between wood cells are lost during first drying and they are never fully recovered. This limits penetration of larger molecules of treatment solution. Chemical explanations of inactivation [76][77] are oxidation of surface bonding sites, chemical interference with bonding and elimination of surface hydroxyl bonding sites. Hydroxyls are responsible for natural hydrophilicity of wood. Modification, removal or blockage of hydroxyls transforms wood from hydrophilic to hydrophobic.

Although all the above explanations are feasible, extractives are the only commonly accepted major physical and chemical cause for surface inactivation over time [78]. When wood is exposed to high temperatures, extractives are migrated to the surface and deposited there as a solid when water is evaporating. Extractives work as contaminants and physically block any solution from contacting wood surface or reaction sites of wood. Moreover, extractives are hydrophobic and thus prevent any water-based solution from wetting and penetrating the wood surface. Chemical bonding of solution and wood are also interfered by acidic nature of many extractives [16][72][79].

Only outer layer of wood is affected by surface inactivation and the problem can be solved by surface modification. The removal of extractives or re-activation of the surface, lowers the contact angle and thus increase the wettability of wood [63][80]. This can happen by chemical or mechanical ways. For example, light sanding or planing immediately before surface treatment are rapid and economical ways to remove most of the surface contaminants [16]. Re-activation is not a permanent state on the surface, extractives migrate again to the surface and re-activation is reversed over time by aging (Figure 9). After 24 hours contact angle is already increased and after four to six days maximum values are reached again [69][81].

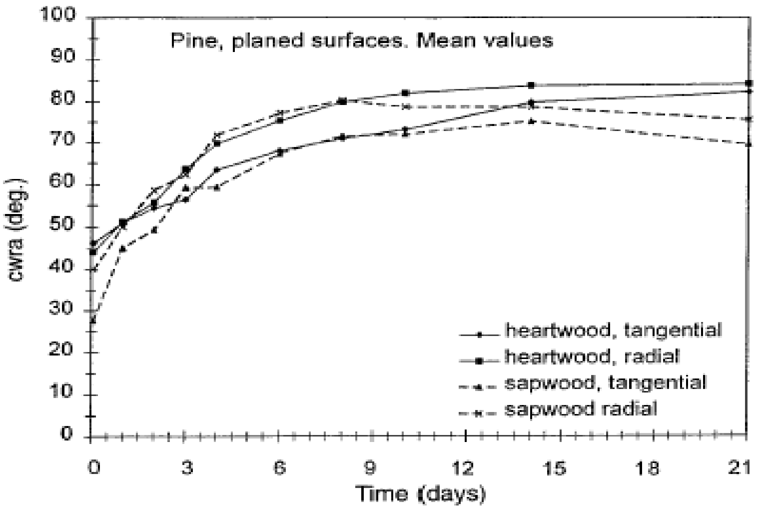


Figure 9. *Constant wetting rate angle (cwra, contact angle defined at the time moment when penetration becomes almost constant) for sessile drops at different times after surface was planed [69].*

4.3 Surface modification of wood

The removal of extractives or re-activation of wood surface can be performed on a chemical or a mechanical way. Chemical treatment can be for example functionalisation of wood with enzymes and thus providing active sites on surface [82]. Or removal of extractives with ethanol soaking [80]. Focus of this thesis is on mechanical ways to modify the wood surface. Presented methods are: planing, sanding, plasma treatment, microwave treatment and steam treatment.

4.3.1 Planing

In planing, a thin layer of wood is removed from the surface. The purpose of planing is to achieve a desired appearance, smoothness and precise measurements to wood. Planing is performed with a planer machine, where the wood moves straight and continuously through the machine. At the same time cutting head turns around its longitudinal axis and blades remove uniform chips from the surface of wood. In a microscopic scale, this will lead to cutting surfaces to obtain a cycloid shape, straight line in cross-section and slice within longitudinal section as shown in Figure 10 [83].

Planing is very effective way to remove extractives and all other physical and chemical contaminants from the surface of wood. When a layer is removed from the surface, a fresh and highly active polar surface is exposed, which allows good wetting with polar solutions, like water. At the same time, planing removes any unevenness and thus allow solutions to flow freely and form a uniform thin layer [16][79].

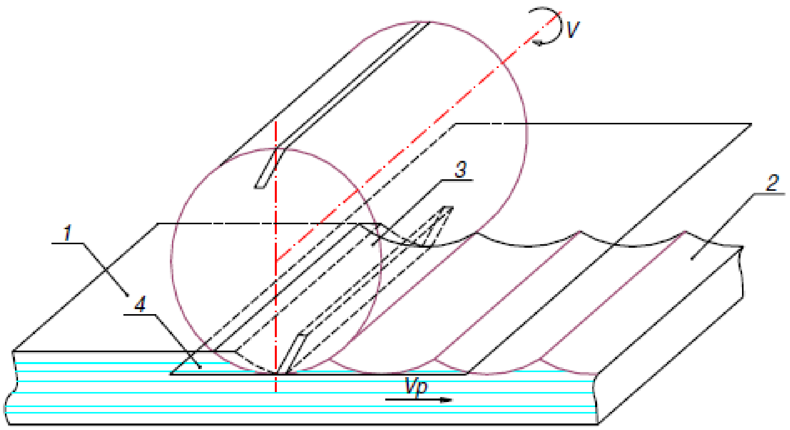


Figure 10. *Movement of rotary blade in planer machine, 1 – surface to be processed, 2-processed surface, 3 – cutting surface, 4 – cutting plane [83].*

Plaining has great impact on the penetration characteristics of the treated surface. Surfaces planed with sharp knives show very little damages. Earlywood is normally cut open without crushing, where slight compression can happen to thick-walled latewood cells. The anatomical structure of wood can usually be easily identified from planed surface. In softwoods, tracheids and rays are cut open. In hardwoods, vessels and rays show exposed lumens [64][68][84][85][86][87]. These open ends of cell lumens facilitate easy penetration for solution, schematically shown in Figure 11. Firstly, those outer longitudinal tracheids or vessels, which have open ends on the surface, are filled. This mainly occurs on earlywood rather than on latewood. Important factor in this mechanism is axis between tracheids and surface, affecting strongly on penetration depth. The second path for penetration is through rays, starting also from open ends of cells. The third penetration way is from ray cells to adjacent tracheids, which is strongly affected by permeability of pits. These three penetration mechanisms implicate that penetration is strongly affected by the way boards are cut out of log. This is due to the number of rays and tracheids ending on surface, width of early and latewood and orientation of grain to the surface. The origin of wood can influence penetration because number of rays and length of longitudinal tracheids, differences in portions of early- and latewood and conditions of pits [64][88].

To achieve these precisely cut open cells on the surface, the sharpness of planing knives plays the important factor. Planing with blunt knives leads to compressed or torn fibres, tracheids and rays. Distortion of cells walls can extend to six or even more layers from the surface. Compression of cells crushes also lumens; and consequently, the penetration of solution is prevented [68][86]. The difference between sharp and blunt knives in the penetration of glue is presented in Figure 12.

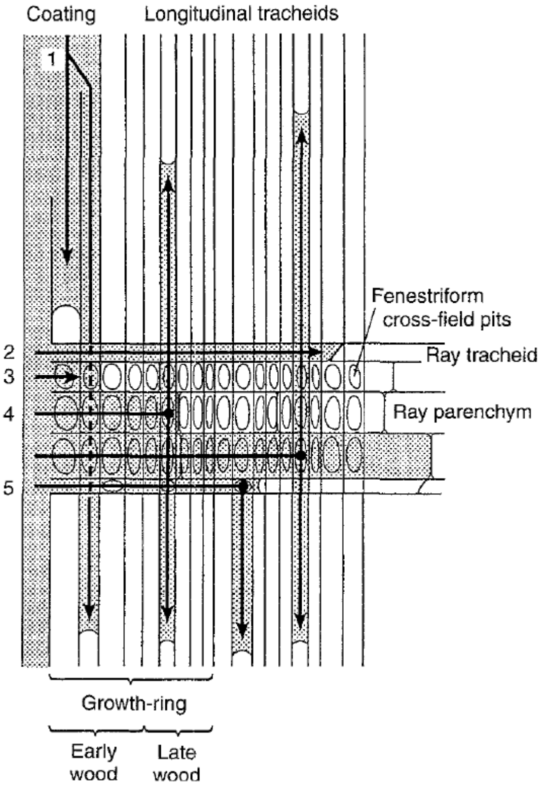


Figure 11. *Presentation of different possible ways for coating to penetrate in softwoods looking from radial cross-section: 1 – penetration into open ended longitudinal tracheids, 2 – penetration into ray tracheids, 3 – penetration into ray parenchyma, 4 – penetration from ray parenchyma into longitudinal latewood tracheids, 5 – penetration from ray tracheids into longitudinal tracheids [64].*

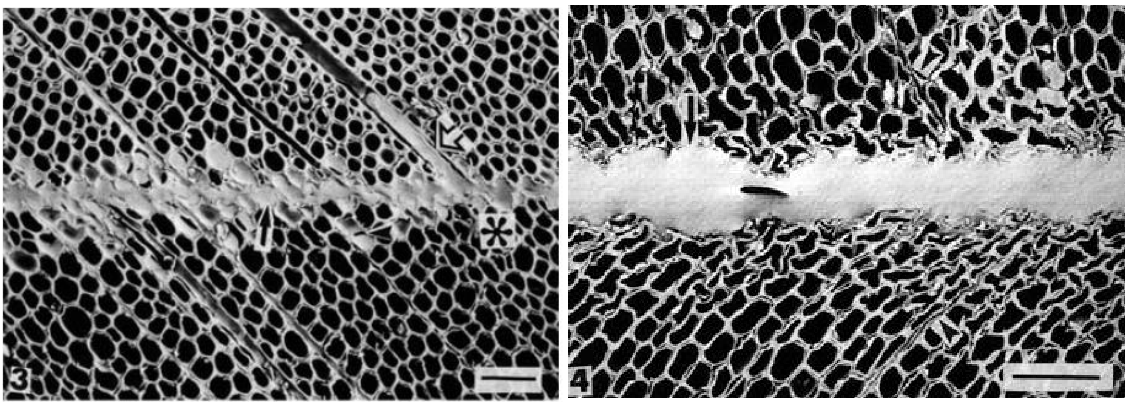


Figure 12. *Left: the wood surface was planed with sharp knives. The glueline is thin and the glue has penetrated to cells, open arrow indicates penetration in a ray. The cells have mostly a normal, intact appearance except some slightly crushed cells which are in the instant vicinity of the glueline (asterisk). Right: the wood surface was planed with dull knives. The glueline is irregular and very thick. The cells are distorted to a depth of several layers and practically no penetration of glue to the cells has occurred. Bar = 100 μm [86].*

Planing studies are mainly focused on adhesive and coating applications, but same penetration behaviour applies on non-film forming fire retardants too. If planing is done with sharp knives and no cells are crushed, then the capillary penetration processes are limited by the increase in viscosity. The micro-pores in the cells allow only low molecular weight materials like solvents and water to penetrate the cell wall. The larger molecules will remain inside the capillary. This selective removal of water will increase the viscosity of solution that is remaining in lumen and thus hinder the penetration any further [88]. This capillary penetration process is presented in Figure 13.

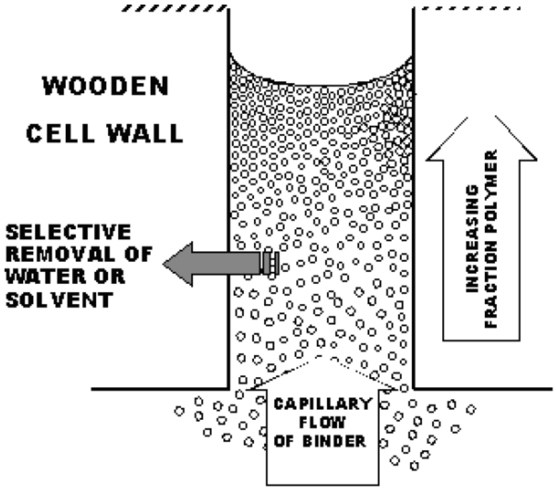


***Figure 13**. Schematic presentation of the penetration process of a liquid containing solid material into a capillary of wood cell [88].*

4.3.2 Sanding

Sanding is a very common operation in the woodworking industry. It is also one of the most time-consuming, skill-based and expensive operations. In sanding, wood is abraded with sanding paper, where abrasive grains work as small knives removing material from the surface. Sanding can be performed on a machine, manually or combination of machine and manual sanding [89][90].

The abrasive tearing action of sanding removes extractives, but it also produces damages on wood surface. Anatomical structures are barely identifiable on sanded surfaces. Earlywood tracheids and rays are compressed and ruptured, fibers are torn, and cells are no longer firmly attached on the surface. Sanding damages latewood as well, but in smaller degree. Damaging effect is not limited only to the outer cells; changes can be observed up to depth of 500-1000 μm from the surface. Sanding also produces large amount of dust particles, which accumulate in lumens obstructing them [64][68][84][85][87][90][91]. This is a particularly strong effect during sanding with a fine grit sand paper. Cleaning of surface removes dust from the outer surface, but not from inside the contaminated lumens. Solution can penetrate to cells which are open to the surface, but deeper penetration is prevented by crushed cells and dust [64][84][91]. Figure 14 presents the different penetration of glue into planed and sanded surfaces.

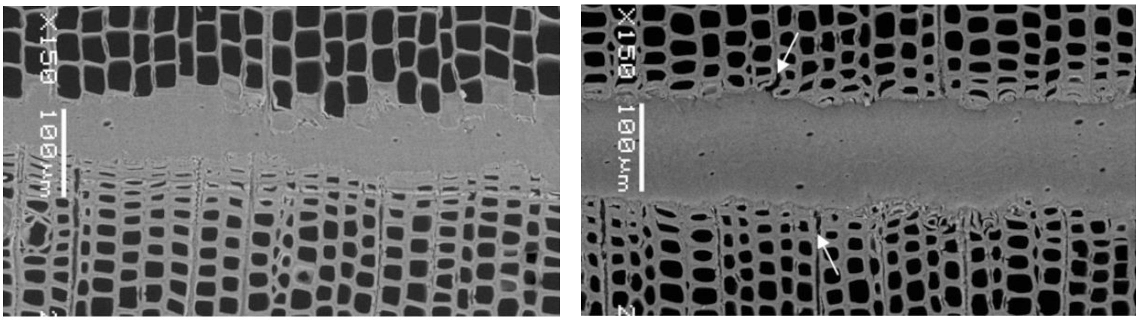


Figure 14. *Transverse environmental scanning electron microscopy micrographs of glued black spruce wood that were planed (left) and sanded (right). Arrows show microruptures in latewood of sanded samples, which are unfilled by the adhesive [87].*

Sanding produces grooves on the surface which are detectable at least at a microscopic scale. They are more pronounced in the perpendicular direction to the abrasive movement and increase roughness of the surface [84][91]. The wetting properties of hydrophilic surfaces are magnified by increased roughness [50]. The grooves on the sanded surface favour and accelerate water conduction due to capillary forces. This surface roughness results in fast wetting of the surface and, therefore, lower contact angles are observed than in smooth surface as it was schematically seen in Figure 7 [68][81][84][91][92].

Although contact angle is low on sanded wood surfaces, studies about surface energy are ambivalent. Some studies report increased surface energy due to longer sanding programs. This is presumed to be due to surface oxidation. Extractives on wood surface could be oxidized at elevated temperatures produced by friction of abrasives on the surface [52][84][90]. Also, opposite results are reported [91], longer sanding program led to smaller surface energy due to decrease in polar part. The longer sanding might increase the surface temperature, which inactivates the wood surface.

Crushed cells and dust prevent good penetration of solutions, but at the same time the roughness with good wettability will provide better adhesion to coatings than planing does. Increased surface area and raised fibers promote good mechanical anchoring of coating to the surface [68][84][85]. Sanding also evens the natural differences on the properties of wood surfaces, resulting in an equal and homogenous coating spread with a smaller amount of coating compared to planed wood [93].

4.3.3 Plasma treatment

Plasma can be called also the “fourth state of matter”, in addition to solid, liquid and gas state of matter. Plasma can be formed by heating the gas. As a result, the gas is ionized, and plasma is formed (Figure 15). Plasma is practically more or less ionized gas.

Normally, gas is an electrical insulator, but when it is heated to appropriate temperature, electrons and ions can move freely in this gas and it becomes electrically conductive. The easiest way to generate plasma in a technological application is through an electrical discharge. Voltage is applied between two metal electrodes, anode and cathode, generating the electrical discharge in the gaseous gap. The electrons in that gaseous gap is being accelerated by the electric field and this kinetic energy of the electrons can be used to stimulate atoms and molecules. This process causes the gas to transform into a plasma state [49][96].

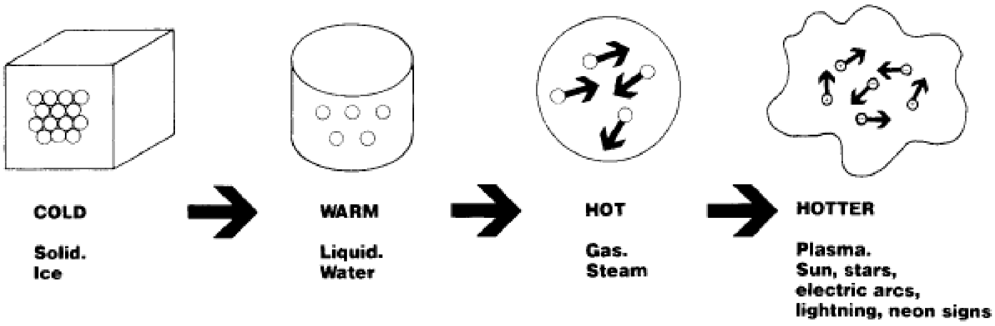


Figure 15. *The four states of matter: solid, liquid, gas and plasma [95].*

There are several different plasma treatment methods. One way to classify them is according to the used pressure; low- or high-pressure or atmospheric pressure. The low-pressure plasma chamber makes it possible to change temperature, power, pressure and reactive gas flow in a controlled environment. However, it has lots of disadvantages, for instance, vacuum system is required and long-time is needed to vacuum process and dehumidification. It is worth noting that, in the vacuum systems, only batch process is possible. Because of these disadvantages, atmospheric pressure plasmas are more suitable for industrial applications [96]. Atmospheric pressure plasmas have lower cost, higher throughput and it is possible to operate in-line without a vacuum system and still use of different gases or gas mixtures is possible [59][96].

Atmospheric plasmas can be classified in various ways, by their electron density or temperature [49]. But principally, there are two possible plasma sources. In corona and dielectric barrier discharge, a wood is used as a counter electrode [96]. Other way to generate plasma is a plasma jet. There plasma is generated between two electrodes and the gas stream is blown directly onto the wood surface at the same time. Used gas can be air, some inert gas or a gas mixture. These are often called “indirect plasma treatment”. This method is not as effective as dielectric barrier discharge because of the combination of charge carriers and the reduction of radicals generated in the gas stream. But these plasmas offer possibility of plasma treatment of small gaps due to their only few millimetres wide jets [49][96]. Different setups for dielectric barrier discharge and atmospheric plasma jets are shown in Figure 16.

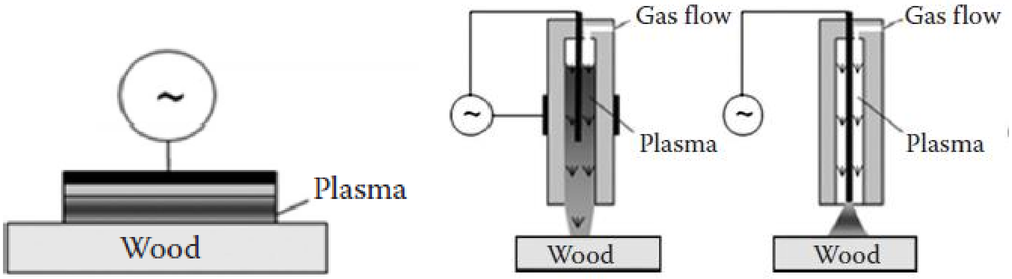


Figure 16. *Setup for dielectric barrier discharge (left) and two different atmospheric pressure plasma jets (centre and right) [96].*

Plasma modification can be used in bulk material treatments, like material machining, fine particles or toxic waste treatments; and in surface treatments like cleaning, etching, functionalization or activation. Cleaning removes contaminants (oil, dust, oxides) from the treated surface. Etching removes a thin layer of material, the chemical and mechanical weak boundary layer, which can be formed during previous mechanical processing. Functionalizing of the surface can be done by depositing functional chemical on the surface without affecting the bulk properties [49]. Activation is done by grafting chemical functions to the material surface in order to get specific properties. This is done by affecting on the surface energy of material [49][97]. The gas composition influences what properties the treated surface will possess after the plasma treatment. All these can be applied also on wooden surfaces, to modify the surface properties without affecting the bulk properties [49][96][97].

Plasma treatment can change the wood surface to a very hydrophilic or hydrophobic, depending on the used gas. The water uptake of the wooden surface can be nearly stopped by using argon plasma where methane or acetylene is added. This can be used as a very environmental friendly method for wood preservation [97][98]. Hydrophilic surface is achieved with oxygen containing (e.g. air) plasma treatment. Extractives are oxidized, degraded and removed by plasma treatment. O/C-ratio of the treated surface is increased partially because of the expose of wood main components, cellulose and hemicellulose, which have high O/C-ratios [99][100], while chemically active oxygen containing polar groups like C–O, O–C–O and C=O are formed on the surface [45][46][101]. This increases the surface energy of the treated surface by increasing the polar part of it, therefore the contact angle is decreased and the wettability is increased [52][73][98][101][102][103].

Plasma treatment can be used to enhance penetration of solutions. Plasma treatment etches cell walls of tracheids causing them to become thinner, also large voids are created between cells when pit membranes and intervening cell walls are eroded by plasma. Not all cells are as easily etched by plasma, for instance, resinous ray cells are quite resistant to plasma and lignin is less susceptible to etching than cellulose. This different etching of cells creates flow paths for solutions to reach deeper penetration into wood [104][105].

Figure 17 shows effect of plasma etching on tangential longitudinal surface of redwood. When lumber is cut to boards, it is typically performed on a tangential longitudinal direction.

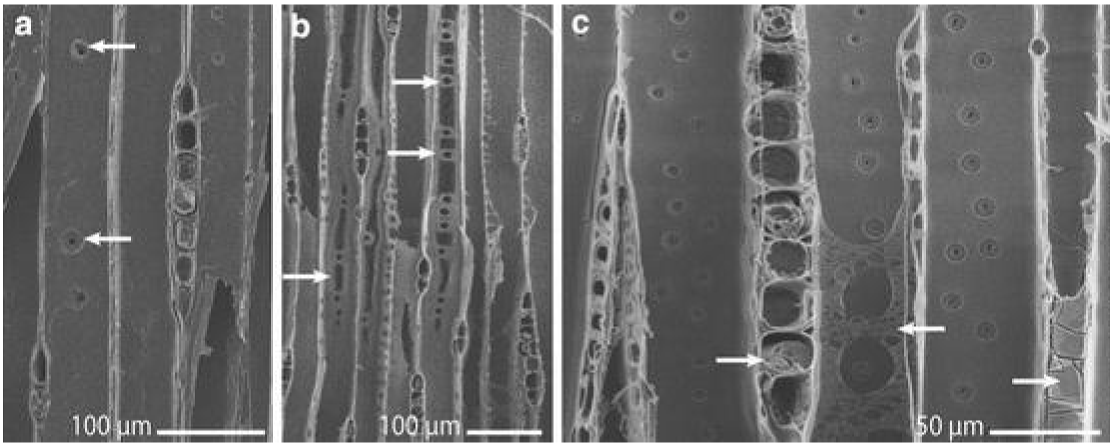


Figure 17. *Redwood seen from tangential longitudinal surface before and after plasma treatment: a. untreated earlywood with rays in a row at the centre and arrows showing pits of cells; b. earlywood and latewood after plasma treatment, arrow at the left showing etched cell walls and arrows at the centre showing remaining outer borders of etched pits; c. earlywood after plasma treatment arrows showing severe thinning and etching of cell walls [104].*

Plasma aided capillary impregnation by dipping, casting, spreading with roll, brush or by spraying with fire retardant water solutions based on nitrogen and phosphorous containing compounds was patented in 2006 [42]. According to the patent, plasma activation of wood surface and adding surfactant to fire-retardant solution provides maximum good spreading and impregnation of the solution, giving an increased fire spread and ignition resistance. Immobilization of fire retardant is claimed to be reached through chemical bonds between solution and chemically active groups formed on the treated surface.

Studies show that plasma pre-treatment of wood before applying fire-retardant results in slightly better fire retardancy. The mass loss is significantly smaller than without fire retardant and also a little smaller than with fire retardant without plasma pre-treatment. The formation of protective char layer starts at lower temperatures, thus the virgin wood within is protected with the char well before the ignition temperature of bare wood is reached [46][106].

4.3.4 Microwave treatment

To most people, microwave heating is familiar from kitchen and cooking. Industrial applications are not so different from the domestic use. Microwave heating is based on rapidly changing electric and magnetic fields. In an electric field, dipolar molecules, like water, are realigned as shown in Figure 18. Rapidly changing field makes the realignment happen a million times per second resulting in internal friction between molecules and causing the material to heat [107][108]. Typical frequencies used in domestic and industrial purposes are 0,922 GHz and 2,45 GHz, these frequencies are suitable for penetration to most of the materials. On wood, deeper penetration is achieved with lower frequency. The 0,922 GHz frequency be used for woods up to 450 mm thick. The 2,45 GHz frequency can be used for processing wood with thickness up to 90 mm or only for surface treatment of thicker woods [109].

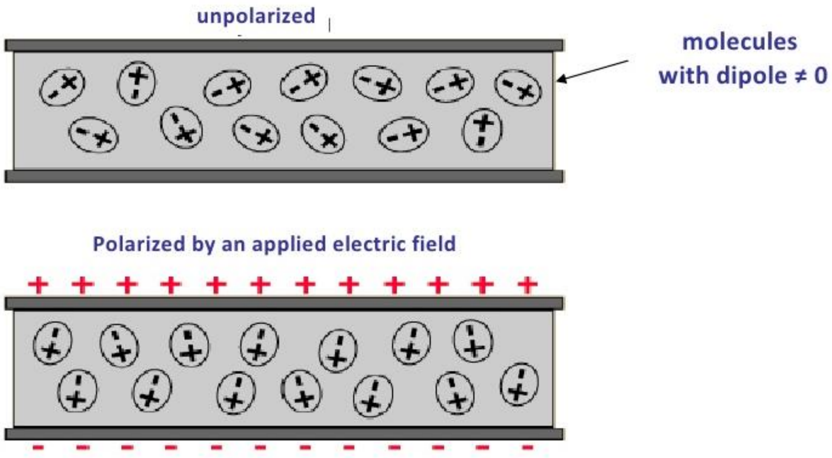


Figure 18. *The dipoles realign themselves according to the direction of the electrical field, and rapidly changing field makes the realignment to change continuously [110].*

The microwave treatment of wood causes the internal water in the wood cells to heat up and boil resulting in steam pressure within the wood cells to increase rapidly and create many small steam explosions. These small explosions cause destruction of the weakest wood cell walls and pit membranes, creating connections between cell cavities (Figure 19); and thus, they provide the easy transportation of vapours and liquids within the wood [111][112]. Resin is also affected by microwave energy. First it is softened by microwave energy and when heating continues, resin starts to melt and finally to boil. Steam pressure causes soft resin to be displaced from rays and leaving pores and cavities of wood. Therefore, microwave method is very effective to increase permeability of woods with high content of resin [111]. Because microwave treatment is based on rapid boiling of water, it works best on moist wood, moisture content of at least 15 %. Preferably method is applied to the “green wood” after sawing where wood´s moisture content varies, depending specie, between 30 % and 200 %, on dry basis [111].

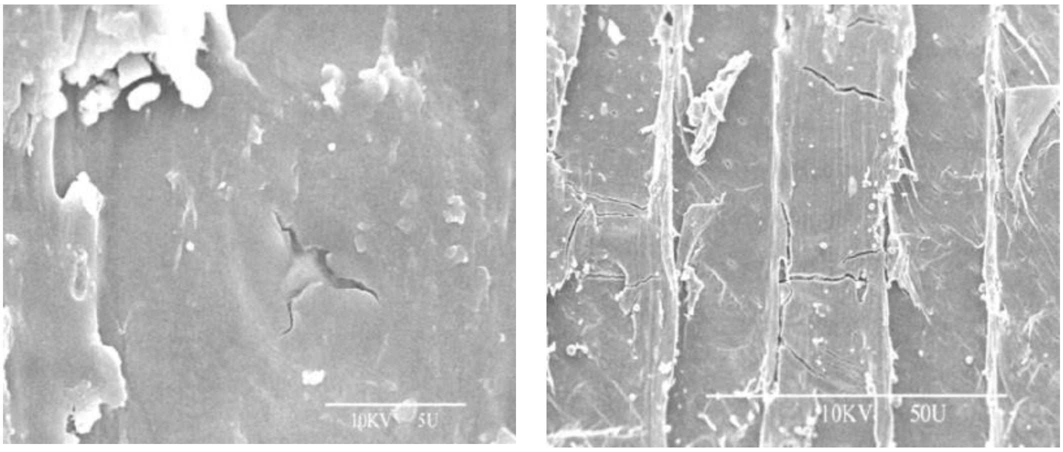


Figure 19. *The broken pit of earlywood (left) and tiny checks in the radial section of larch wood after microwave treatment [113].*

In wood industry, microwave energy is mainly used for drying of wood. It decreases significantly the drying time of timber compared to other methods. Microwave treatment results in less drying checks, more uniform moisture content profile of the wood and lower residual drying stresses [109][111][114][115]. For drying purposes, very low radiation intensities must be used to avoid any damages on wood. These low microwave intensities used for drying do not affect the strength properties of wood significantly, but permeability is increased in the range of 1,1 to 1,5 times [111][112][116]. Moderate intensity of microwave radiation can be used in the modification of wood. Wood permeability can be increased by a thousand fold, but mechanical strength is decreased. The strength loss increases as applied microwave energy increases. The high degree of modification can convert wood into a highly porous, almost sponge like, material with high number of cavities mainly in radial-longitudinal plane [111][112][115]. This high intensity microwave modification has an industrial application; it results in porous material, called Torgvin (Figure 20). It is infused with resin which flows to voids created by microwave radiation. Wood is then compressed to its original dimensions and resin is cured. End product, called Vintorg, has improved structural properties and resistance to decay [117].

Many wood species have naturally a very low permeability. This causes problems in timber processing when preservative or other chemical treatment is performed on wood. With microwave modification of wood, impermeable wood species become permeable and can be impregnated easily with resins, preservatives or other chemicals [109]. To get required degree of modification to wood, enough intensity has to be used to create high steam pressure within cells for rupturing the wood microstructure, but too much microwave power can lead to wood burning [109].

Figure 20. *Messmate sample after intensive microwave modification: natural wood (left) and a high degree microwave modified wood – Torgvin (right) [118].*

Microwave treatment before fire retardant impregnation increases permeability and thus higher loading and deeper penetration of fire retardant is obtained. Increase in these also improves performance in fire tests [119][120]. The microwave treatment does not have great impact on leaching. Test conducted with preservative treatment showed increase in penetration depth when exposure time increased, but on leaching, microwave pre-treatment had only minor effect [121]. This leaching can be assumed to apply on fire retardants too, if they do not react with wood or make complex inside the wood.

4.3.5 Steam treatment

Steam is used in wood industry to control the drying of lumber. Use of steam reduces the drying time and reduces drying checks. During heating period of drying, use of steam accelerates warming of wood without overdrying of the surface. This reduces microcracking of the surface. During drying period, steam prevents overdrying of the surface by delaying the evaporation of water from the surface. After drying, moisture gradient is typically very large, and lumber is not suitable for further processing. Drying stresses would cause deformations in planing and splitting. Conditioning wood with steam, the moisture gradient between surface and centre can be equilibrate. Surface absorbs some moisture at the same time as centre continues drying. [122]

Alexiou et al. [123] proposed that the steam pre-treatment accelerates drying due to increased air permeability and diffusivity of wood. Several studies have confirmed increase in both mentioned properties [124][125][126]. In these studies, the permeability is proposed to increase due to internal cracking and hydrolysis of pit toruses (Figure 21) [124][125]. On the contrary, Hukka et al. [122] did not notice the pre-steaming to accelerate drying and therefore did not agreed about increased permeability. Although, permeability was not measured in the study.

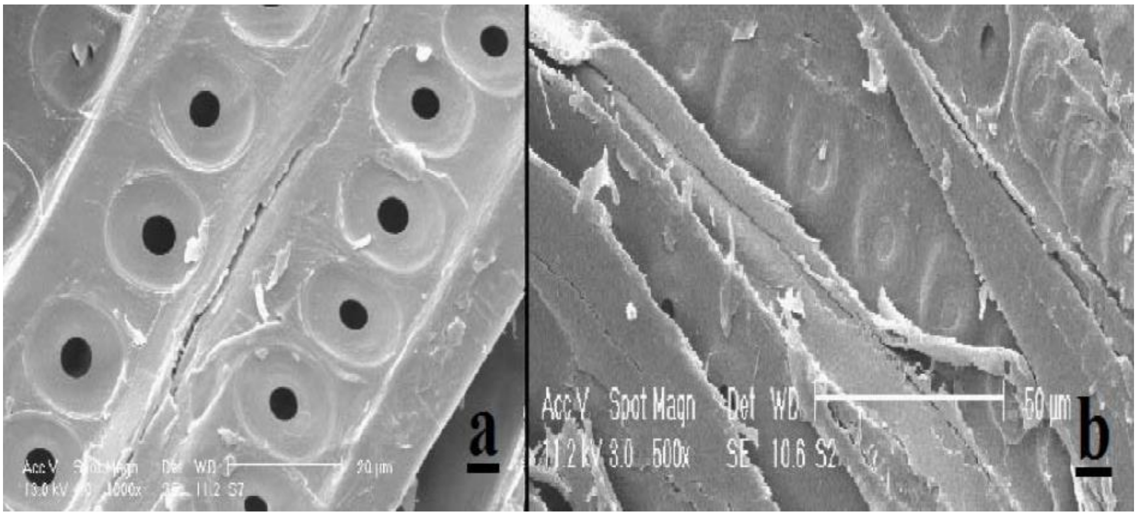


Figure 21. *Pits of fir wood specimen a. after steaming at temperature of 160°C compared to b. control specimen [124].*

Internal cracks and open pits create pathways to liquid flow resulting in increased uptake and deeper penetration of liquid [127][128][129]. Increase in solution uptake is higher right after steam treatment, but it does not last. After 24 hours solution uptake is at the same level as on untreated specimens [128]. Differences in solution uptake between heartwood and sapwood of the same wood were noticed by Matsumura et al. [129]. On sapwood, pre-steaming had only very minor effect, but on heartwood, the liquid uptake increased from 0,1 to 0,4 g/cm^2. Specimens with the highest solution uptake reported to have the highest degree of damages on pits and cell walls and lowest amount of extractives. Similar notes about removal of water soluble extractive have done also different authors [123][125][130], but also opposite results are reported [124].

Increase in penetration depth is reached only after several days of storage after treatment, not directly afterwards. This could be due to two reasons: 1) vacuum created in the center of the samples by continuous heating and cooling, this draws solution inside the wood during storage; and 2) elevated temperature of pre-steamed samples leads to faster rate of diffusion [127][128]. The increased penetration depth can be seen when steaming green wood. In dry specimens there are no significant difference between steamed and control samples [128]. Instead, steaming of dry wood increases surface roughness due to raised fibers [131], which could increase wettability of steamed surfaces.

Very different results about effects of steaming are reported. This indicates that wood specie and steaming condition have high impact on steaming effects. If steaming can impact on porous structure of wood in such a way that it facilitates fluid transfer, the permeability of wood is increased. Here the extractives play the important part. Higher extractive content is affected more by steam treatment [124][129]. On higher temperatures, decomposition of lignin was observed and loss of C=O groups, resulting in samples to become less water absorbent, but similar changes were not detected when steaming was performed at lower temperatures [132]. Depending author, temperature in steam treatment varies between 100°C and 180°C, and used pressures varies between atmospheric pressure and 3 bar pressure [124][125][126][128][129].

5. LEGISLATION, CLASSIFICATION AND TESTING OF FIRE RETARDANT WOOD

5.1 Health concerns of fire retardants

REACH regulation assesses registration, evaluation, authorisation and restriction of chemicals in EU region and it binds all the member countries. The main purpose of REACH is protection of human health and environment by placing more responsibility to industry. Instead of authorities, the industry is now accountable for safety of chemicals. All substances that are produced or imported to EU must be registered. Authorities can prohibit or restrict the use of dangerous chemicals if risks cannot be managed. Aim is to substitute most hazardous substances with less dangerous ones [134].

Over the past decades halogenated, especially bromine containing, fire retardants have been used very widely in different materials because of their effectiveness. But studies have shown that some of the halogenated compounds are harmful to human DNA and certain organs. They can also cause cancer and degenerative diseases. And during fire, some halogenated compounds form toxic gases causing environmental pollution which can sometimes be more disastrous than fire itself. Many of the halogenated fire retardants are mobile in the environment and are now found accumulated in the food chain, indoor air, dust and other common materials, causing serious human health concerns; exposure to halogenated fire retardants can happen through digestion, skin contact or inhaling [5][135][136]. These health concerns and growing awareness of environmental change have led restriction of many halogen containing substances [28] or they are added on the candidate list of very high concern for authorisation [137].

Restriction of halogen containing substances have risen a demand for non-halogenated, eco-friendly and effective fire retardants. Phosphorous and nitrogen-based fire retardants are commonly used alternatives for cellulosic materials as discussed earlier. Nitrogen does not evolve smoke or release dioxins and halogen acids during combustion. Combining nitrogen with phosphorus would provide good fire retardancy by covering the surface with a non-flammable char during combustion resulting an eco-friendly fire retardant with very limited smoke production. Good leach resistance could be achieved through a permanent chemical bond between phosphorus and cellulose [5].

5.2 European classification system

The European commission introduced Commission decision 2000/147/EC in February 2000 [138]. The purpose of this harmonized Euroclass system is to remove trade barriers by removing differences in classification and test methods between member countries of

EU. Previously, every country had their own national standards and classification system. Member countries can still decide the required fire performance of construction products, but the requirements have to be expressed according to harmonized standards [6].

The Euroclass system consists of two subsystems, one is meant for classifying construction products excluding floorings. This mainly means the products that are used in walls and ceilings. Another similar system classifies floorings. Both systems have classes from A to F, classes A1 and A2 are meant for non-combustible products. Classifications for floorings are denoted with $_{fl}$, for example B_{fl} [139]. Additional classification for smoke production are s1, s2 and s3, and for burning droplets/particles d0, d1 and d2 [138]. Natural wood with a sufficient density and thickness are usually classified into Euroclass D. Fire retardant wood can reach the requirements of Euroclass B, with additional classifications s1 and d0 [6].

5.3 Euroclass testing methods

Commission directive defines the classification of fire performance for construction products excluding floorings (Table 2) and classification for floorings (Table 3). Standard EN13501-1 [140] describes the harmonized testing procedure. The classification of construction products excluding floorings is based on four standardised test methods: the non-combustibility test EN ISO 1182 [141], the gross calorific potential test EN ISO 1716 [142], the single burning item test (SBI) EN 13823 [143], and the single-flame source test (the small flame test) EN ISO 11925-2 [144]. For floorings, the same tests are used excluding the SBI test and with addition of the radiant panel test EN ISO 9239-1 [145].

5.3.1 Non-combustibility test SFS-EN ISO 1182

The non-combustibility test EN ISO 1182 [141] is developed for testing homogenous products and identify the construction products that are inert or nearly inert to a fire. Cylindrical shape specimen is placed into a furnace with a temperature of 750 °C. Changes in temperature (ΔT) are measured with thermocouples and flaming is observed during the test. Mass loss (Δm) is recorded and calculated after the test. For A1 classification temperature rise must be less than 30 °C, mass loss under 50 % and no flaming can occur during the test. A2 classification allows 50 °C change at temperature, 20 second flaming during the test. Mass loss must be under 50 % as in A1 classification.

Table 2. *Classification of reaction to fire performance for construction products excluding floorings [140].*

Class	Test method(s)	Classification criteria	Additional classification
A1	EN ISO 1182 [a] and	$\Delta T \leq 30$ °C; and $\Delta m \leq 50$ %; and $t_f = 0$ (i.e. no sustained flaming)	-
	EN ISO 1716	$PCS \leq 2,0$ MJ/kg [a] and $PCS \leq 2,0$ MJ/kg [b c] and $PCS \leq 1,4$ MJ/m^2 [d] and $PCS \leq 2,0$ MJ/kg [e]	-
A2	EN ISO 1182 [a] or	$\Delta T \leq 50$ °C; and $\Delta m \leq 50$ %; and $t_f \leq 20$ s	-
	EN ISO 1716 and	$PCS \leq 3,0$ MJ/kg [a] and $PCS \leq 4,0$ MJ/m^2 [b] and $PCS \leq 4,0$ MJ/m^2 [d] and $PCS \leq 3,0$ MJ/kg [e]	-
	EN 13823	$FIGRA \leq 120$ W/s and $LFS <$ edge of specimen and $THR_{600s} \leq 7,5$ MJ	Smoke production [f] and Flaming droplets/particles [g]
B	EN 13823 and	$FIGRA \leq 120$ W/s and $LFS <$ edge of specimen and $THR_{600s} \leq 7,5$ MJ	Smoke production [f] and Flaming droplets/particles [g]
	EN ISO 11925-2 [i]: Exposure = 30 s	$F_s \leq 150$ mm within 60 s	
C	EN 13823 and	$FIGRA \leq 250$ W/s and $LFS <$ edge of specimen and $THR_{600s} \leq 15$ MJ	Smoke production [f] and Flaming droplets/particles [g]
	EN ISO 11925-2 [i]: Exposure = 30 s	$F_s \leq 150$mm within 60 s	
D	EN 13823 and	$FIGRA \leq 750$ W/s	Smoke production [f] and Flaming droplets/particles [g]
	EN ISO 11925-2 [i]: Exposure = 30 s	$F_s \leq 150$ mm within 60 s	
E	EN ISO 11925-2 [i]: Exposure = 15 s	$F_s \leq 150$ mm within 20 s	Flaming droplets/particles [h]
F	No performance determined		

[a] For homogeneous products and substantial components of non-homogeneous products.

[b] For any external non-substantial component of non-homogeneous products.

[c] Alternatively, any external non-substantial component having a $PCS \leq 2,0$ MJ/m^2, provided that the product satisfies the following criteria of EN 13823: $FIGRA \leq 20$ W/s, and $LFS <$ edge of specimen, and $THR_{600s} \leq 4,0$ MJ, and s1, and d0.

[d] For any internal non-substantial component of non-homogeneous products.

[e] For the product as a whole.

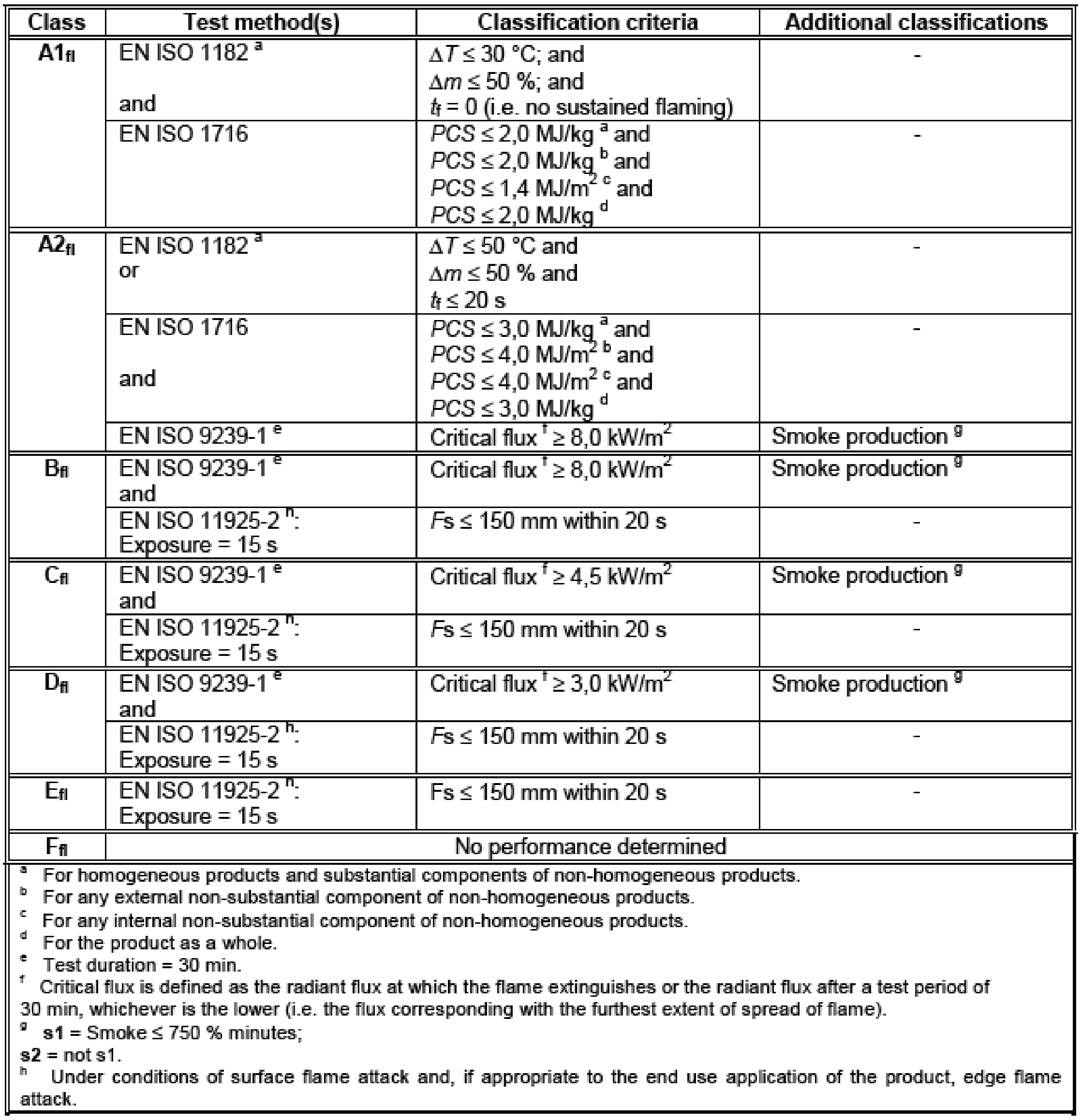
[f] In the last phase of the development of the test procedure, modifications of the smoke measurement system have been introduced, the effect of which needs further investigation. This may result in a modification of the limit values and/or parameters for the evaluation of the smoke production.
s1 = $SMOGRA \leq 30$m^2/s^2 and $TSP_{600s} \leq 50$m^2 ; **s2** = $SMOGRA \leq 180$m^2/s^2 and $TSP_{600s} \leq 200$m^2; **s3** = not s1 or s2

[g] **d0** = No flaming droplets/ particles in EN 13823 within 600 s;
d1 = no flaming droplets/ particles persisting longer than 10 s in EN 13823 within 600 s;
d2 = not d0 or d1.
Ignition of the paper in EN ISO 11925-2 results in a d2 classification.

[h] Pass = no ignition of the paper (no classification);
Fail = ignition of the paper (**d2** classification).

[i] Under conditions of surface flame attack and, if appropriate to the end–use application of the product, edge flame attack.

Table 3. *Classification of reaction to fire performance for floorings [140].*



Class	Test method(s)	Classification criteria	Additional classifications
A1$_{fl}$	EN ISO 1182 ^{a} and	$\Delta T \leq 30$ °C; and $\Delta m \leq 50$ %; and $t_f = 0$ (i.e. no sustained flaming)	-
	EN ISO 1716	$PCS \leq 2{,}0$ MJ/kg ^{a} and $PCS \leq 2{,}0$ MJ/kg ^{b} and $PCS \leq 1{,}4$ MJ/m^{2} ^{c} and $PCS \leq 2{,}0$ MJ/kg ^{d}	-
A2$_{fl}$	EN ISO 1182 ^{a} or	$\Delta T \leq 50$ °C and $\Delta m \leq 50$ % and $t_f \leq 20$ s	-
	EN ISO 1716 and	$PCS \leq 3{,}0$ MJ/kg ^{a} and $PCS \leq 4{,}0$ MJ/m^{2} ^{b} and $PCS \leq 4{,}0$ MJ/m^{2} ^{c} and $PCS \leq 3{,}0$ MJ/kg ^{d}	-
	EN ISO 9239-1 ^{e}	Critical flux ^{f} $\geq 8{,}0$ kW/m^{2}	Smoke production ^{g}
B$_{fl}$	EN ISO 9239-1 ^{e} and	Critical flux ^{f} $\geq 8{,}0$ kW/m^{2}	Smoke production ^{g}
	EN ISO 11925-2 ^{h}: Exposure = 15 s	$Fs \leq 150$ mm within 20 s	-
C$_{fl}$	EN ISO 9239-1 ^{e} and	Critical flux ^{f} $\geq 4{,}5$ kW/m^{2}	Smoke production ^{g}
	EN ISO 11925-2 ^{h}: Exposure = 15 s	$Fs \leq 150$ mm within 20 s	-
D$_{fl}$	EN ISO 9239-1 ^{e} and	Critical flux ^{f} $\geq 3{,}0$ kW/m^{2}	Smoke production ^{g}
	EN ISO 11925-2 ^{h}: Exposure = 15 s	$Fs \leq 150$ mm within 20 s	-
E$_{fl}$	EN ISO 11925-2 ^{h}: Exposure = 15 s	Fs ≤ 150 mm within 20 s	-
F$_{fl}$	No performance determined		

[a] For homogeneous products and substantial components of non-homogeneous products.
[b] For any external non-substantial component of non-homogeneous products.
[c] For any internal non-substantial component of non-homogeneous products.
[d] For the product as a whole.
[e] Test duration = 30 min.
[f] Critical flux is defined as the radiant flux at which the flame extinguishes or the radiant flux after a test period of 30 min, whichever is the lower (i.e. the flux corresponding with the furthest extent of spread of flame).
[g] **s1** = Smoke ≤ 750 % minutes;
s2 = not s1.
[h] Under conditions of surface flame attack and, if appropriate to the end use application of the product, edge flame attack.

5.3.2 Gross calorific value test SFS-EN ISO 1716

The calorific value test SFS-EN ISO 1716 [142] is suitable for homogenous and non-homogenous products. The test determines the gross heat combustion (PCS) of a sample when burned completely. Sample that is grinded to powder is placed inside the calorimetric bomb which is surrounded by water jacket. Sample is then ignited in pressurized oxygen atmosphere. The gross heat of combustion is calculated based on the sample mass, temperature rise, and correction factors related to the specific test arrangement. Required values for the gross heat combustion for different classifications are shown in Table 2 and Table 3.

5.3.3 Single burning item test SFS-EN 13823

The single burning item test SFS-EN 13823 [143] is new fire testing method developed for Euroclass classification system. The specimen is constructed from two wings of sizes 1,0 m x 1,5 m and 0,5 m x 1,5 m and the testing material is mounted on non-combustible boards. The thermal exposure of test comes from triangle-shaped propane burner placed at the corner formed by the specimen wings. During the test, the heat release rate (HRR) and the smoke production rate (SPR) is measured. Additionally, flaming droplets and lateral flame spread (LFS) on the long wing are observed. The fire growth rate (FIGRA) and total heat release rate during first 10 minutes (THR_{600s}) are calculated. Based on FIGRA, LFS and THR_{600s} the product is classified in accordance with Table 2.

5.3.4 Single-flame source test SFS-EN ISO 11925-2 (small flame test)

In the single-flame source test SFS-EN ISO 11925-2 [144] the sample is subjected to direct impingement of a small flame. It demonstrates ignition of a product when exposed to a match size flame. The test is performed in a combustion chamber, where the test specimen of size 250 mm x 90 mm is vertically attached to a holder. Small flame height of 20 mm is tilted to angle of 45 degrees and brought into contact with the sample. The contact point of flame is either 40 mm above the bottom edge at the centreline of sample surface or at the centre of bottom edge. The filter paper is placed beneath the sample to observe falling of flaming particles.

The exposure time for flame is 15 seconds for classification E and 30 seconds for classification B, C, D. The 15 second test is terminated 20 seconds after the first application of flame and the 30 second test is terminated after 60 seconds. To pass the test, flame is not allowed to spread over 150 mm height from application point during the test. Also, time to possible ignition of the sample, burning droplets and ignition of the filter paper below the sample are observed and registered.

5.3.5 Radiant panel test SFS-EN ISO 9239-1

In the radiant panel test SFS-EN ISO 9239-1 [145] a sample size of 230 mm x 1050 mm is placed horizontally under a radiant panel tilted by 30 degrees. The purpose of the test is to estimate the behaviour of floorings at early stages of a fire when upper surfaces are heated by flames or hot gases. The radiant panel exposes the sample to a heat flux of 10,9 kW/m^2 at hotter end, which is closer to the panel, and decreasing to 1,1 kW/m^2 at further end of the sample. To the hotter end of the sample, a pilot flame is applied on the sample surface for 10 minutes time. The spread of flame is observed, and the distance is converted to critical heat flux. The samples which do not ignite, or flame spread is less than 110 mm have critical heat flux of $\geq 11\ kW/m^2$. Test specimens flame spread over 910 mm have critical heat flux of ≤ 1,1 kW/m^2. The test ends when the sample extinguishes, or 30 minutes time is reached, whichever is happens first. The classification is determined based on the critical heat flux according to Table 3.

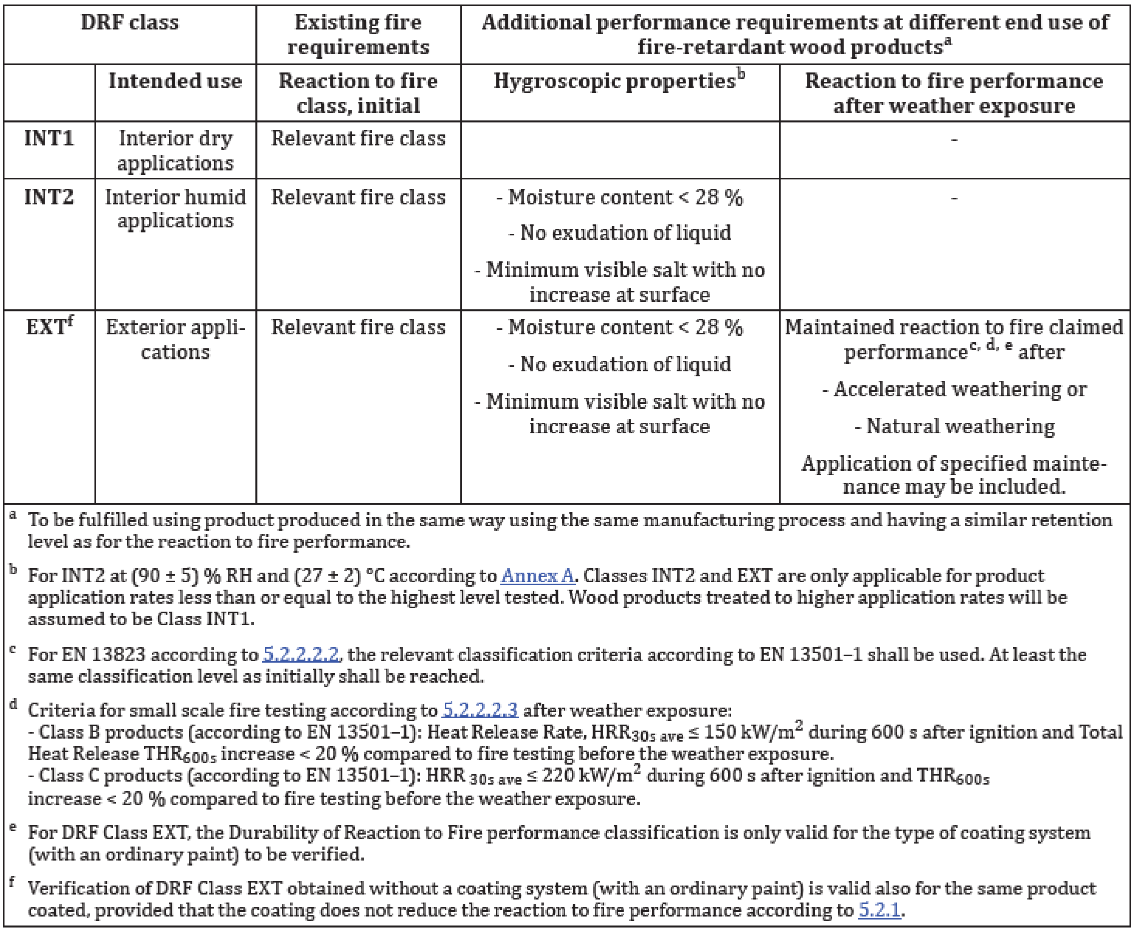
5.4 Durability of fire-retardant treated wood

The standard SFS-EN 16755:2017 [146] durability of reaction to fire performance describes the characteristics which fire-retardant treated wood should fulfil so that the fire-retardant properties are maintained through the desired service life in the estimated use conditions (Table 4). There are three classes for the durability of reaction to fire performance (DRF). DRF class INT1 is for permanent indoor use for dry applications and only initial fire class is reported. DRF class INT2 is for permanent indoor use for humid applications and hygroscopic properties at (90 ± 5) % and (27 ± 2) °C is tested. The equilibrium moisture content shall be less than 28 %.

For permanent exterior applications, the standard is DRF class EXT. In addition to hygroscopic properties testing, products intended for outdoor use should maintain their fire performance after weathering. The standard gives two test methods for accelerated weathering. In a method A the specimens are exposed to twelve one-week cycles. Each cycle consists of 96 hours of water exposure and 72 hours of drying. In method B the specimens are exposed to a 24-hour cycle which consists of 4 hours wetting, 4 hours drying, 4 hours wetting, 4 hours drying and 8 hours rest. Exposure to the ultraviolet lamp is continuous through the drying period. This cycle is carried out for six weeks. The maintained fire class performance is tested with the SBI-test. It is also possible to perform a small-scale testing with a cone calorimeter. To compare fire performance before and after weathering also testing the product before weathering is needed.

In the cone calorimeter test, the specimen size of 100 x 100 mm is placed vertically in a sample holder, which is then placed on a loading cell. A cone heater exposes sample to a constant heat flux and pyrolysis products released from the sample are ignited with an electric spark igniter. All the combustion gases are collected into a fume hood above the heater and smoke production is measured. These are analysed, and test report provides data about heat release, ignitibility, smoke production and mass loss [147].

Table 4. *Requirements for durability of reaction to fire performance classes of fire-retardant treated wood products used in interior and exterior applications [146].*



DRF class		**Existing fire requirements**	**Additional performance requirements at different end use of fire-retardant wood products**[a]	
	Intended use	**Reaction to fire class, initial**	**Hygroscopic properties**[b]	**Reaction to fire performance after weather exposure**
INT1	Interior dry applications	Relevant fire class		-
INT2	Interior humid applications	Relevant fire class	- Moisture content < 28 % - No exudation of liquid - Minimum visible salt with no increase at surface	-
EXT[f]	Exterior applications	Relevant fire class	- Moisture content < 28 % - No exudation of liquid - Minimum visible salt with no increase at surface	Maintained reaction to fire claimed performance[c, d, e] after - Accelerated weathering or - Natural weathering Application of specified maintenance may be included.

[a] To be fulfilled using product produced in the same way using the same manufacturing process and having a similar retention level as for the reaction to fire performance.

[b] For INT2 at (90 ± 5) % RH and (27 ± 2) °C according to Annex A. Classes INT2 and EXT are only applicable for product application rates less than or equal to the highest level tested. Wood products treated to higher application rates will be assumed to be Class INT1.

[c] For EN 13823 according to 5.2.2.2.2, the relevant classification criteria according to EN 13501–1 shall be used. At least the same classification level as initially shall be reached.

[d] Criteria for small scale fire testing according to 5.2.2.2.3 after weather exposure:
- Class B products (according to EN 13501–1): Heat Release Rate, $HRR_{30s\ ave} \leq 150\ kW/m^2$ during 600 s after ignition and Total Heat Release THR_{600s} increase < 20 % compared to fire testing before the weather exposure.
- Class C products (according to EN 13501–1): $HRR_{30s\ ave} \leq 220\ kW/m^2$ during 600 s after ignition and THR_{600s} increase < 20 % compared to fire testing before the weather exposure.

[e] For DRF Class EXT, the Durability of Reaction to Fire performance classification is only valid for the type of coating system (with an ordinary paint) to be verified.

[f] Verification of DRF Class EXT obtained without a coating system (with an ordinary paint) is valid also for the same product coated, provided that the coating does not reduce the reaction to fire performance according to 5.2.1.

6. MATERIALS AND METHODS

6.1 Wood materials

Commercially available pine boards were used in the tests. The wood boards were planed and delivery length was approximately 240 cm, width and thickness were 9,2 cm and 1,5 cm, respectively. The preparation of wood for each test is described later with the description of each test setup. Only boards without knots and visibly identifiable parts of heartwood were selected.

Wooden commercial tongue depressors were used in quick and small-scale leaching tests to evaluate the leaching properties of the fire retardants applied on wood. They were made from birch and their size was 150 x 18 x 1,6 mm^3. Testing of these is described in the chapter 6.7.2 In-house UL 94.

In the cone calorimeter and the radiant panel tests, bigger pine board and spruce plywood samples were used. The bigger pine boards had length, width and thickness of 105 cm, 12 cm and 2,8 cm, respectively. To achieve adequate width for the radiant panel test, two pine boards were glued together. The spruce plywood had length, width and thickness 160 cm, 160 cm and 1,8 cm, respectively. Suitable sample sizes for both tests were cut and planed from these boards. The spruce plywood was used for comparative purposes; due to its absorption properties, higher loadings of fire retardants were attained.

6.2 Fire retardant chemicals

In this study, two fire retardants - reactive and two-component - were used. In both, the fire retardancy is based on synergistic effect of phosphorus and nitrogen. The reactive fire retardant (FR-R1) was expected to bond with some of the active sites of wood. Working method of the two component fire retardant (FR-TC) was to form a metallic salt inside wood cells. Based on first tests, the reactive fire retardant looked more promising and therefore more testing was performed by using that one. Also, some development in the recipe of the reactive fire retardant was done along testing. Surfactants were added to achieve more uniform spreading and deeper penetration into the wood surface. Catalyst was added to enhance bonding of fire retardant and wood compounds. Activation of the catalyst was done by placing samples at 190°C for five minutes after applying the fire retardant. This new recipe for the reactive fire retardant was named FR-R2.

The reactive fire retardant was manufactured through synthesis with chemicals containing phosphorous and nitrogen. The end product was powder, from which 30 % water solution was made. This solution was very acidic, pH under 1. Very acidic solution will degrade wood surface, therefore pH was adjusted with ammonium hydroxide. Finally, the solid content of the solution was 25,2 %. In the two-component fire retardant, the first component was 20 % water solution containing phosphorous and nitrogen. The second component was 25 % water solution containing metallic cation, and phosphorus and nitrogen.

6.3 Surface treatment methods

External claddings are installed heartwood side out because it is less susceptible to crack than sapwood side [149][150]. It is also more difficult to get penetration on the heartwood side [66][151]. If good penetration is achieved on the heartwood side, the sapwood side should be even easier to treat. And as discussed earlier, both sides of the material should be fire retardant treated to prevent the back-side ignition due to heat. Therefore, heartwood side was chosen to be the testing side in this study.

Before applying fire retardant on the surface, a surface pre-treatment was performed. Purpose of the pre-treatments was to re-activate the wood surface to achieve more even spreading and deeper penetration of the fire retardant. The used methods were planing, sanding, plasma treatment, microwave treatment, steam treatment and steam treatment followed by roasting. Samples without a pre-treatment were prepared to compare effectiveness of the pre-treatments. Also soaking was used as a one fire retardant adding method to compare achieved penetration depths.

6.3.1 Planing

Planing was performed with Olsa D951 planer. Approximately one millimeter was planed away from the surface. After the planing, fire retardant was applied on the surface during the same day.

6.3.2 Sanding

Sanding was performed with an electric handheld sander, Powerplus pow400 (Figure 22). Vibrating speed was 13000/min and used sandpaper was 150 grit. After the sanding, dust was removed from the surface with pressurised air. After the cleaning, fire retardant was applied on the surface during the same day.

Figure 22. *The electric handheld sander was used for sanding of samples.*

6.3.3 Plasma treatment

Plasma treatment was performed with Tantec Plasma Tec-X (Figure 23). The nozzle was kept in 45 degrees angle and the distance to the sample surface was one centimeter. The sample was moved under the nozzle so that the whole surface of the sample was treated. This took 2,5 minutes per sample. After the plasma treatment, the treated samples were let cool down at 23 °C and RH 50 % approximately 15 minutes before applying fire retardant to the surfaces so that heat of the surface did not have effect on the penetration.

Figure 23. *The setup of the plasma treatment device.*

6.3.4 Microwave treatment

Samples were microwave treated in a domestic Kenwood microwave oven, model K30CSS14E. Oven works at 2450 Hz frequency and power output is 900 W. Samples were treated individually in the oven (Figure 24). Treatment time was one minute at the full 900 W power. The treated samples were let cool down at 23 °C and RH 50 % approximately 30 minutes before applying fire retardant. The samples heated more in the microwave treatment than in the plasma treatment, thus longer stabilizing time was needed.

Figure 24. *The setup of the microwave treatment.*

6.3.5 Steam treatment

Steam treatment was performed in atmospheric conditions by heating a water bath to the boiling point. Samples were supported above boiling water so that they were subjected to rising steam. Samples were kept exposed to the steam for one hour. After the steam treatment, the samples were kept in a plastic bag at 23 °C for one hour to cool down and still prevent drying. After one hour, fire retardant was applied on the surfaces.

6.3.6 Steam treatment and roasting

The steam treatment was combined with roasting (thermal treatment) to inactivate surfaces after applying a fire retardant. Inactivation makes wood surface more hydrophobic; and thus, it prevents water from penetrating inside the wood and then leaching out of a fire retardant.

Steaming was performed similarly to 6.3.5 Steam treatment, meaning that the samples was kept one hour above the boiling water bath. Fire retardant was applied on the sample surfaces and samples were stabilized at 23 °C and RH 50 % for three days. The samples were then roasted in an oven at 160 °C for 30 minutes and cooled down in a desiccator.

6.3.7 Soaking

For soaking purposes, ends of the samples were sealed with the two component glue to prevent solution from penetrating from end grains. In practice, the board are longer, and penetration reaches only certain distance from the ends. Coating the ends simulated the situation in the middle parts of the board where fire retardant is able to penetrate only from the surface.

The samples were immersed in the fire-retardant solution for four hours when the reactive FR-R1 fire retardant was used. For the two-component FR-TC fire retardant, the samples were immersed in the first solution for two hours and then kept for three days at 23 °C and RH 50 % before they were immersed in the second solution for two hours. After the second immersion, the samples were again stabilized for three days at 23 °C and RH 50 %.

6.4 Contact angle measurement

For contact angle measurements, 5 cm long samples were cut from the 9,2 cm wide wood boards and prepared with different pre-treatments. Four samples from four different boards were treated the same way and 10 measurements were performed for each sample. This resulted in at least 40 measuring points for each pre-treatment. Contact angel measurement was used to test different parameters for pre-treatments and sometimes measurements were conducted again to verify results. When trying to find these suitable treatment parameters for each pre-treatment, always the not pre-treated wood was included to the contact angle measurements as a starting point. At the end of the measurements, total of 200 contact angle values had been measured for not pre-treated wood.

Contact angle measurements were performed with an automatic contact angle measurement device (Attension Theta tensiometer), which was equipped with an automatic video measuring system. The used probe liquid was distilled water. A sample was positioned on a sample stage and a sessile drop volume of 3 µm was placed on the sample surface with an automatic syringe. At the same time, the camera started to record, and the program measured the angle between the surface and the sessile drop. The program recorded the left and the right side angle of the sessile drop and calculated the average of these. Five seconds after the sessile drop had been dropped on the surface the value of this average was recorded as the contact angle. The sessile drops were placed in a row from one side to another, regardless of latewood or earlywood. Measuring direction was parallel to fiber orientation (Figure 25). Measurements were done within an hour after surface pre-treatment to avoid the aging of the surface.

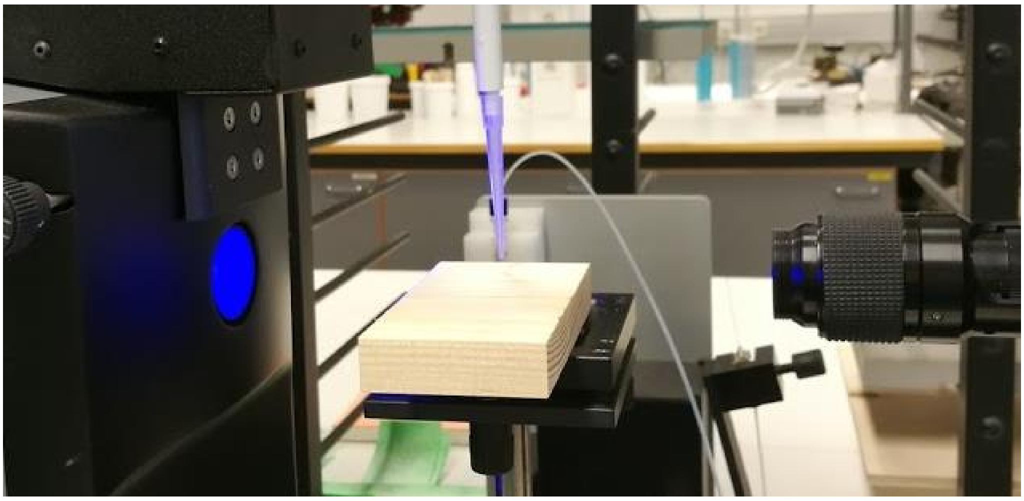


Figure 25. *Contact angle measurement. A sessile drop was placed on the surface with an automatic syringe (middle), camera (right) started to record the contact angle formed by the drop. Camera detects the drop on a direction parallel to the fiber orientation. Measurements were done in a row from one side (back in the figure) to another (front in the figure).*

6.5 Liquid uptake

The 9,2 cm wide boards were cut to 25 cm long samples, this is standard sample size for the small flame testing. After a pre-treatment of surface, fire retardant solution was applied on the treated surface with a brush. The samples were kept in a vertical position when fire retardant was applied. This way real differences in absorption properties can be observed when the excess fire retardant flows away. In the horizontal application position, some of the applied fire retardant would stay as a puddle on the surface and would penetrate slowly to the porous wood. Application of the fire retardant was done twice; the second layer was applied after drying of the first one (1-2 hours). In the two-component FR-TC fire retardant, the component number one was applied first and the component number two was used as the second layer. The liquid uptake of each sample was calculated by weighting samples before and after the fire retardant was applied.

6.6 Penetration depth

The amount of fire retardant on the surface of sample does not give any information about the penetration depth. Therefore, scanning electron microscope (SEM) analyses were performed. Small, 1,5 cm x 1,5 cm, samples were cut with a circular saw from the differently pre-treated samples on which FR-R1 fire retardant was applied. Also, a sample from not pre-treated wood with FR-R2 on the surface was prepared. Samples were prepared in a way that it was possible to analyse the penetration depth of the fire retardant from a cross-section surface. An epoxy resin was applied on the surface and impregnated into the cells with vacuum to prevent the cells from collapsing. The resin surface was grinded to achieve a perfectly smooth surface for the SEM analysis.

The SEM analyses of the samples was performed at Åbo Akademi University using LEO Gemini 1530 SEM. It had x-ray detector that was able to detect elements onwards from beryllium. It was also equipped with a SE (secondary electron), a BSE (backscattered electron) and an In-Lens detector. The SEM analysis made it possible to get a high magnification image from the surface and x-ray imaging gave information about the position of phosphorus in the sample.

The x-ray imaging was used to collect information about the penetration depth of the fire retardant. The x-ray gave atomic percentage values of phosphorus in every pixel. Through histogram analyses, 0,03% was chosen to be a significant value for phosphorus. The average penetration depth of the fire retardant was calculated by counting the all the pixels containing phosphorus and calculating the average depth of these. The width of every image was 512 pixels and the height was 389 pixels. Also, the deepest individual penetration depth of every sample was recorded.

6.7 Burning methods

Different burning methods were used to find a suitable in-house test method. Single burning item (SBI) test is the test which determines the classification of wall materials. It is a big and expensive test and thus it is not sensible to build for an in-house method. Therefore, fast and small-scale burning methods are needed for research and development purposes. Cone calorimeter and radiant panel tests are smaller, but testing can take time up to one hour per sample. The cone calorimeter test results can give some indication about performance in SBI test, but they are not always directly comparable. The radiant panel test is a standard method for floorings, but results do not correlate with performance in the SBI test.

To compare fire performance of large series, a fast and easy burning method was needed. The small flame test and the blow torch method was used in this study to evaluate the fire performance of samples. Also, the in-house UL 94 test was used to compare the fire retardants.

6.7.1 Small flame test

For the small flame test, 25 cm long pieces were cut from the 9,2 cm wide boards. Seven samples of each pre-treatment were prepared. This makes total of 56 samples for FR-TC and FR-R1 fire retardant solutions excluding references. Later, five samples with improved recipe of the reactive fire retardant with additives (FR-R2) were tested without any surface pre-treatment, as well. The samples were stabilized at 23 °C and RH 50 % for three days after the fire retardants were applied. Before performing the small flame test, the samples were dried in an oven at 105 °C temperature for two hours and cooled in a desiccator. This was done to remove the effect of water on the fire performance and so moisture content of the wood demonstrated "the worst-case scenario" when the humidity of air is very low. The humidity of air changes depending of the weather and the season, and the moisture content of the wood follows this cycle.

The small flame test setup is shown in Figure 26. Differing from the standard, the samples were exposed to a flame for three minutes to see more differences; 30 seconds is a very short time for wood. The samples were extinguished after two minutes the flame was removed if no self-extinguishment happened. The mass changes of the samples were recorded, also other observations were made during the burning, including formation of black area, ignition of the sample, flame reaching 10 and 15 cm lines and afterburn time.

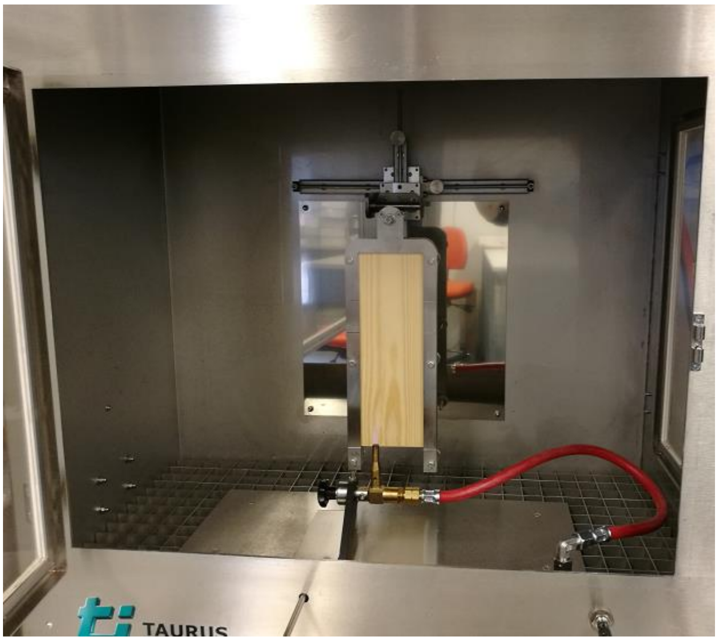


Figure 26. *Test setup of the small flame test. At the beginning of the test the flame was tilted to the 45-degree angle, the door was closed, and the flame was moved to touch the surface of the sample.*

6.7.2 In-house UL 94

UL 94 [152] test is meant for testing flammability of polymer materials that are used for parts and devices. In the test, the sample size of 125 x 13 x 3 mm^3 is subjected to a flame height of 20 mm. The test is performed on horizontally and vertically position samples. In the horizontal test, a sample is exposed to the flame for 30 seconds and proceeding of burning is recorded. In the vertical test, the sample is exposed to the flame for 10 seconds.

As soon as flaming of the sample ceases, the flame is brought back under the sample and kept there for an additional 10 seconds. Afterflame and afterglow times are recorded.

Parameters of the vertical UL 94 test was used to test commercial wooden tongue depressors in the small flame cabin. The fire retardants were applied on the surface by dipping the tongue depressors into the fire retardant solution for 1-2 seconds. After three days conditioning at ambient environment, the samples were tested in the small flame cabin. The samples positioned in the vertical position were exposed to the flame for 10 seconds as shown in Figure 27. If fire ceased after removal of the flame, the sample was exposed to the flame for additional 10 seconds. The mass changes of the samples in burning was recorded.

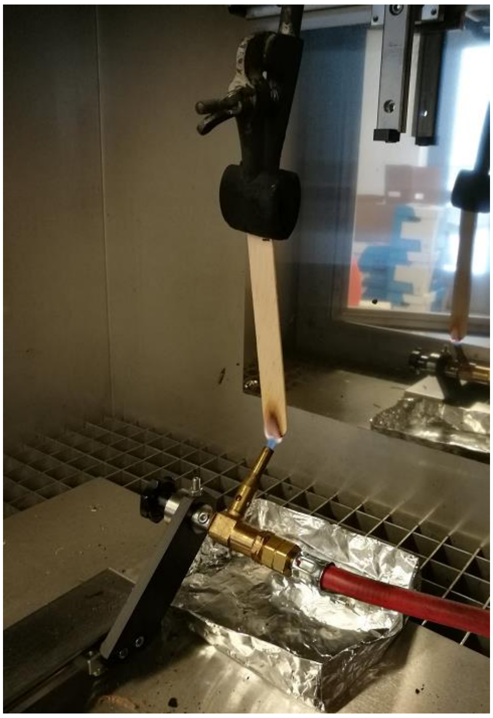


Figure 27. *The test setup for the in-house UL 94 test. The small flame cabin and the two centimeter flame was used. A clamp was used to attach the sample to the cabin´s frame holder.*

6.7.3 Blow torch burning

The small flame test was quite inefficient to burn wooden boards, so efficient but still fast burning method was needed for further testing of the wood samples. Blow torch produced big flame but testing principle was the same as in the small flame testing. The test setup for the blow torch testing is presented in Figure 28. The samples were prepared similarly as on the small flame test; a 25 cm long piece was cut from the 9,2 cm wide boards, a pre-treatment was performed, and a fire retardant was applied on the surface. Distance of the torch nozzle from the sample surface was 11 cm and height from the table surface was

8,5 cm. The sample was subjected to the flame for 30 seconds, the mass change in burning was measured for each sample.

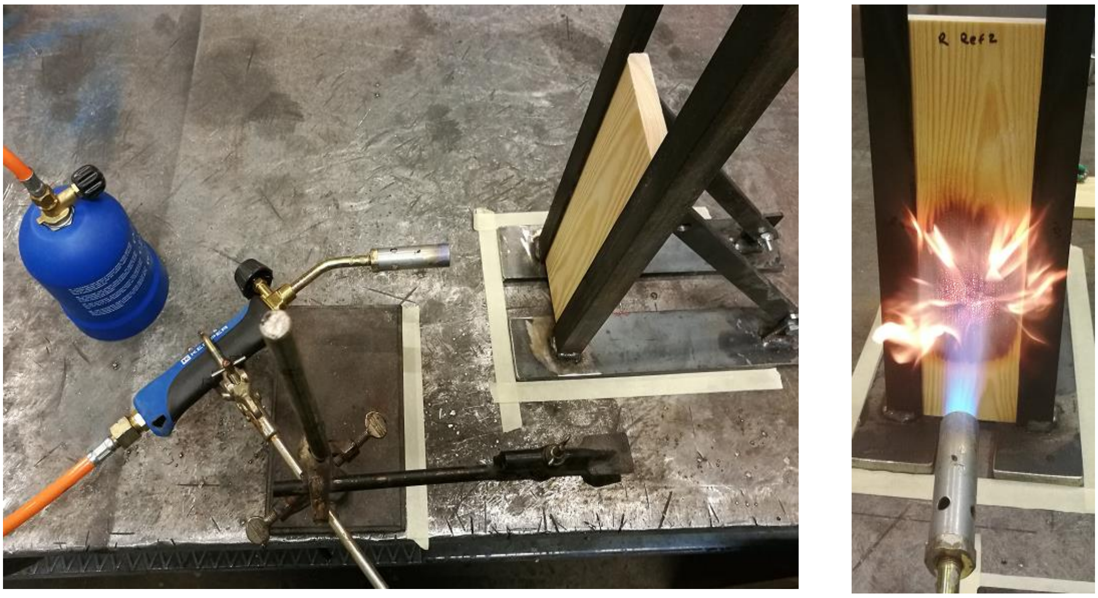


Figure 28. *Left: the test setup for the blow torch testing. Right: the blow torch flame on a fire retarded wood surface.*

6.7.4 Cone calorimeter test

Cone calorimeter tests were performed at Åbo Akademi University using the cone calorimeter manufactured by Fire Testing Technology. The samples, size of 10 x 10 cm^2, were placed on a horizontal position. The samples were 25 mm from the conical heat source and exposed to a 50 kW heat flux. Recorded values were heat release rate (HRR) and total smoke release (TSR). Schematic presentation of the cone calorimeter test is shown in Figure 29.

The cone calorimeter test was performed for FR-R2 fire retardant. The fire retardant amounts of 250 g/m^2 and 300 g/m^2 were applied on the planed pine board samples. Thickness of these samples was 2 cm. Heartwood and sapwood sides were both tested. Also tests for 1,8 cm thick spruce plywood samples were performed with 300 g/m^2 and 400 g/m^2 fire retardant loadings.

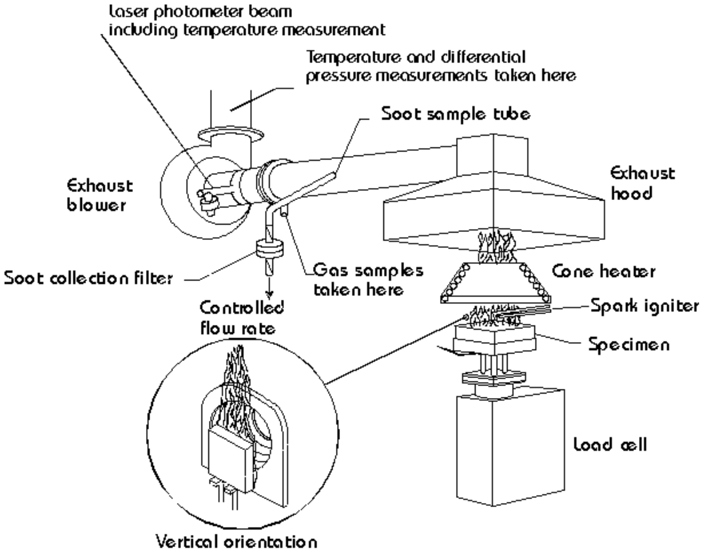


Figure 29. *Schematic presentation of the cone calorimeter test setup [148].*

6.7.5 Radiant panel test

Radiant panel test (Figure 30) was performed with the radiant panel device, manufactured by Fire Testing Technology. The tested samples were pine boards size of 2,8 x 23 x 105 cm^3. For these samples FR-TC and FR-R1 were used. Later, the radiant panel test was performed to FR-R2 fire retardant which was applied on a spruce plywood. Used sample size was 1,8 X 23 x 60 cm^3, rest of the sample holder opening was covered with a rock sheet. Shorter sample size can be used if it is expected that the sample do not burn to the end. Direct classification propose was given by the test program. The tests were performed according to the standard.

Figure 30. *Radiant panel test equipment. A reference sample is burning inside the cabin.*

6.8 Leaching

To determine which fire retardant should be used to more comprehensive leaching studies, a fast leaching test was performed with the tongue depressors. Fire retardant treated samples were immersed to distilled water for two hours. After drying three days in ambient conditions, the samples were tested using the in-house UL 94 test.

Leaching of the fire retardants from the solid pine boards was tested by immersing the treated samples to distilled water and the blow torch burning was performed after drying. Three to five parallel samples were prepared for different leaching times, which were 1, 3, 7, 16, 31 and 79 hours. This test method was modified from standard ENV 1250-2 meant for leaching studies for preservatives [34]. In that test, five small 25 x 15 x 50 mm^3 size test pieces are immersed in 500 ml of distilled water. Water is stirred thorough the whole test and changed after one hour. Second water change is two hours after the first change. Later the time interval for water change is 4, 8, 16 and 48 hours. In this study, no water change or stirring was performed. According to Lebow et al. [153] the stirring of water had no significant effect on leaching tests.

Five parallel samples of FR-R2 fire retardant without pre-treatment were prepared for the first leaching test. The parallel samples were placed in the same container where was 6,9 litres of distilled water. This water amount was calculated from the standard ENV 11250-2 to correlate the treated surface area used in this study. Both sides of the samples were treated with the fire retardant to obtain the adequate water amount where the samples could be immersed. Five samples without fire retardant were also immersed to distilled water for 79 hours to test the effect of water immersion on the burning properties of plain wood. After leaching, the samples were dried to constant mass at 60 °C and stabilized 3-5 days at 23 °C and RH 50 % before the blow torch burning. Leachate waters of these samples were collected and leached phosphorus amount was analysed with the inductively coupled plasma, ICP (Agilent Technologies 5110 ICP-OES) at Tampere University of Technology. In order to develop an in-house method for analysing leachate waters, these same waters were analysed at Kiilto Oy with X-ray fluorescene, XRF (PANanalytical Epsilon3-XL).

Further leaching tests were performed for FR-TC and FR-R2 fire retardants. For FR-R2 retardant, the used pre-treatment methods were planing, sanding, plasma treatment, steam treatment and steam treatment followed by roasting. Also no pre-treatment method was performed for repetitive purposes. Three parallel samples for the different leaching times were prepared and the parallel samples were placed in the same container where was 3,5 litres of distilled water. After leaching, the samples were dried to a constant mass at 60 °C and stabilized 3-5 days at 23 °C and RH 50 % before the blow torch burning. For FR-TC fire retardant, the leaching test was performed on the samples without any pre-treatment method.

7. RESULTS AND DISCUSSION

In this study, the surface pre-treatments methods before the fire retardant treatment was investigated. The purpose of the pre-treatments was to enhance the wettability and penetration of the fire retardant into the wood, and thus achieve better and more durable fire retardancy inside the wood. Wettability of the pre-treated surfaces was evaluated by the contact angle and liquid uptake measurements. The penetration depth was investigated by the SEM-analyses and the burning properties was studied with different burning methods. The burning methods were also compared in order to find a good in-house burning method before more extensive testing at an official testing facility. The durability of the fire retardants was evaluated by performing the leaching test.

The used pre-treatment methods were planing, sanding, plasma treatment, microwave treatment and steam treatment. Steam treatment was also combined to roasting to evaluate the impact of the surface inactivation on the leaching of the fire retardant. Not pre-treated surface was used as a starting point and attained results were compared to that. Also, soaking without any pre-treatment was used to evaluate the penetration of the fire retardant solution when enough time and fire retardant is available.

Two differently acting fire retardants were used in this study. One was the two-component fire retardant (FR-TC) which should form a water insoluble compound inside the wood. Other was the reactive fire retardant (FR-R1) which should react with active sites of wood. Development of this fire retardant was done by adding the surfactants and the catalyst on the recipe (FR-R2).

7.1 Impact of treatment on contact angle

The contact angle tells the wetting behaviour of the surface. The contact angle below 90 degrees indicates the hydrophilic surface, meaning easy spreading of water-based solutions on the surface [48]. The contact angles measured after the different treatments are shown in Figure 31. The number of measuring points is not the same for all the treatments, because some pre-treatments were repeated to verify the results attained with the certain parameters. However, all the results that were obtained with the chosen parameters are presented.

On box plot graphs, like in Figure 31, a lower whisker represents a lowest quartile (25 % of values fall to this category), a lower box represents a second quartile. Two boxes together represent middle 50 % of the values. A median line divides a middle box in half and marks a midpoint of the data; the half of the values fall below this line and the half above. An upper box and whisker both represent also 25 % of the values. Crosses are the averages of measured values. Possible individual points are outliers. This means a value that is an abnormal observation in that group.

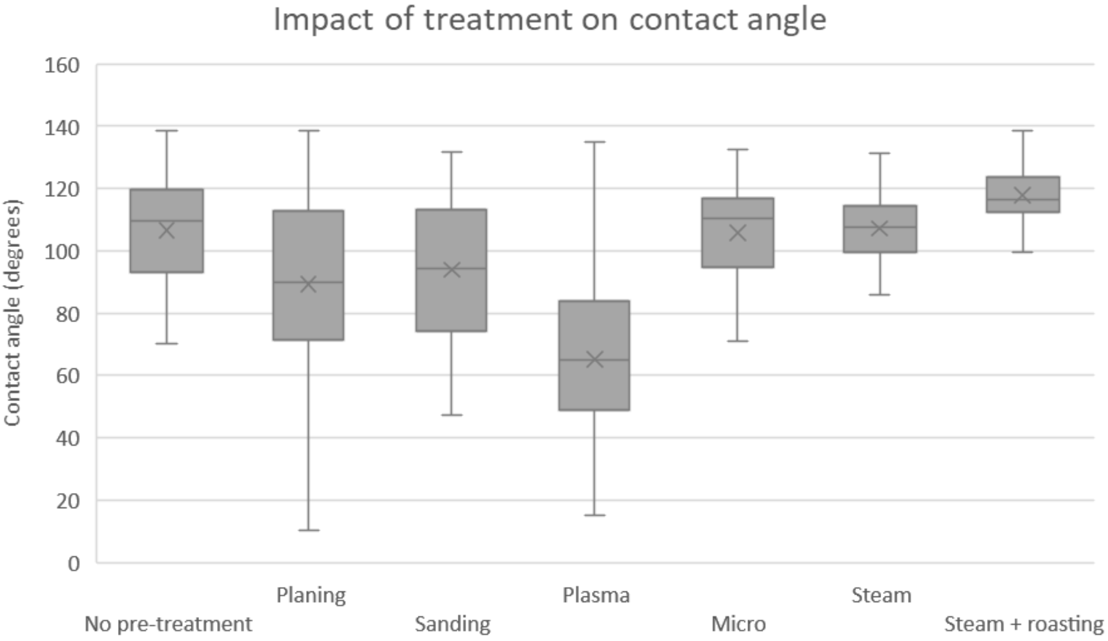


Figure 31. *Contact angle measurement results. Red line is at 90 degrees which is the limit between a hydrophobic and a hydrophilic surface. Number of measurements: no pre-treatment n=200, planing n=80, sanding n=40, plasma n=120, micro n=120, steam n=40, steam + roasting n=40.*

The average contact angle for samples with no surface pre-treatment was 107 degrees. Navickas et al. [154] measured the contact angles between 100 and 110 degrees for the pine surfaces inactivated with heat. In this study, industrially dried boards were used, so it can be expected that heat has been used for drying of woods and the inactivation of these samples is happened due to heat treatment.

As seen in Figure 31, planing lowered the average contact angle by 17,4 % to 89 degrees. The variation of the contact angles increased substantially on the planed surfaces; and consequently, the standard deviation increased from 16,6 degrees to 28,7 degrees compared to not pre-treated samples. One explanation for increased variation is the different wettability of earlywood and latewood. According to Shupe et al. [66] and Hse [155] porous earlywood exhibits lower contact angles and better wettability than smooth latewood. They measured the contact angle five seconds after the water was dropped on the surface. Maldas et al. [156] argued that the contact angle of earlywood is higher than the contact angle of latewood when the initial contact angle is used. These different arguments are actually in agreement due to their different measuring method. Initial contact angle is attained by extrapolating the contact angle to the beginning of time. Thin cell walls and big lumens of earlywood facilitate fast water penetration by capillary action, resulting in rapidly decreasing contact angle and deep slope on the contact angle curve. Thus, fast penetration results in a high initial contact angle, but low contact angle is observed if some later point of time is used on measurement. According to Maldas et al. [156] difference between earlywood and latewood was statistically significant. This difference between earlywood and latewood was even increased by extraction of extractives which increased also the standard deviation of the contact angles. These results are consistent with findings of this study. Planing removed the effect of extractives from the surface and revealed the fresh surface of earlywood and latewood rings which resulted in the increased variation of contact angles.

In Figure 32, the contact angles of the planed samples are compared to the corresponding references. Even though the average contact angle decreased, the planing effect varied greatly depending on the board. On board number 23, planing even increased the average contact angle. This can be due to surface geometry of latewood and earlywood rings which varies even within the board.

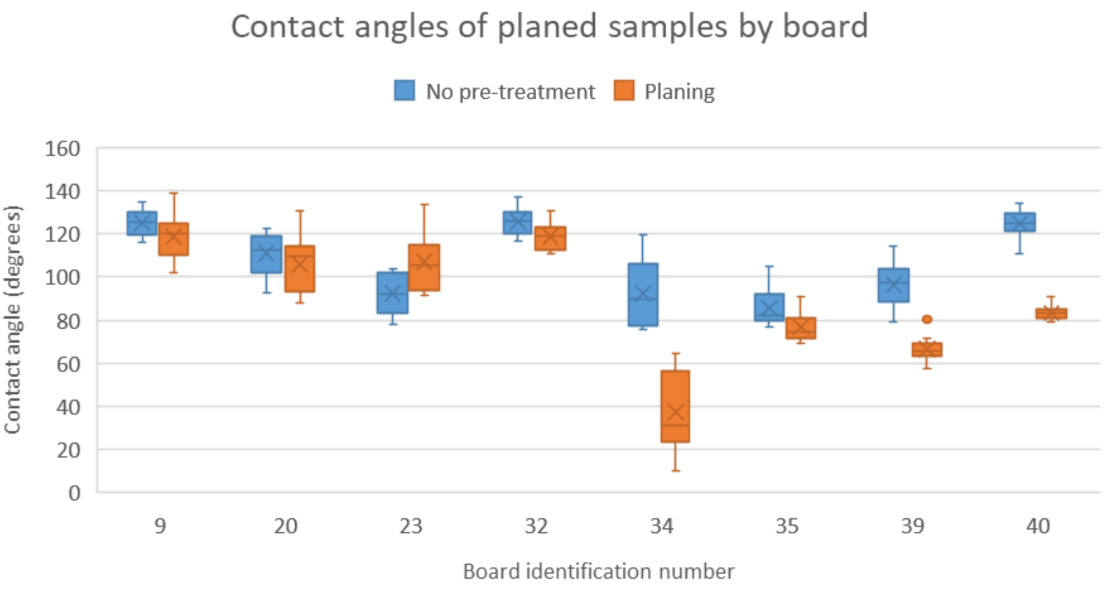


Figure 32. *Contact angles of planed samples compared to not pre-treated samples grouped by the board.*

Figure 31 shows that sanding yielded an average contact angle of 94 degrees, the decrease was 12 % compared to the not pre-treated samples. The average contact angle of the sanded surfaces was slightly higher than the planed ones. Typically in literature, sanding has resulted in lower contact angles than planing [68][92], but opposite results have been reported as well. Generally it can be concluded that the results are dependent on the wood specie [60][81].

It is practically impossible to compare contact angle results obtained after sanding performed by different authors. The used grit of a sandpaper affects the contact angle. A finer sandpaper causes more grooves, but their small width and depth cannot facilitate the water spread and penetration as well as larger grooves can [58][91][92]. Sanding direction (across or parallel to grains) and a hardness of an abrasive mineral yield different surface roughness which affects the contact angle [89]. The contact angles measured on a groove direction have quite different values than the contact angles measured on a parallel direction. In this thesis, the handheld sanding machine was used, which produced a vibrating circular movement. Therefore, the measuring direction is irrelevant in these results but might be the reason for the variation of the results; the standard deviation increased to 23,6 degrees. Figure 33 shows that despite the increased standard deviation, sanding decreased the average contact angles regardless of the board.

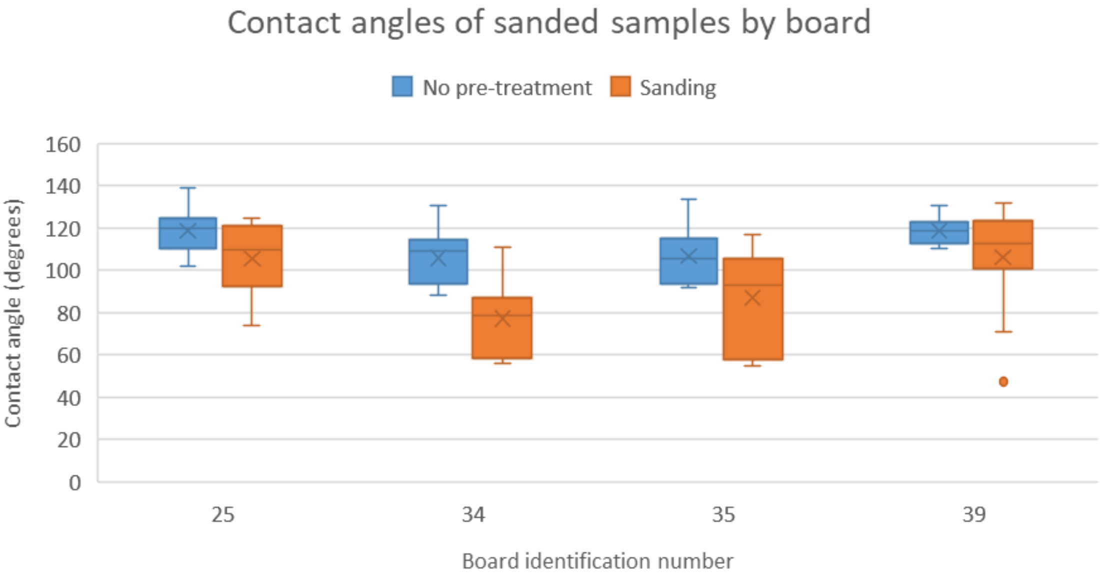


Figure 33. *Contact angles of sanded samples compared to not pre-treated samples grouped by the board.*

It is seen in Figure 31 that the plasma treatment lowered the contact angle significantly, where both average and median were 65 degrees. This is 39,3 % decrease compared to the not pre-treated samples. Plasma treatment was the only pre-treatment method which had 75 % of the contact angle values below 90 degrees. In the study made by Podgorski et al. [73], 30 minutes treatment with the dielectric barrier plasma lowered the contact angle of fir wood from 115 degrees to 10 degrees. Air-based plasma jet treatment of sugar maple lowered the contact angle from 68 degrees to 51 degrees, but the same treatment had no effect on the contact angle of black spruce [102]. Also, Ivanov et al. [158] observed that the decrease in contact angles significantly depends on wood specie. In their study, the contact angle of tzalam decreased 80,3 % but decrease of cedar´s was only 24,2 %.

The great variation in a response of different species to a plasma treatment can be explained with extractives. A plasma treatment removes extractives, reveals the main components of wood and create active groups on the revealed surfaces which increases the surface energy. However, the plasma treatment cannot impact on the surface energy of extractives [99][101]. Thus, if the plasma treatment has not been able to remove the extractives from the surface, no great change can be observed on the contact angle. And on highly porous wood species, wood extractives can migrate very rapidly on the surface and the wood quickly returns to a orginal state, and thus no change of the contact angle can be measured [102].

In this study, plasma treatment increased the standard deviation of the contact angles to 24,7 degrees, which was signifigantly more than the not pre-treated samples. Most likely the plasma treatment removed the extractives from the surface and revealed the latewood and earlywood rings, just as planing did – section 7.1, p. 54 – and thus the variation increased. The outcome on a plasma tretment is also affected by a plasma device and used parameters including, treatment time, distance and used power [73]. In this study, plasma treatment was performed with the plasma jet. Therefore, very small area, could be treated at once, and thus the sample has to be moved under the plasma nozzle to treat every spot and still avoid burning of the surface. Despite of the same time which was used on the certain area, some variation occured on the surface due to a movement speed and preciseness of an operator. When plasma results are analyzed by boards, a decrease on the contact angles of all boards could be seen as shown in Figure 34. This indicated that treatment with a plasma jet could enhance the wettability of pine, but the final impact depends on the initial surface charcteristics and operation parameters.

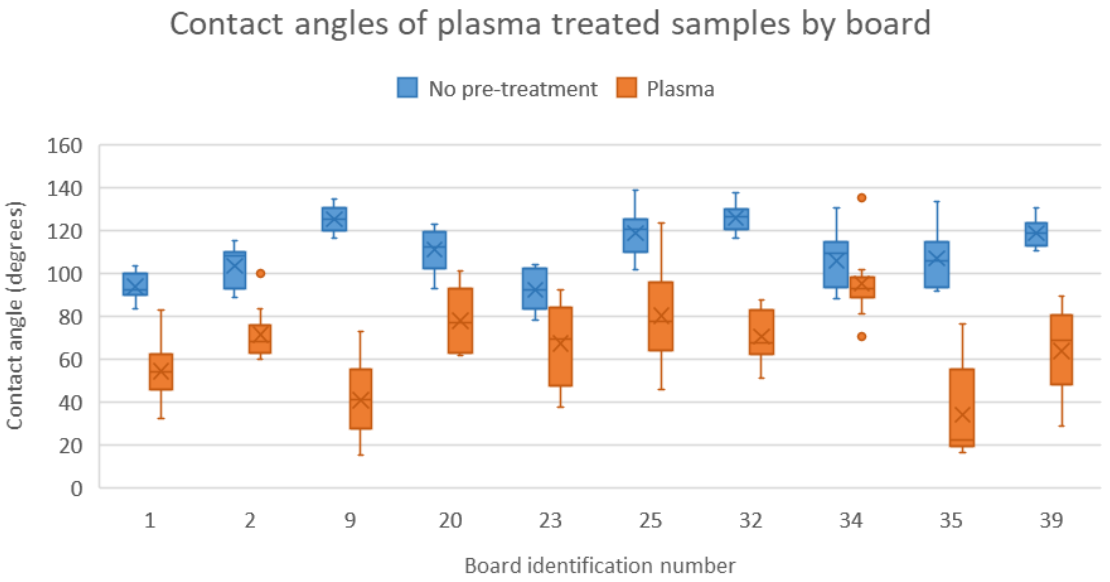


Figure 34. *Contact angles of plasma treated samples compared to not pre-treated samples grouped by the board.*

The microwave treatment did not increase the wettability of pine wood in this study. As seen in Figure 31, the average contact angle of the microwave treated samples was 106 degrees. The microwave treatment is meant for moist wood. The working mechanism is based on creating cavities with small explosions of boiling water [111]. The boards used in this study were already industrially dried, and thus the moisture contents were 10-12 %, which were not enough for the effective microwave treatment. The increase of the treatment time was tested to achieve a more intensive effect. By using one minute microwave treatment followed by one minute cooling and then one minute microwave treatment again, the wood sample started to form char and produce smoke even at the lower power of 720 W.

The steam treatment did not have any effect on the wettability; the average contact angle was 107 degrees as seen in Figure 31. Steam treatment increases permeability of green wood, it has no significant effect on surface characteristics of dried lumber [128]. Roasting after steam treatment increased the contact angle to 118 degrees. This was expected, because temperature inactivates wood surface and makes it hydrophobic. Podgorski et al. [73] measured a doubled contact angle of fir wood after one hour thermal treatment at 160 °C, as was shown in Figure 8. In this study, a great change was not observed. But it needs to be considered that the wood specie was different, the shorter time was used, the initial contact angle was already on the hydrophobic region and the steam treatment was performed before roasting.

De Meijer et al. [51] explained the large part of the variation in contact angle observations was due to the complex nature of wood. Porous structure, chemical heterogeneity, surface roughness and difference between porous earlywood and smooth latewood, all cause variation to the contact angles. According to Rossi et al. [159] a surface energy of wood log can change 37,9 % over a distance of 14 meters. If this kind of change is possible within the wood, variation between woods can be even greater.

7.2 Impact of treatment on fire retardant uptake

The amount of fire retardant has great impact on fire performance of wood. Even an excellent fire retardant with too low loadings cannot protect the wood from burning. To reach the highest classification of combustible products, high loadings of a fire retardant is usually needed. This loading needs to be higher than in a traditional preservative treatment [6].

Figure 35 presents the results for the liquid uptake of the two-component fire retardant (FR-TC) and the reactive fire retardant (FR-R1) after different pre-treatments. There are no significant differences on the liquid uptakes between the two fire retardants. With the exception of soaking (not presented in the figure), which resulted 379 g/m^2 of FR-TC and 262 g/m^2 of FR-R1 fire retardant. The difference in the uptake results in soaking was probably due to time of measurement. After soaking, fire retardant was dripping from wood, so too early weighing gave more fire retardant than in reality was achieved. Additionally, too late measurement gave lower result because some water has already evaporated. And drying wood with paper can lead to paper to draw fire retardant away from wood cells.

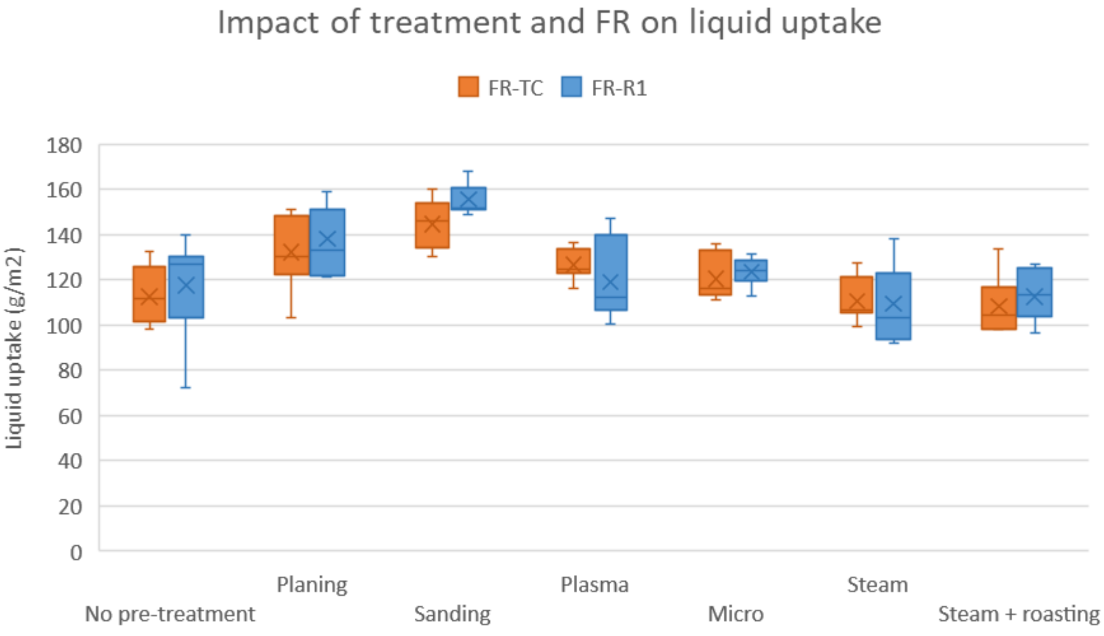


Figure 35. *Liquid uptake (g/m^2) of FR-TC and FR-R1 fire retardants after the different pre-treatments.*

Planing and sanding of samples increased significantly the liquid uptake compared to the not pre-treated samples. Without any pre-treatment, the average liquid amount of FR-R1 was 118 g/m^2, while planing and sanding led to 139 g/m^2 and 156 g/m^2 fire retardant amounts, respectively. Likewise, the achieved fire retardant amounts with FR-TC without pre-treatment was 113 g/m^2, while planing and sanding resulted in 132 g/m^2 and 145 g/m^2 fire retardant amounts, respectively.

Many studies [64][84][85][87] have shown that planing cuts open cells and thus exposes cell lumens to the surface. This allows easy penetration of liquid into the open cells, which explains increased liquid uptake of the planed surfaces. The increased liquid uptake of sanded surfaces is explained by grooves produced on the surface. They were able to facilitate and accelerate liquid conduction by capillarity [84][91][160]. According to de Moura et al. [84][160] complete wetting of sanded surfaces requires less time than wetting of planed surfaces. They suggested that a capillary effect provided by roughness dominates over chemical aspects of wetting.

Plasma treatment increased slightly the liquid uptake of FR-TC to 127 g/m^2, but with FR-R1 the liquid uptake was 119 g/m^2, practically the same as without any pre-treatment. This was a quite surprising result, because the plasma treatment resulted in the lowest contact angle. Although, variation in the contact angles after the plasma treatment was quite large and thus the variation occurred in the liquid uptake as well. Geometry of the growth rings [161] and uniformity of the treatment has also effect on the liquid uptake.

Neither microwave nor steam treatment had any effect on the liquid uptake. This was quite expected, because these treatments had no effect on the contact angle either. In Figure 35 the steam treated, and the steam and roasted samples were presented in different columns, but at this point they were still treated the same way, roasting was performed later. The liquid uptake of the samples was statistically the same.

The solid contents of FR-TC and FR-R1 fire retardants were not the same. FR-R1 had slightly higher concentration. FR-R1 was applied twice with the same solution which had the concentration of 25 %, but the first solution of the FR-TC system had only 20 % concentration. Due to this difference, a higher solid amount of fire retardant was achieved with FR-R1 as shown in Figure 36. Increasing the concentration of FR-TC on the same level as FR-R1 was not possible; even with these concentrations, salt precipitated on the surface of the FR-TC samples. With FR-R1 even slightly higher concentrations could be possible; no salt precipitation was observed on these samples.

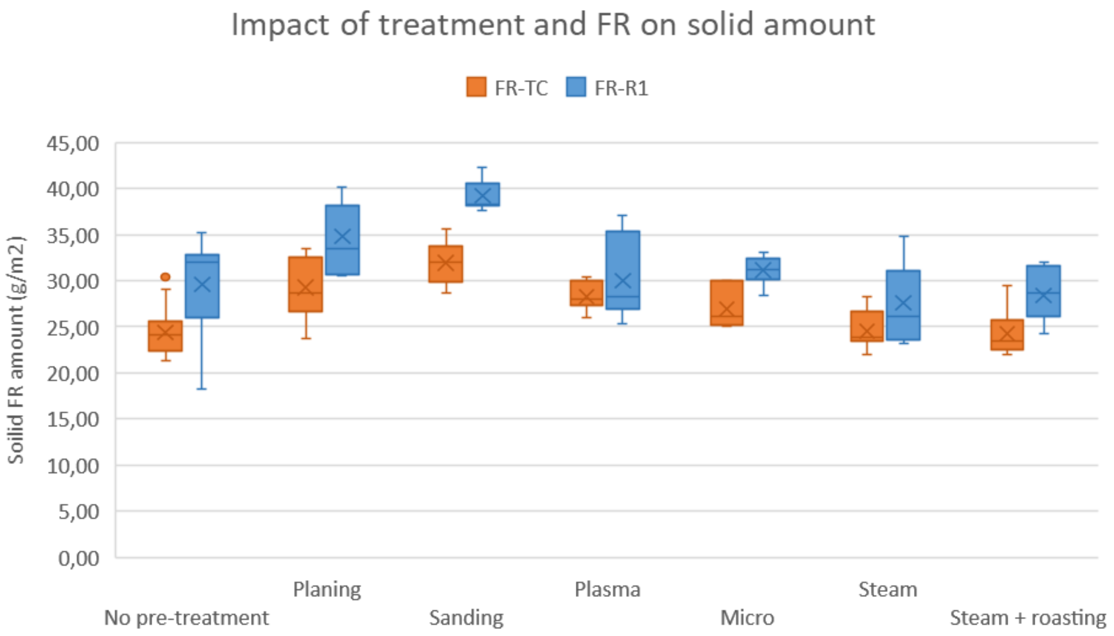


Figure 36. *Achieved solid amounts (g/m^2) of FR-TC and FR-R1 fire retardants in the samples after the different pre-treatments (soaking excluded).*

Wetting properties of a liquid can be altered by changing the tension of the liquid by using surfactants, meaning that the lower surface tension results in enhanced wetting properties [50]. Dineff et al. [157] and Ivanov et al. [158] reported decreased contact angle and increased penetration rate when surfactant were used in phosphorus and nitrogen containing fire retardants. According to Desmarais et al. [161] pure water is absorbed to cell walls causing swelling which slows down the penetration process, but solvent does not cause swelling; thus, penetration is more linear than with water. In this study, adding solvent based surfactants and a catalyst to the reactive fire retardant increased significantly the liquid uptake regardless of the pre-treatment (Figure 37). The liquid uptake of the samples without pre-treatment was 151 g/m^2 when FR-R2 was used. This was 28 % increase compared to FR-R1.

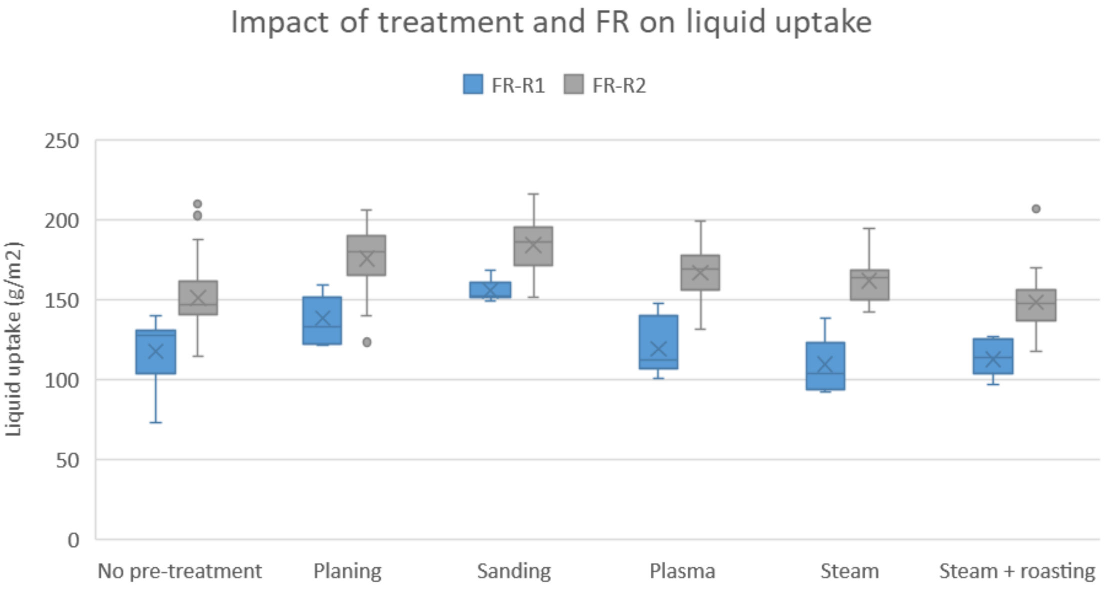


Figure 37. *Liquid uptake (g/m^2) of FR-R1 and FR-R2 fire retardants after the different pre-treatments. No microwave treatment or soaking was performed with FR-R2.*

For sanded surfaces, the increase in the liquid uptake was the smallest, about 20 %; however, the liquid uptake of sanded surfaces was still the highest, 184 g/m^2. For the planed surfaces, the increase was 27 % to 176 g/m^2. The liquid uptake of the plasma treated surfaces increased from 119 g/m^2 to 167 g/m^2, meaning 42 % increase. The liquid uptakes of the plasma treated samples and the not pre-treated samples were practically the same when FR-R1 was used. But with FR-R2 the liquid uptake on the plasma treated samples was 10,5 % more than on the not pre-treated. This dissimilarity might be caused by natural variation of the wood. The samples treated with FR-R1 were from the same boards. Due to the test arrangements with FR-R2, the plasma treated and the not pre-treated samples were from different boards. Average density of the not pre-treated samples was 569 kg/m^2 and for the plasma treated samples 507 kg/m^3. The plasma samples were clearly the lightest samples that were used in this study.

The steam treated, and the steam and roasted samples were both only steamed before fire retardant was applied, thus the liquid uptake of the samples should be the same. This was the case with FR-R1. The liquid uptake of FR-R2 was 162 g/m^2 for the steam treated samples and 148 g/m^2 for the samples which were determined to be roasted afterwards. The average density of the steam treated samples was 545 kg/m^3, while for the steam and roasted samples it was 538 kg/m^3, thus density does not offer explanation for the difference. Again, with FR-R1 the samples were from the same boards but with FR-R2 from different boards due to the test arrangement, thus most likely the difference is due to natural variation and geometry of growth rings on the surface of wood. Liquid uptake is different in grain direction than in perpendicular direction [161].

Slight salt formation was observed on the surface of some samples which were treated with FR-R2. Salt was formed on the surface of the not pre-treated, sanded and plasma treated samples. On the planed and steam treated samples no salt formation was perceived.

7.3 Impact of treatment on penetration depth

SEM imaging was used to study the penetration depth of the fire retardant. The position of phosphorus was analysed with x-ray. The average penetration depth of phosphorus was calculated based on these analyses. Also, the deepest individual penetration of phosphorus in each sample was recorded. These results are presented in Table 5. The variation in the deepest individual penetration is greatly affected by structural differences of wood. The rays provide the pathway for the deepest penetration in pine. Solution encounters less resistance when penetrating through a ray than when penetrating through connecting pits of tracheid cells [64]. In these image sizes (4 x 3 mm^2), typically one deeper penetration was observed.

Table 5. *Penetration depth of FR-R1 measured by phosphorus in wood after the different pre-treatments and penetration depth of FR-R2 without a pre-treatment.*

Treatment	**Average penetration depth (µm)**	**Deepest individual penetration (µm)**
No pre-treatment	93	652
Planing	92	895
Sanding	172	1092
Plasma treatment	96	770
Microwave treatment	91	1319
Steam treatment	154	778
Soaking	710	3015
FR-R2, no pre-treatment	357	2372

The penetration depth of not pre-treated sample (Figure 38) was the same as was the penetration depth of planed sample (Figure 39). Planing provided higher liquid uptake but did not allow deeper penetration. Knorz et al. [85] reported similar results obtained with adhesive. Planing provided easy access into the cells that were open to the surface, but no deep penetration was observed. As can be seen from Figure 38 and Figure 39, growth rings on the not pre-treated and planed sample are very differently oriented, but other identifications of the cells is hard to do. More studies are needed to understand whether the difference is caused by coincidental structural difference or did planing provide deeper penetration.

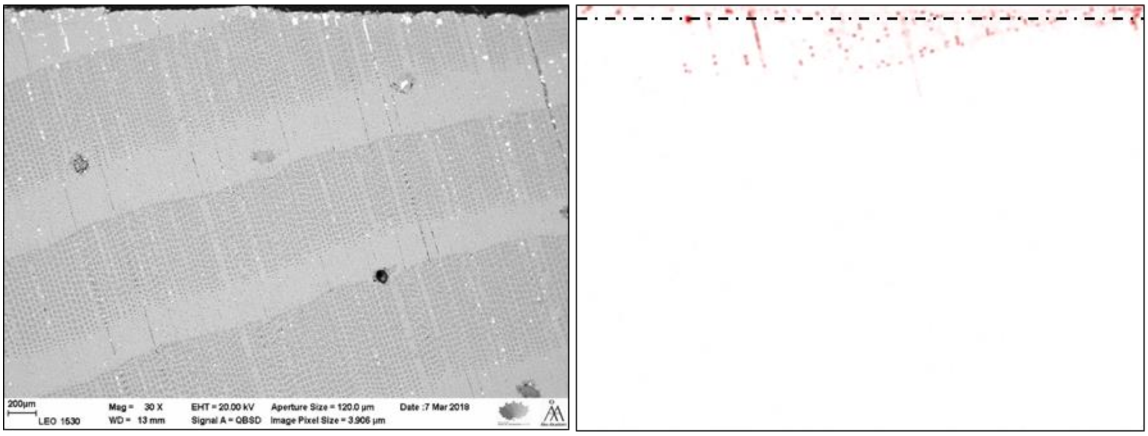


Figure 38. *SEM-images (30x) of not pre-treated sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

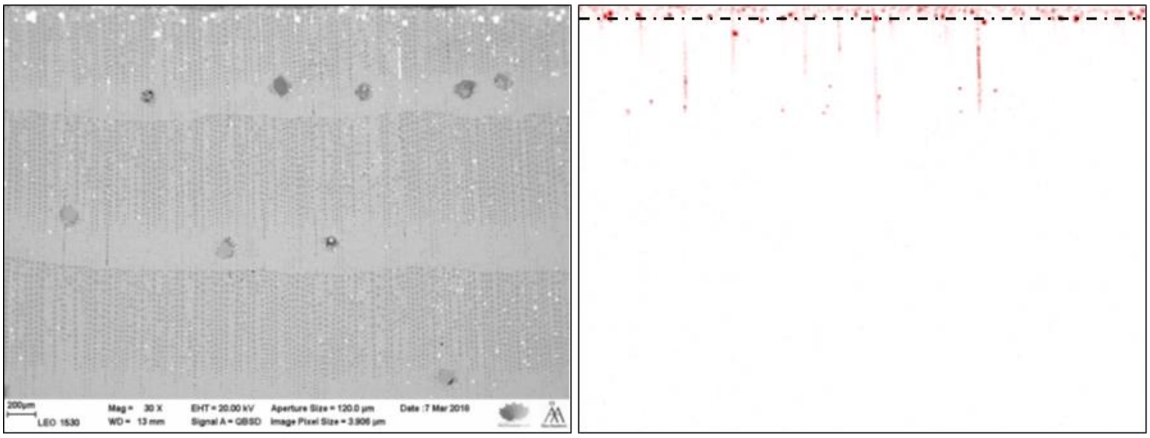


Figure 39. *SEM-images (30x) of planed sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

Sanding (Figure 40) resulted surprisingly deep penetration, 172 µm. In most studies sanding had crushed cells on the surface and thus prevented penetration of the solution; however, most studies about penetration of sanded surfaces were conducted with a glue or a high viscous coating [68][91]. When coatings with different solid contents have been compared, differences in penetration depth were observed, both on non-sanded and sanded surfaces. Unpigmented coatings with a small solid content resulted in deeper penetration than pigmented coatings [64]. This can be explained by principles of the capillary penetration process shown in Figure 13; water penetrates to the cell walls and the solid content remains in lumens. This capillary penetration process requires open cells on the surface which are usually crushed by sanding. Crushing of cells was not studied in this thesis. It is possible that sanding was not very severe because the handheld sander was used and therefore lots of cells could remain uncrushed on the surface.

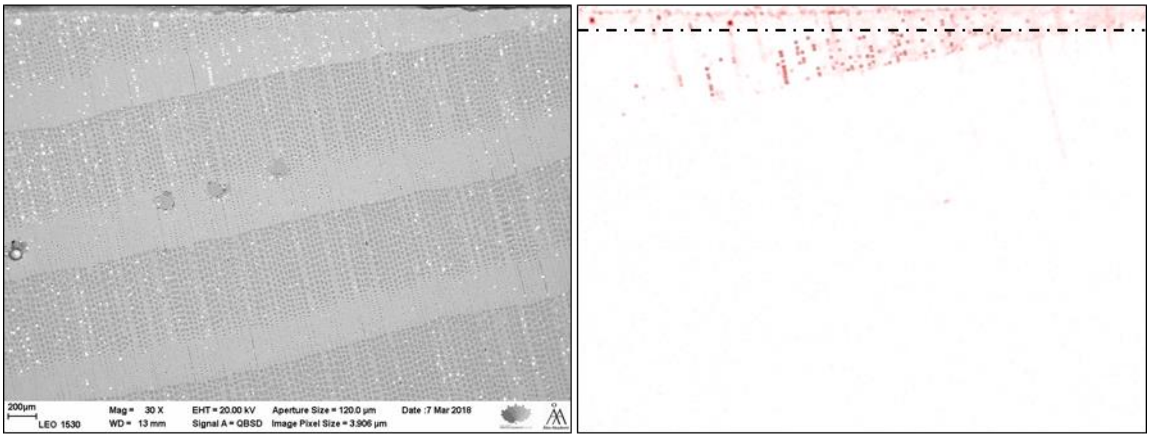


Figure 40. *SEM-images (30x) of sanded sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

Plasma treatment (Figure 41) provided the penetration depth of 96 µm which was similar to the not pre-treated sample. This shows why the liquid uptake was not improved during the plasma treatment. The effective depth of plasma treatment can be less than one micrometer on a surface of an organic material [49]. This could explain why change on the contact angle was observed, but increased penetration depth or liquid uptake was not achieved. It must be noted that, as can be seen in Figure 41, there was a latewood ring on the surface of plasma treated sample. This could have affected on the penetration depth.

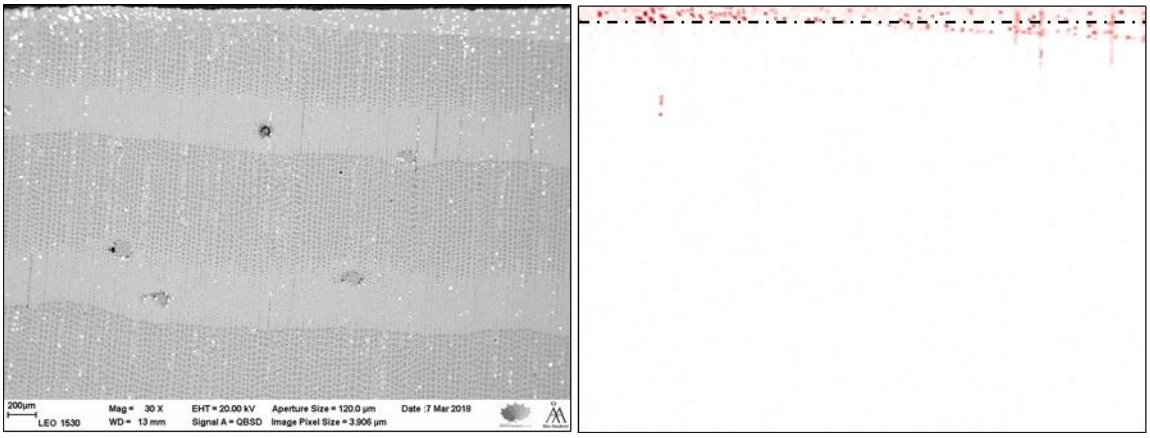


Figure 41. *SEM-images (30x) of plasma treated sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

The penetration depth was 91 µm in the microwave treated sample. As seen from the SEM image (Figure 42), one deep individual penetration was observed, most likely through a ray cell. If this is excluded from the calculations, average penetration depth is

86 µm. As stated earlier, the working mechanism of the microwave treatment requires moist wood [111]. Thus, it was expected, that no change on the penetration of a liquid into a dry lumber would be observed.

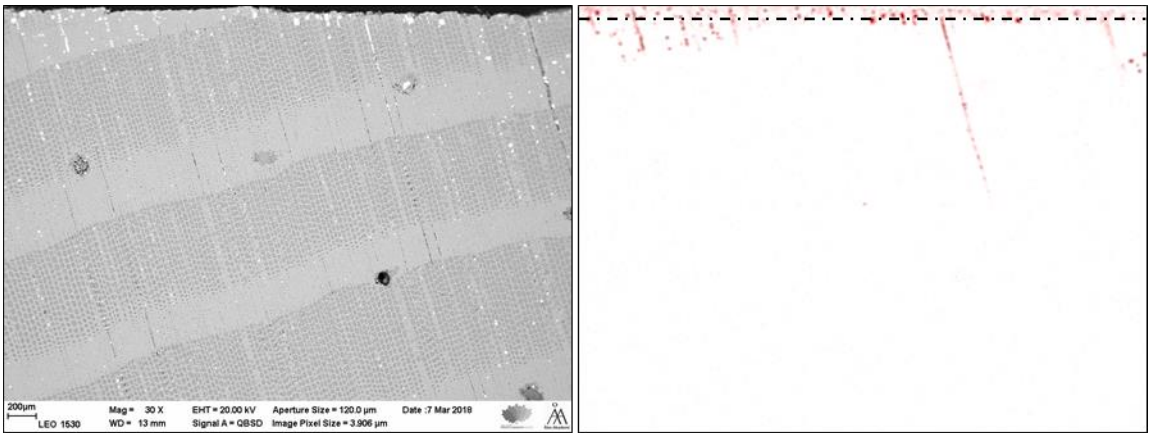


Figure 42. *SEM-images (30x) of microwave treated sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

The steam treated (Figure 43) sample had the penetration depth of 154 µm. This was not expected based on the contact angle and the liquid uptake results. Lebow et al. [128] noticed that steam treatment did not improve the penetration of boron to dry lumber, although they did not provide any numerical values. It is worth noting that they used Douglas fir heartwood in their studies. In this study, deeper penetration by using the steam pre-treatment can be firstly explained by the use of pine sapwood; and secondly, the longer penetration time provided by moisture, which came from steaming. According to Desmarais et al. [161] water-based solutions are first immersed slowly inside the first layer of pine sapwood cells. Later liquid penetrates more quickly and steadily to deeper cells. Moisture from steaming offered additional water to the fire retardant and provided more time for the penetration before water was evaporated. This could also explain the deep penetration of the sanded surfaces. Grooves from sanding facilitated a higher amount of liquid and thus the evaporation of water took longer, and the fire retardant had more time for the penetration.

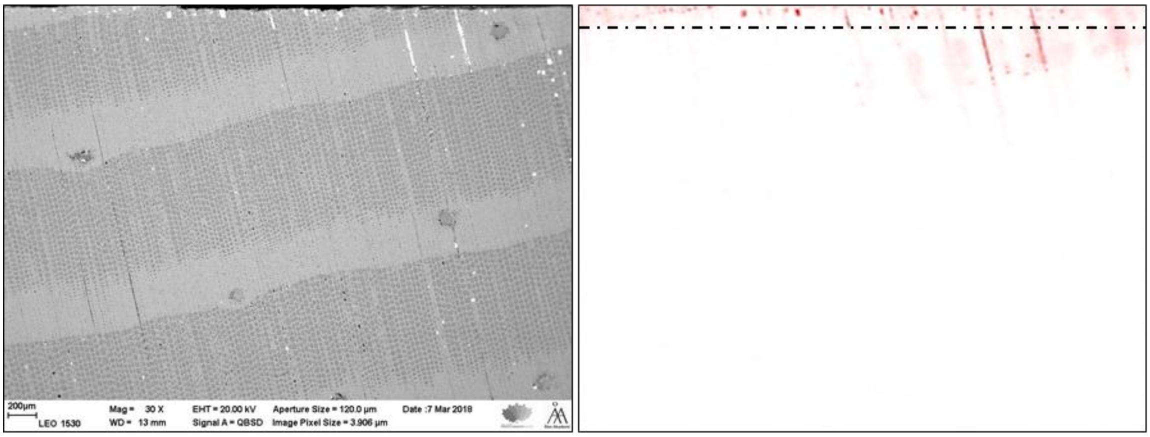


Figure 43. *SEM-images (30x) of steam treated sample on which FR-R1 fire retardant was applied. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

Soaking of the samples resulted in the deepest penetration (Figure 44). Samples were immersed into the fire retardant solution for four hours. Water-based solutions penetrate easily to pine sapwood after first few minutes. If enough time is used, penetration through whole board is possible [161].

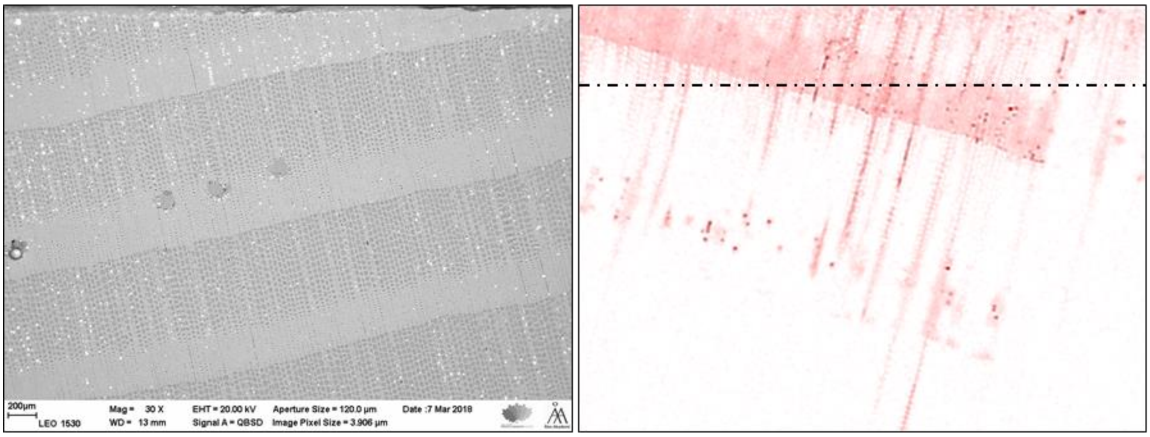


Figure 44. *SEM-images (30x) of sample soaked in FR-R1 fire retardant. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

Adding the surfactants (Figure 45) increased significantly the penetration depth. The average penetration depth of FR-R2 was 2,8 times deeper than the penetration of FR-R1 on the not pre-treated surface. This is in agreement with the earlier studies; use of surfactants lowers the surface tension of fire retardant and allows faster [157][158] and deeper [64][161] penetration into the cells of pine.

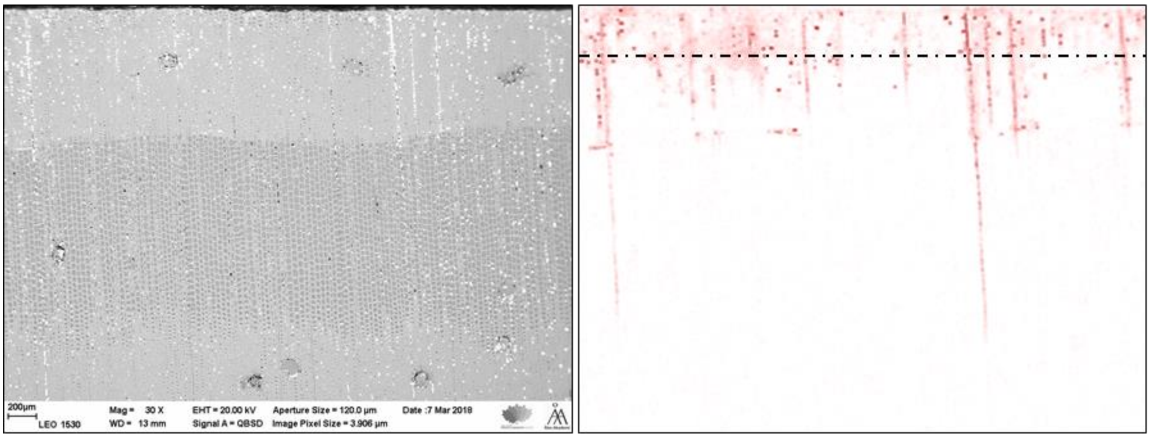


Figure 45. *SEM-images (30x) of not pre-treated sample on which FR-R2 fire retardant. Left: image of wood structure, right: elemental mapping of phosphorus (red) of the same area. Dotted line: the average penetration depth.*

According to de Meijer et al. [64] penetration of solution was greatly influenced by the growing conditions of the timber and the way boards were sawn out of the log. The differences in penetration came from the flat and standing growth rings, the width of latewood and earlywood bands, the grain orientation and the number of rays ending on the surface. The origin of wood had influence because the growing conditions effect on the portions of latewood and earlywood, the number and length of rays and tracheids and the condition of the pits.

Propositions of de Meijer et al. [64] supports findings of these SEM images. Penetration followed clearly the shape of the growth rings. Earlywood penetration had been easy, but phosphorus cumulated into the latewood cells indicating decelerated penetration. This also affected on the penetration depth; on parts where latewood ended on the surface, the penetration was quite shallow. On the soaking sample (Figure 44) effect of the growth rings could be seen clearly; the fire retardant was penetrated through the earlywood and filled the latewood cells before it continued to the next growth ring.

7.4 Impact of treatment on burning properties

The burning properties of the pre-treated samples were tested by the small flame test. The fire retardants FR-TC and FR-R1 were used in this study. The samples were weighed before and after burning. The percentage of remained mass was calculated from the mass change.

It is seen in Figure 46 that the different pre-treatments could not change the burning properties of the samples in the small flame test. The average remained mass of the reference samples was 98,77 % and the standard deviation was 0,40 %. The remained mass of the samples treated with the FR-R1 fire retardant was 99,65 % and the standard deviation was 0,06 %. For FR-TC samples the remained mass was 99,57 % and the standard deviation was 0,09 %. Both fire retardants increased the fire performance of wood and decreased the variation in the percentage of remained mass. The standard deviation was significantly smaller when fire retardant was used. Thus, the fire retardants prevailed over properties of wood in burning.

FR-R1 had higher average remained mass than FR-TC treated samples had. Statistical analysis confirmed difference of these two groups, thus FR-R1 had better fire retardancy than FR-TC did. Clear difference was especially in soaked samples. FR-TC samples was first soaked in solution number one and when these samples were immersed to solution number two, some of the first solution was most likely leached out. This could explain why FR-TC had poor fire retardant properties after soaking.

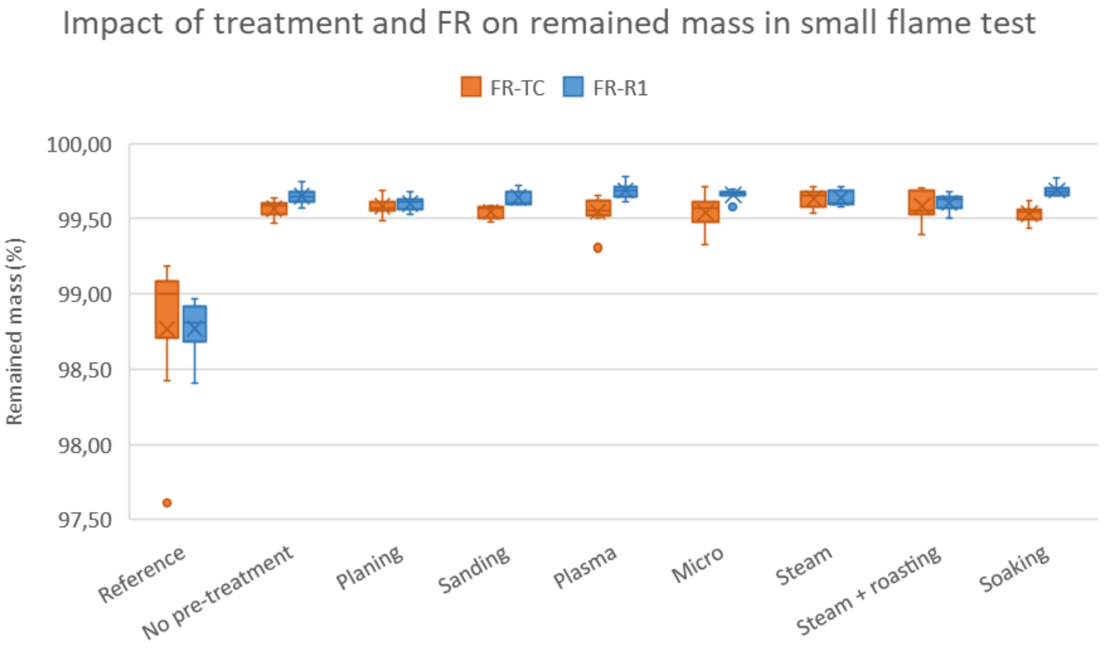


Figure 46. *Remained mass of samples with the different pre-treatments after the small flame test.*

Overall, soaking was not preferable method for adding fire retardant. It required long time and large quantities of fire retardant, thus all superior aspects of surface treatment were lost and still penetration was shallower than what could be achieved with a pressure impregnation.

The development of the FR-R1 recipe was done by adding surfactants and a catalyst, the new fire retardant recipe was named FR-R2. The impact of these additives on the fire retardant properties was tested without any surface pre-treatment and the burning test was performed with the small flame test. Also, necessity for activation of catalyst at 190°C was tested by preparing FR-R2 samples with and without activation (Figure 47). The remained mass of FR-R1 samples on the not pre-treated surfaces was 99,61 %. With the not activated FR-R2 samples, the remained mass increased to 99,66 % and activation increased the remained mass to 99,72 %. These results indicated that increasing the liquid uptake by use of surfactants could result in better fire performance.

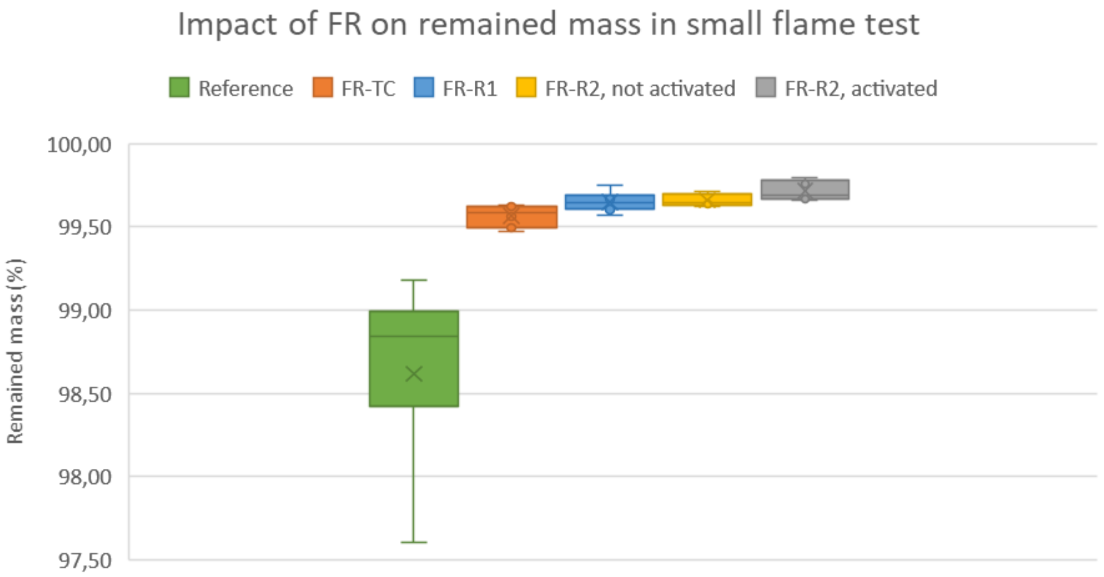


Figure 47. *Remained mass of not pre-treated samples with the different fire retardants after the small flame test.*

Fire retardant FR-TC did not provide as good fire protection as FR-R1 and FR-R2 did. One reason was the smaller solid amount achived with FR-TC and no higher amount was possible because of the salt formation on the surface. Higher solid amount of fire retardant seemd to provide slightly better fire retardancy (Figure 48). The fire retardancy depends also from the mechanism of fire retardant. To confirm the root cause for difference of these two fire retardant would require more testing.

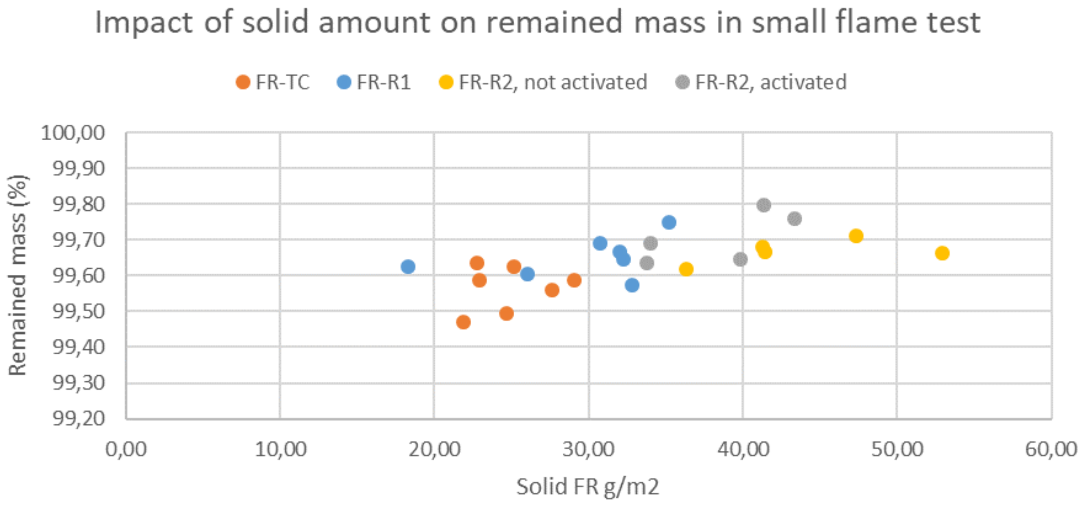


Figure 48. *Impact of solid fire retardant amount on the remained mass in the small flame test (not pre-treated samples).*

In order to remove the effect of different chemistry of the fire retardants, the remained masses of the samples were observed by one fire retardant at the time. Figure 49 shows the results of FR-R1. No correlation between the remained mass and the solid amount of fire retardant could be found. Figure 50 shows the remained mass after burning of FR-TC treated samples. Compared to FR-R1, this fire retardant resulted in even slightly descending trend; however, no correlation was found.

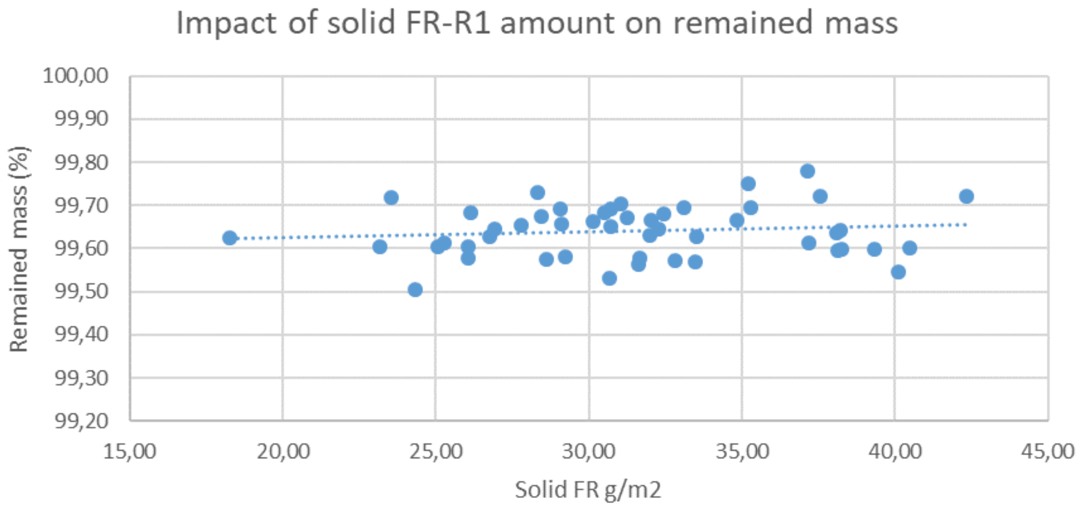


Figure 49. *Impact of solid FR-R1 amount on the remained mass in the small flame test, soaking excluded.*

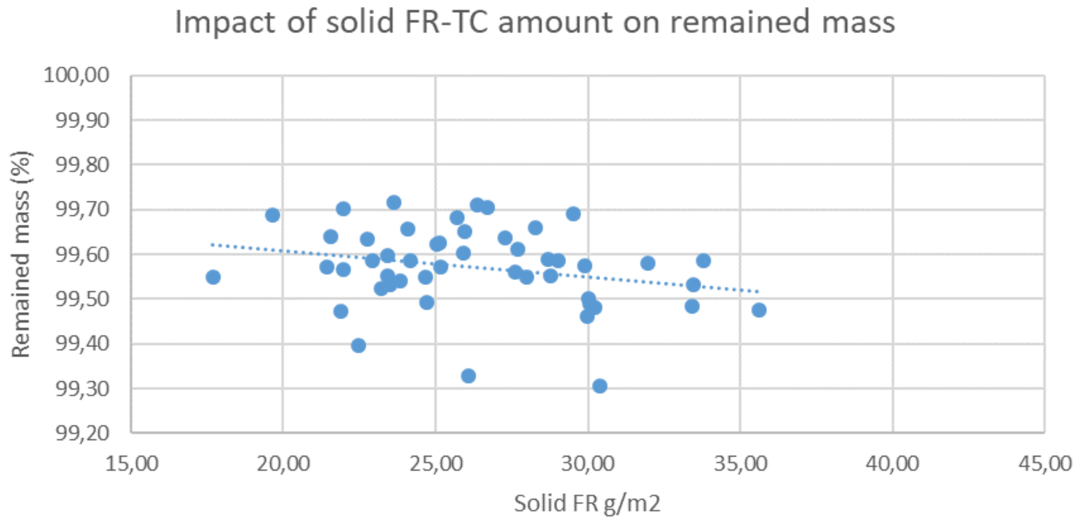


Figure 50. *Impact of solid FR-TC amount on the remained mass percent in small flame test, soaking excluded.*

Soaking was excluded from previous figures, but adding soaking to presentations did not bring out any correlation between the remained mass and the solid amount of fire retardant (Figure 51).

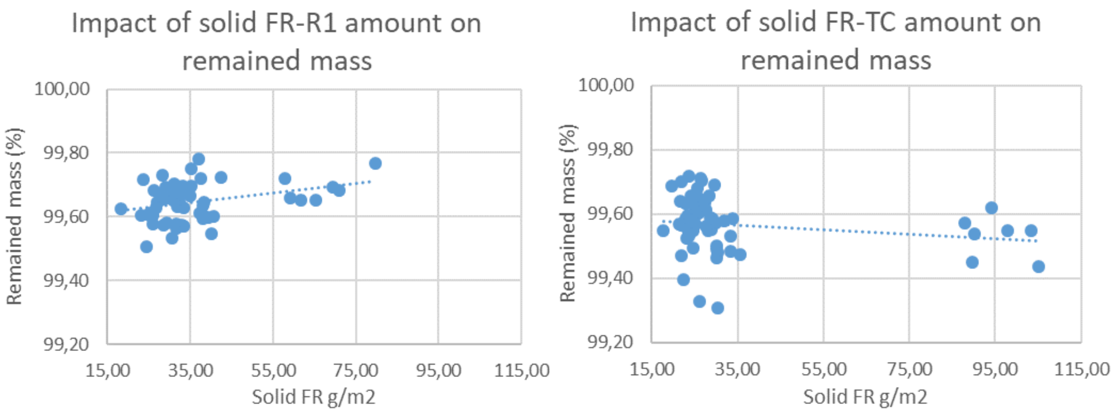


Figure 51. *Impact of solid FR-R1 and FR-TC amounts on the remained mass in the small flame test, soaking included.*

A pre-treatment of the surface did not have any influence on the fire performance of wood. The results from the small flame test indicate that ±10 g/m^2 of solid fire retardant cannot affect the fire property of wood; however, fire retardant treatment increased the remained mass compared to references. Even the smallest achieved fire retardant amounts in this study were sufficient to prevent burning with the small flame test.

7.5 Comparison of different burning methods

Different burning methods were tested to find a good in-house method for wood burning. The small flame test is a standard procedure, but the flame is too small for the standard sized wooden samples. In many occasion, water inside the cells of wood is enough to prevent burning with the small flame test. Therefore, the samples were dried before burning. Even though drying represented the “worst case”-scenario, it did not represent the real-life situation.

The use of small flame cabin to perform the in-house UL 94 test, was a fast and easy way to test fire retardants on wood. The sample size and the flame size are more in the same proportion which was not the case in the small flame test. Therefore, in-house UL 94 test was not that sensitive to moisture as the small flame test was. Variations occurred in the density of the used tongue depressors, but it is the same case with all wood samples.

The small size of tongue depressors was also a disadvantage. Due to the small size, surface pre-treatments were not even tried to perform on them. And even though, the tongue depressors were made of wood they did not represent the real wood material used in construction and furniture industry. Therefore, a bigger flame to test real boards was needed. The bunsen burner produced a bigger flame, but it was discarded, because adjustments of the flame easily left uncharred area on the surface. This would affect the results. The blow torch produced also a bigger flame and it was easier to get repeatable parameters for the testing compared to the bunsen burner.

The results of the small flame test are shown in Figure 47, the in-house UL94 test results are in Figure 52 and the blow torch burning results are in Figure 53. The actual remained mass is of course different in different burning methods due to dissimilar sample and flame sizes. But in all methods FR-TC performed worst and activated FR-R2 had the highest remained mass. All these methods seem suitable for the in-house use to evaluate and compare fire performance of different fire retardants.

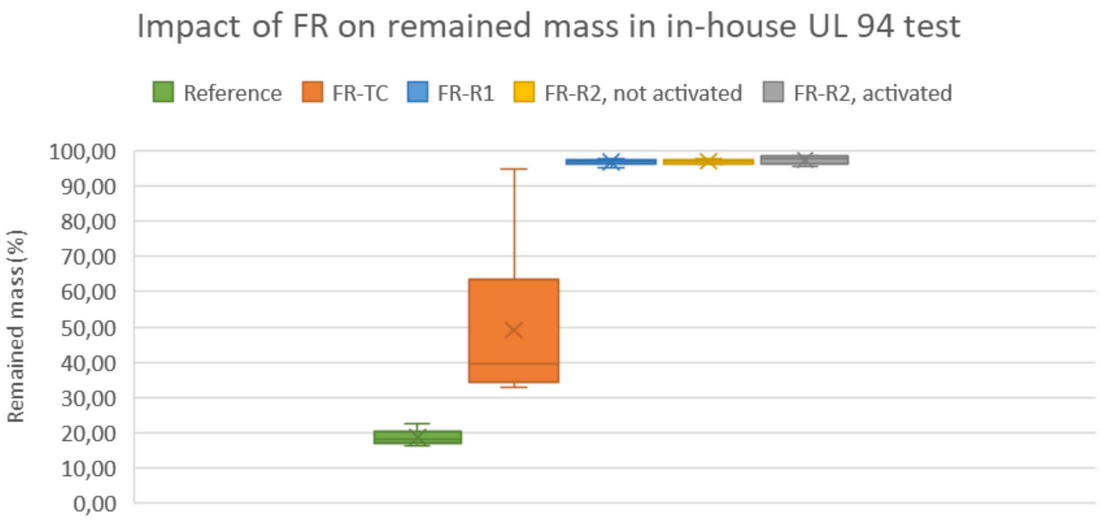


Figure 52. *Remained mass of samples treated with the different fire retardants after the in-house UL 94 test.*

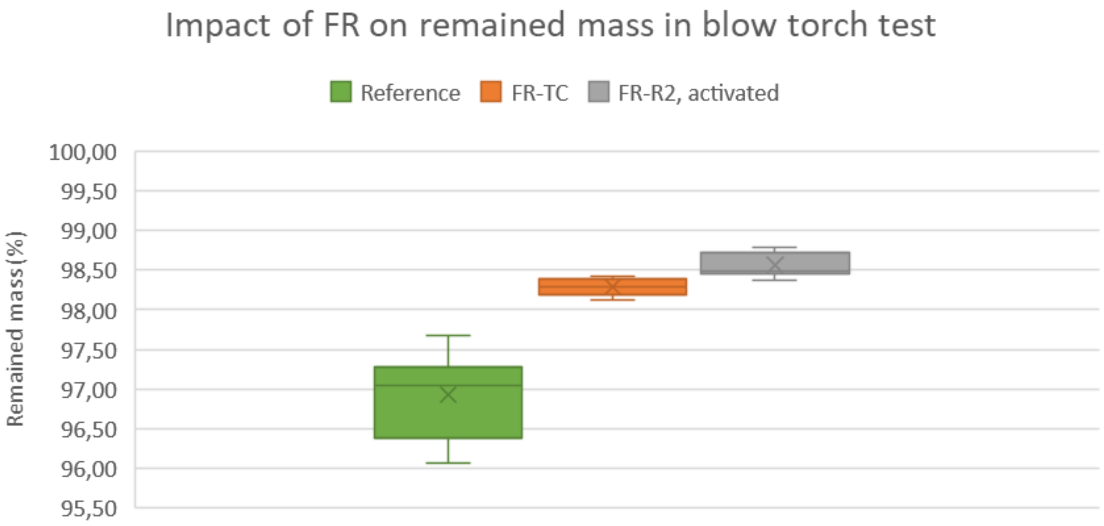


Figure 53. *Remained mass of not pre-treated samples with the different fire retardants after the blow torch test.*

The in-house UL 94 test presented the clearest difference between the fire retardants. Figure 54 shows the effect of the in-house UL 94 test on the tongue depressors protected with FR-TC and FR-R2. The samples with FR-TC burned to the clamp, but the samples with FR-R2 did not even ignite. The fire retardants were applied on the tongue depressors by dipping them into the solutions. Therefore, it is possible that the same phenomenon happened here to FR-TC as what was suspected with soaking; dipping in the second solution caused leaching of the first solution. This can explain in part the big difference of the remained masses.

Additionally, good intumescent layer was formed on the FR-R2 samples during the in-house UL 94 test as seen in Figure 54. Also, in blow torch testing the different surface behaviour of the fire retardants was observed clearly (Figure 55). The small tendency to make intumescent char was noticed in the small flame tests with FR-R1 and FR-R2, but the intumescent layers were not very clear.

Figure 54. *Remains of tongue depressors protected with FR-TC (left) and FR-R2 (right) after the in-house UL 94 burning. Intumescent layer was formed on the FR-R2 samples.*

Figure 55. *Samples of FR-TC (left) and FR-R2 (right) after the blow torch burning. Thin intumescent layer was formed on the surface of FR-R2 sample.*

In the radiant panel test, the fire retardants FR-TC and FR-R1 were tested on pine boards. For the untreated pine board critical flux was 3,27 kW/m^2 which led to the classification D$_{fl}$. The critical flux for FR-TC was 7,67 kW/m^2 which resulted in the classification C$_{fl}$. FR-R1 had critical flux >10,9 kw/m^2 which corresponded to the classification B$_{fl}$. Again, in this test, FR-R1 performed better than FR-TC. FR-R1 reached the best possible classification for wood, but FR-TC improved the classification of pure wood only by one step.

Later, the radiant panel test was performed on FR-R2 which was applied on a spruce plywood. The two plywood references gave critical fluxes 5,16 kW/m^2 and 4,46 kW/m^2, corresponding to classes C$_{fl}$ and D$_{fl}$, respectively. To get the smoke classification s1, total smoke production has to be under 750 %. The smoke classification for reference was s1, because the measured smoke results were 9,15 % and 7,47 %. The same plywood with 330 g/m^2 of FR-R2 on the surface gave critical flux >10,9 kW/m^2 resulting in the classification B$_{fl}$. Also, the smoke classification s1 was passed easily with the result of 4,92 % smoke.

Cone calorimeter tests were performed at Åbo Akademi University on the pine and the plywood samples treated with FR-R2. On pine, FR-R2 was tested by applying it on the heartwood side (Figure 56) and on the sapwood side (Figure 57). The used liquid amounts were 250 g/m^2 and 300 g/m^2. These high loadings were possible to achieve probably due to planing of the samples. To get suitable sample size for the cone calorimeter testing, the samples were cut and planed from bigger boards. On the thinner boards this high loading had caused salt formation on the surface.

In the heartwood side testing of pine samples, there was quite big difference between the two references, the maximum heat release rates (HRR) were 249 kW/m^2 and 199 kW/m^2. For the sample where fire retardant amount was 250 g/m^2, the HRR was 179 kW/m^2. And for the 300 g/m^2 samples,16 the HRR were 149 g/m^2 and 184 g/m^2. Results on sapwood side were more constant. The HRR peaks of references were 235 kW/m^2 and 246 kW/m^2. The sample with 250 g/m^2 of fire retardant had the HRR peak of 163 kW/m^2 and the samples with 300 g/m^2 had the HRR peaks of 142 kW/m^2 and 143 kW/m^2.

As a rule of thumb, cone calorimeter result <100 kW/m^2 indicates the possibility of getting classification B in the SBI test [162]. These results are still quite far from that class and adding more fire retardant only by surface application is quite demanding. Higher amounts or higher concentration of the fire retardant leads easily to salt formation on the surface.

More constant results of sapwood side might be because of more even fire retardant layer, it is easier to get penetration on the sapwood side. On small samples there is also a high risk that some of the solution flows to sides and penetrates from there, resulting in less solution on the testing surface. This might have had effect on these results as well.

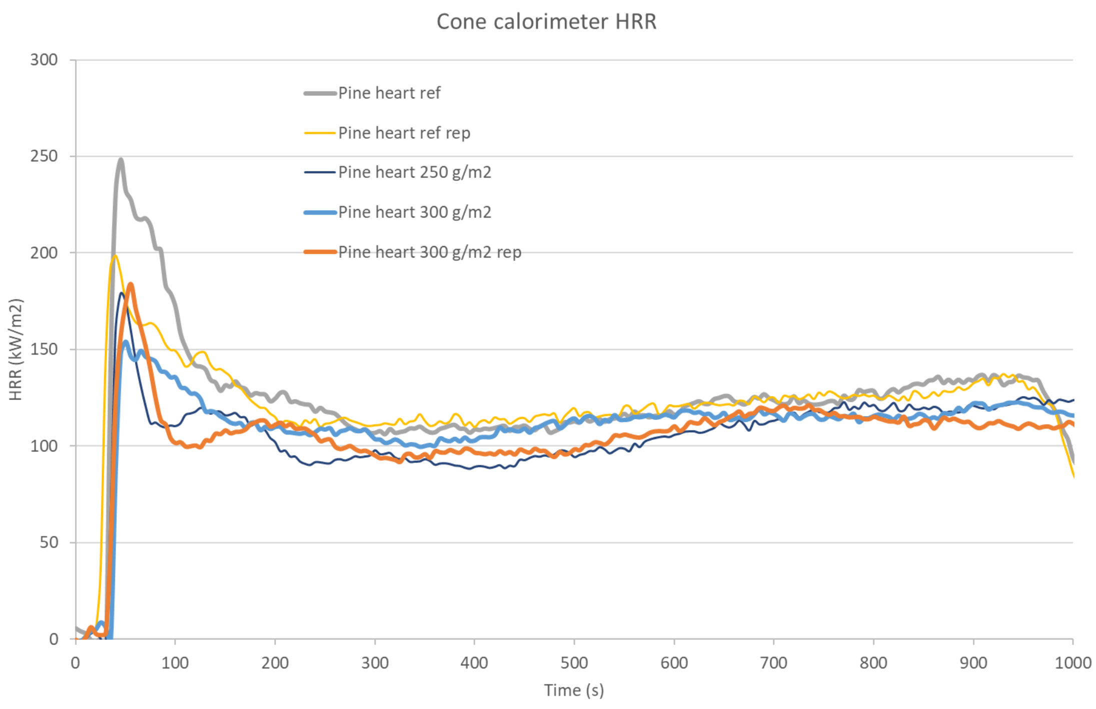


Figure 56. *Cone calorimeter HRR results of FR-R2 applied on the heartwood side of pine board.*

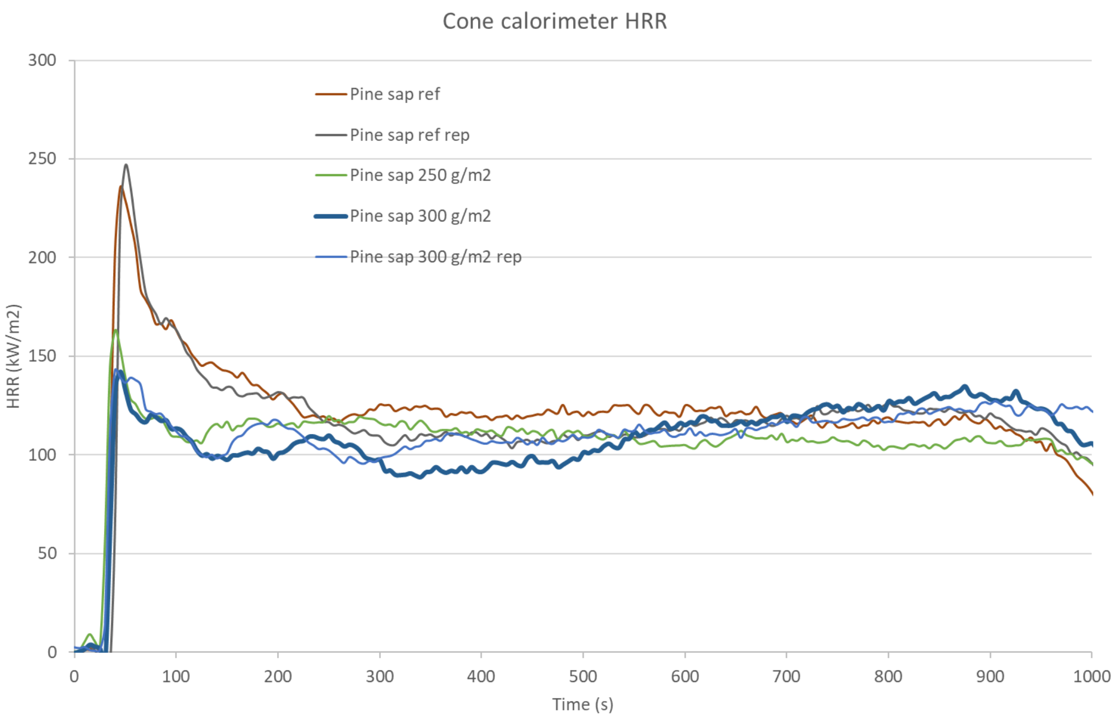


Figure 57*. Cone calorimeter HRR results of FR-R2 applied on the sapwood side of pine board.*

On spruce plywood it was possible to reach higher loadings of FR-R2, where the tested amounts were 300 g/m^2 and 400 g/m^2. These resulted in the maximum heat release rate of 184 kW/m^3 and 110 kW/m^3 when reference had the maximum of HRR 277 kW/m^2 (Figure 58). On this kind of material where it is easier to reach deeper penetration and higher loading of fire retardant it could be possible to reach the class B in the SBI-test. Higher loading or higher concentration does not lead so easily on salt formation on plywood as on solid wood.

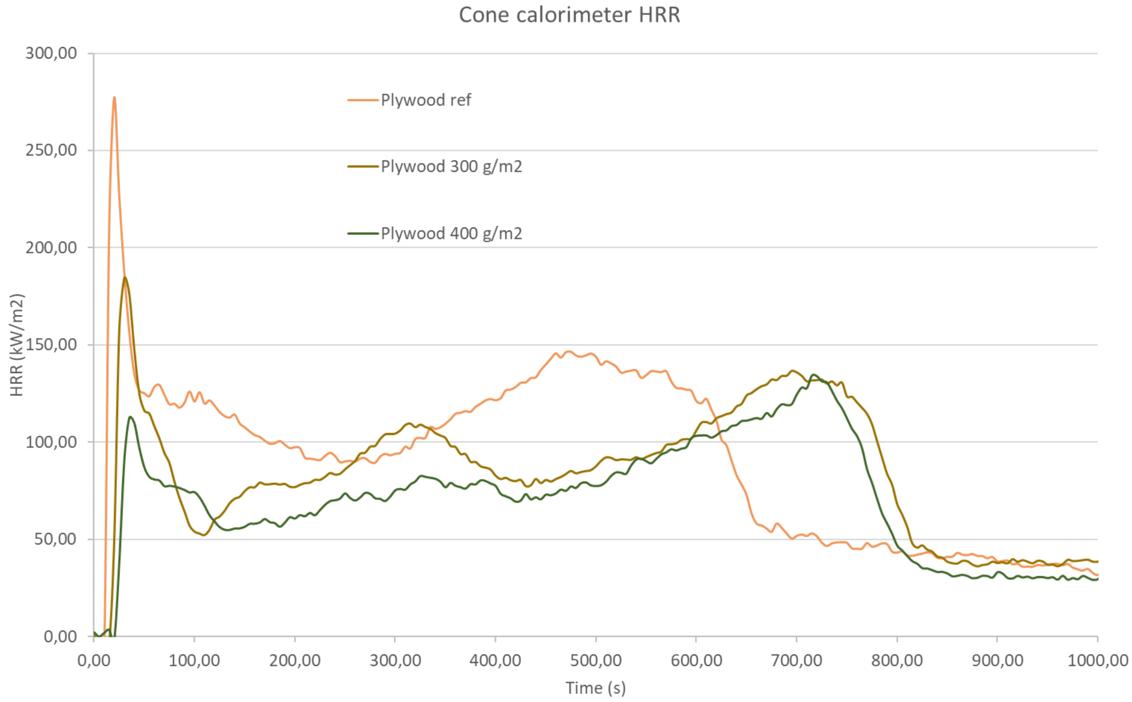


Figure 58. *Cone calorimeter HRR results of FR-R2 applied on the spruce plywood.*

Total smoke release (TSR) of the samples is presented in Figure 59. During the 1000 seconds test, the heartwood side references had the TSR values of 252 m^2/m^2 and 290 m^2/m^2, quite big difference as was expected based on the maximum HRR results. FR-R2 treated heartwood side gave TSR 366 m^2/m^2 for 250 g/m^2 sample and 395 m^2/m^2 and 370 m^2/m^2 for the samples with 300 g/m^2 of the fire retardant. The use of the fire retardant increased the total smoke release on the heartwood side of the pine samples. The sapwood side samples acted the same way. References had the TSR values of 293 and 320 m^2/m^2. The sample with 250 g/m^2 of FR-R2 had TSR 410 m^2/m^2. The samples with 300 g/m^2 of FR-R2 had TSR values of 397 m^2/m^2 and 389 m^2/m^2.

On the plywood, the use of FR-R2 fire retardant decreased the total smoke release. The reference had the TSR value of 387 m^2/m^2. FR-R2 with the amount of 300 g/m^2 had the

TSR of 256 m^2/m^2, and 400 g/m^2 loading resulted the TSR 199 m^2/m^2. Also, in the radiant panel test the smoke production was decreased on the plywood when FR-R2 was used.

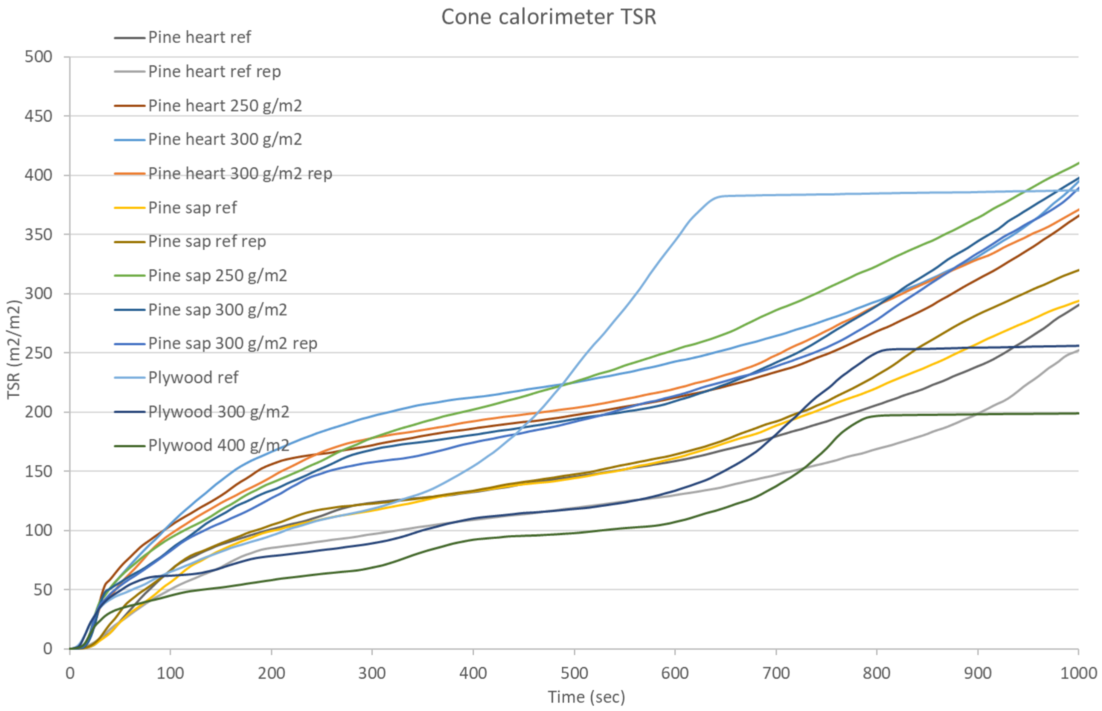


Figure 59. *Total smoke release results of the cone calorimeter samples.*

7.6 Impact of treatment on leaching properties of fire retardant

In order to test the durability of the fire retardants in rain and humid conditions, the leaching test was performed on the selected surface pre-treatment methods. The samples were immersed in distilled water for different times and dried afterwards. Fire performance of the samples after leaching was tested by the blow torch test. Leached phosphorus was analysed from the selected leaching waters.

A fast leaching test with tongue depressors was performed on the fire retardants before the full scale leaching tests. Based on the burning results of the in-house UL 94, the fire retardants were leached out in water immersion (Figure 60). Still, the fire performance of the leached samples was slightly better than the fire performance of the reference samples. This indicated that not all the fire retardant was leached out.

The remained masses of FR-R1, not activated FR-R2 and activated FR-R2 samples were 38,4 %, 36,2 % and 34,9 %, respectively. The remained mass of FR-TC sample was 28,0 %. All the leached samples burned to the clamp and looked like the FR-TC sample in Figure 54. The part which was protected by the clamp was the major part of the remained mass, therefore comparing small differences of the remained masses is not very reliable.

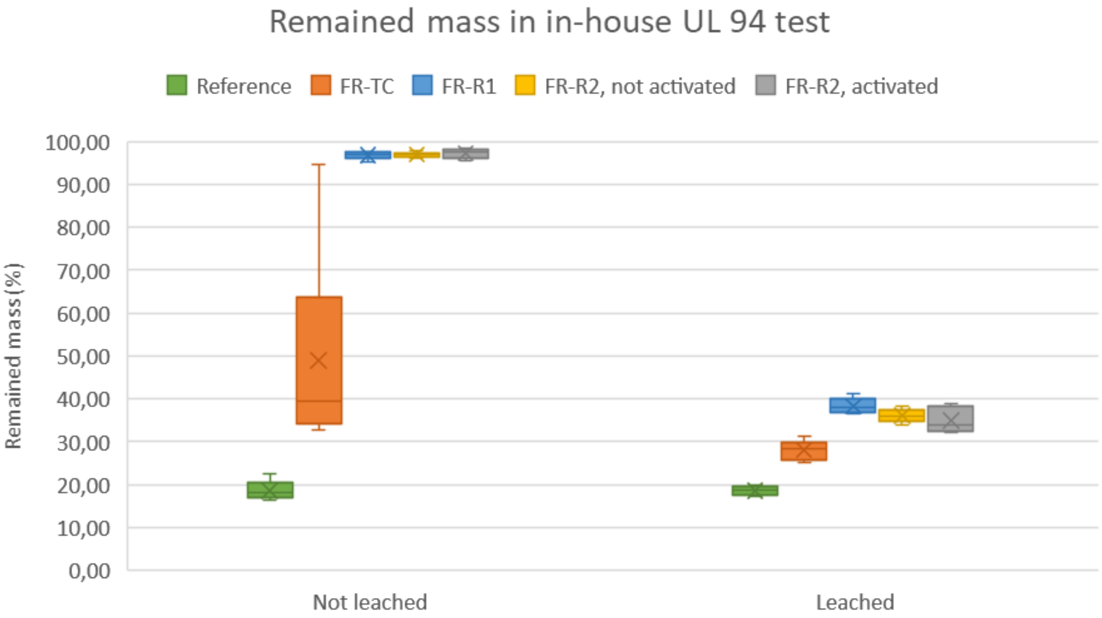


Figure 60. *Remained mass of tongue depressors after the in-house UL 94 test, before and after leaching.*

The leaching tests were performed on FR-R2 and FR-TC which were applied on the not pre-treated samples. Based on the highest liquid uptake, good penetration characteristics and reactive bonding capabilities of FR-R2, the leaching test was performed on FR-R2 also with different surface pre-treatment methods including: planing, sanding, plasma treatment, steam treatment and steam treatment followed by roasting. FR-R2 was applied on the pre-treated surface and then leaching test was performed.

In the result charts (for example Figure 63) blank reference indicates samples which had no fire retardant, and leaching was not performed on them. FR reference samples contain fire retardant, but leaching was not performed on them. 1 h, 3 h, 7 h, 16 h, 31 h, 79 h show the time that the fire retardant treated samples were under the leaching process. Blank 79 h are the samples which do not contain fire retardant, but they were in the leaching process for 79 h as a reference to study behaviour of plain wood during leaching.

The leached phosphorus of FR-R2 was analysed at Tampere University of Technology with ICP from the leaching waters of the not pre-treated samples. Figure 61 shows the amount of applied FR-R2 on the samples and the fire retardant amount remained in the samples after leaching (calculated from the ICP-results). It can be seen in Figure 61, that about half of the fire retardant had been already leached out after one hour. The remained amount (90 g/m^2) is hardly enough to provide protection in wood. After three hours of leaching, the curve of remained fire retardant amount seemed to level off to about 40 %. Some irregularities in the amount of leached fire retardant are likely due to the structure of wood which enabled easier leaching on those samples or a statistical error.

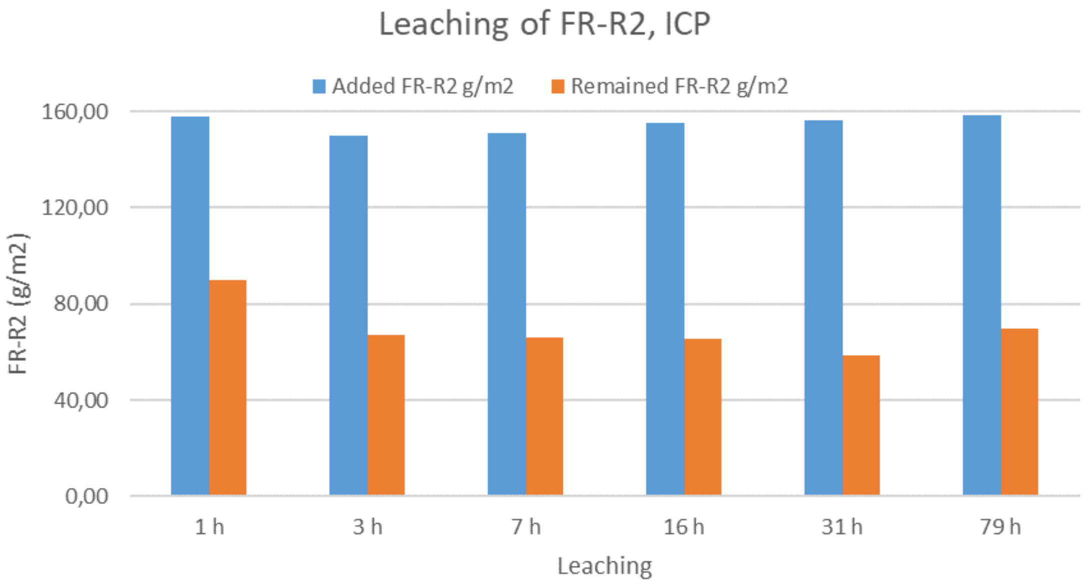


Figure 61. *Leaching of FR-R2 in water immersion measured from the leaching waters with ICP and calculated to g/m*^{2}.

In order to develop an in-house method for performing leaching test and analyse the leachate waters, samples from the same waters were analysed at Kiilto Oy with XRF. The results are quite comparable to the ICP results as seen in Figure 62. Only relevant difference is at 79 h sample. ICP gave as the remained FR-R2 amount 70 g/m^2 while XRF gave 56 g/m^2. Samples were diluted for the ICP testing; thus it is possible that some error had occurred at that stage. The result attained by XRF seems more logical.

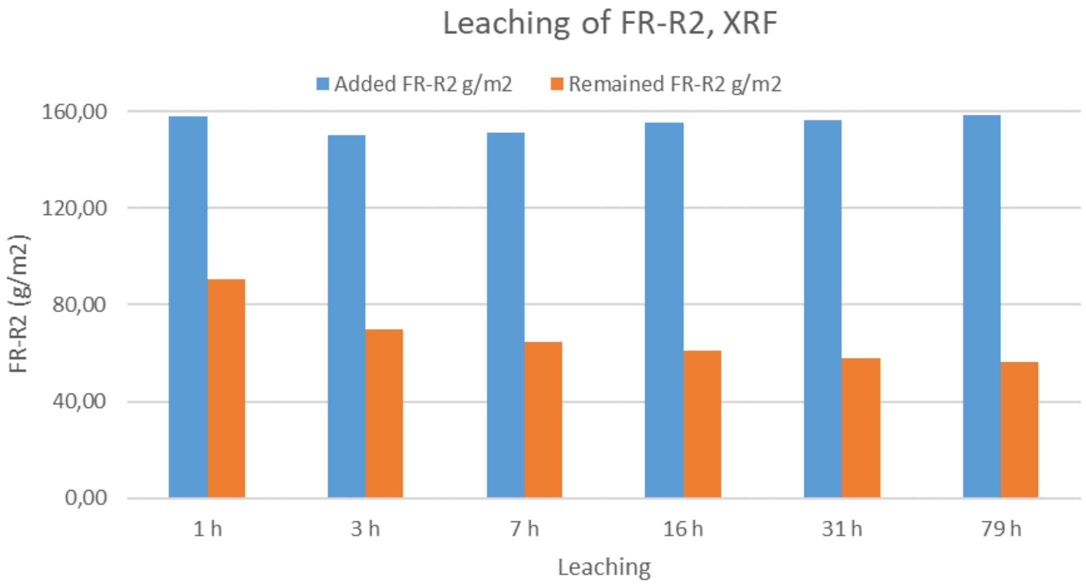


Figure 62. *Leaching of FR-R2 in water immersion measured from the leaching waters with XRF and calculated to g/m*^{2}.

The leached samples were burnt with the blow torch and the remained mass of the samples is shown in Figure 63. The blank samples without leaching had the lowest remained mass, 96,4 %. The fire retardant treated samples without leaching had logically the highest remained mass, 98,4%. The leached samples had the remained mass 97,4 - 97,8 %. This is in agreement with the ICP and XRF-results, that most of the fire retardant have leached out and did not affect burning.

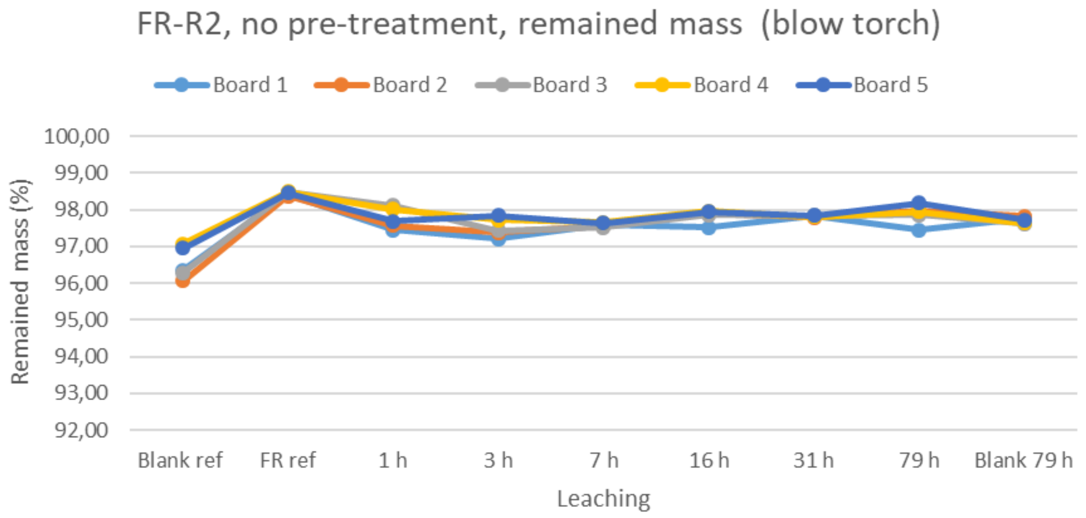


Figure 63. *Leaching results of FR-R2 applied on the not pre-treated surfaces.*

Phosphorus was analysed with XRF also from the leaching waters of the not pre-treated FR-TC samples. Figure 64 shows that about 70 % of the fire retardant had leached out after one hour and only about 30 g/m^2 of fire retardant remained on the surface. This is hardly a sufficient amount to prevent the burning of wood. Figure 65 shows the burning results performed on leached FR-TC samples. The remained mass of the blank and fire retardant reference samples were 97,4 % and 98,3 %, respectively. For the leached samples the remained masses were 97,4 – 97,7 %. After one hour leaching, the remained mass was 97,6 %, thus stable level of the burning was reached. This indicates that FR-TC cannot be used as an efficient leach resistant fire retardant.

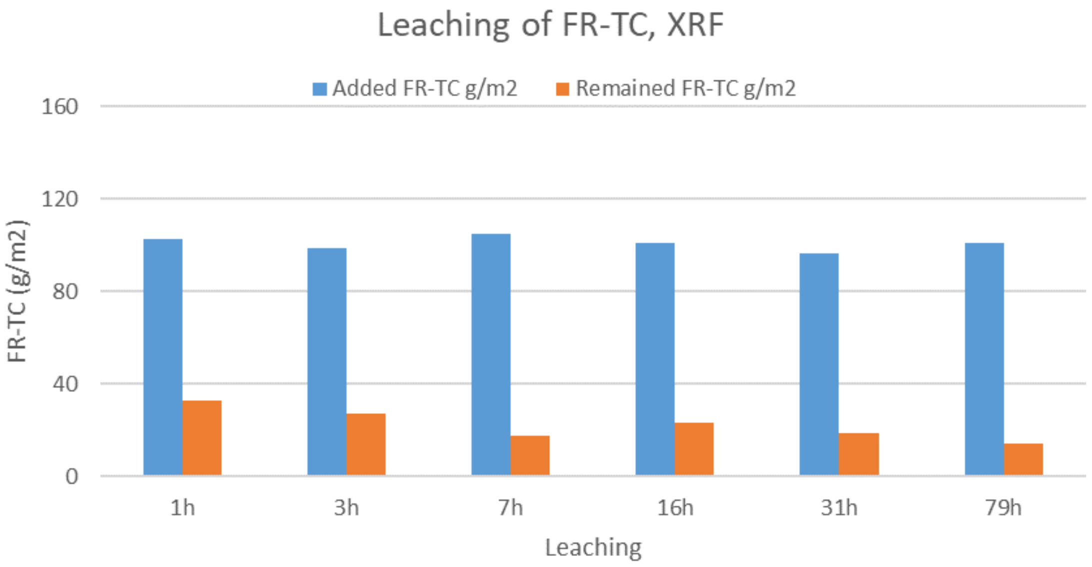


Figure 64. *Leaching of FR-TC in water immersion measured from the leaching waters with XRF and calculated to g/m^2.*

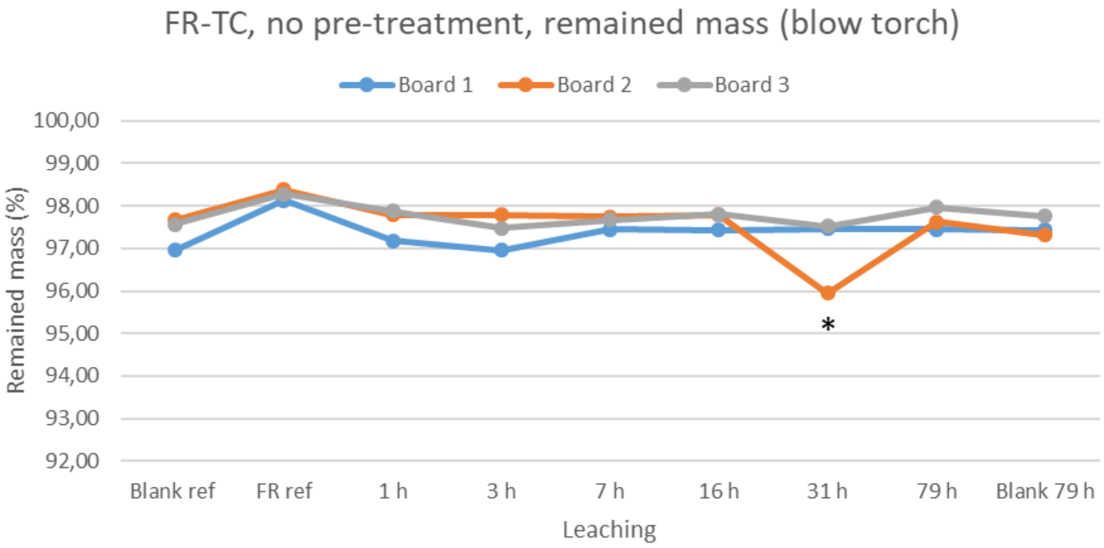


Figure 65. *Leaching results of FR-TC applied on the not pre-treated surfaces. Asterisk: extinguished after 5 min afterburn.*

In the next step, the pine wood pieces were planed and FR-R2 was applied on them. Figure 66 shows the burning results of the planed samples. On the planed samples the stable remained mass was reached after one hour leaching. As it was seen in Figure 39, planing did not provide deep penetration and based on these results, no bonding between wood and the fire retardant seemed to happen.

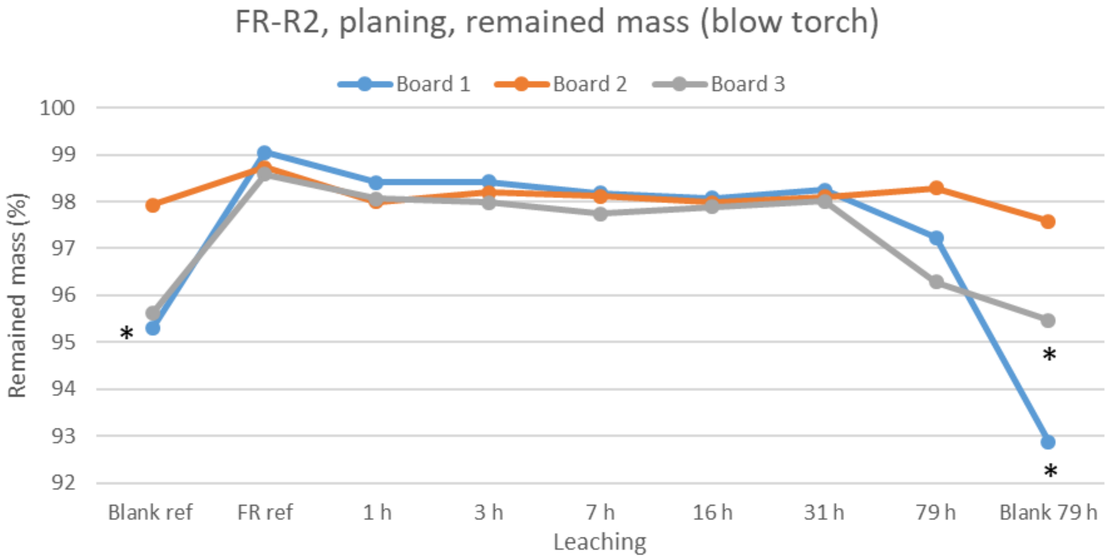


Figure 66. *Leaching results of FR-R2 applied on the planed surfaces. Asterisk: extinguished after 5 min afterburn.*

Sanding as a pre-treatment gave deeper penetration than planing as was seen in Figure 40, but based on the leaching test, sanding did not provide any better leach resistant properties (Figure 67). Again, after one hour leaching, the steady 97,5 – 97,7 % remained mass was reached. The blank and reference samples had the remained mass of 97,0 % and 98,4 % respectively.

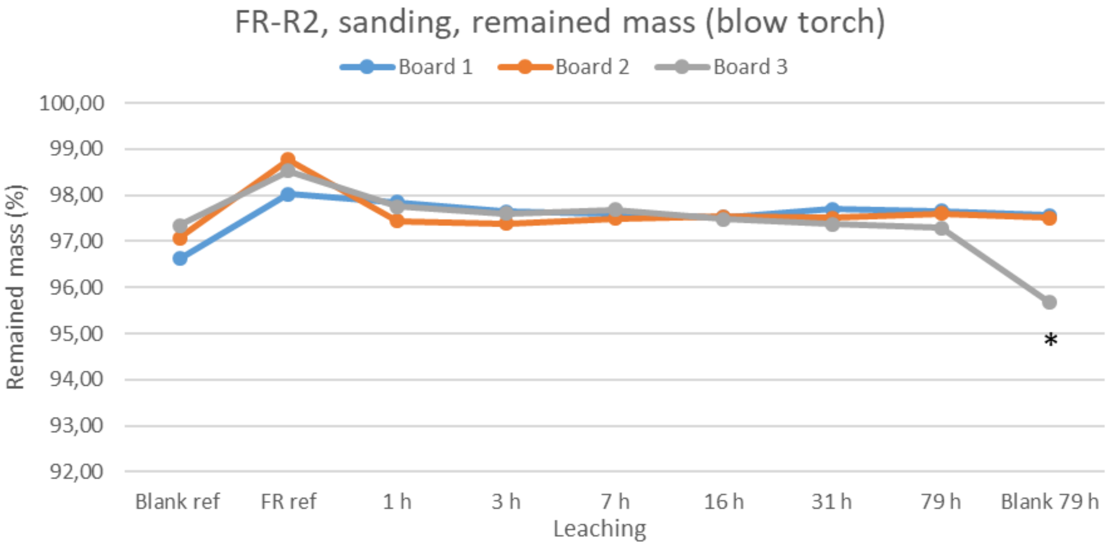


Figure 67. *Leaching results of FR-R2 applied on the sanded surfaces. Asterisk: extinguished after 5 min afterburn.*

The plasma pre-treatment did not provide deep penetration, but its ability to form functional groups on the treated wood surface was promising for the reactive fire retardant. More active groups could lead to a strong bond between wood and the fire retardant. Figure 68 shows that in this study, such strong bond was not achieved. After one hour leaching the remained mass was in the same level as on the blank sample. Slight increase in the remained mass towards longer leaching times was due to malfunction of the blow torch. Later it was discovered that the nozzle was partly blocked by dirt and thus the flame was smaller and did not cause as severe burning as on the earlier burned samples.

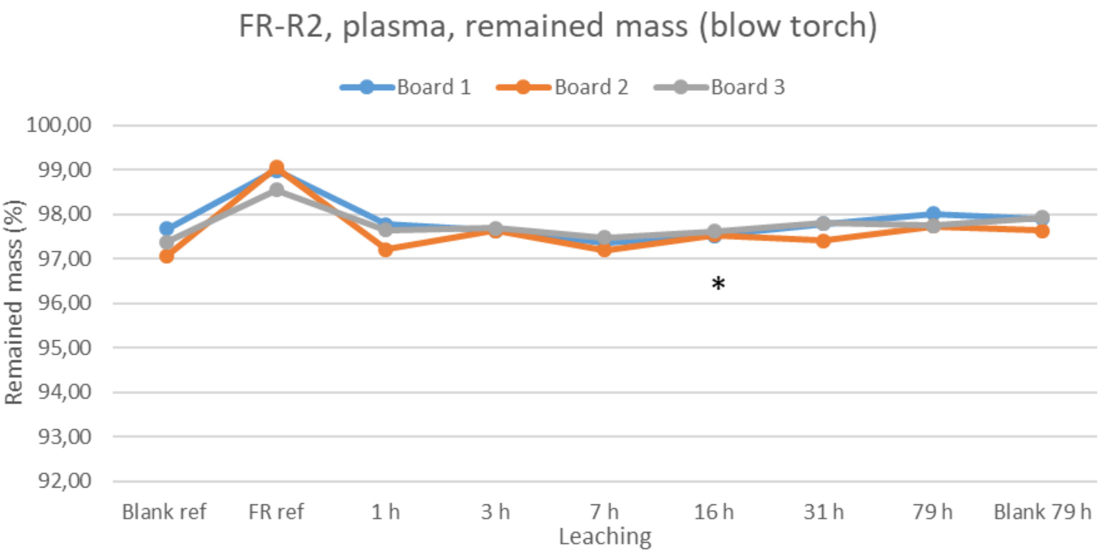


Figure 68. *Leaching results of FR-R2 applied on the plasma treated surfaces. Asterisk: the blow torch flame looked smaller after 16 h samples.*

Figure 69 shows the burning results of the steam treated samples. The reference samples containing fire retardant had the remained mass of 98,3 %. And leaching stabilized the remained mass to about 97,0 – 97,4 % already after one hour leaching. This is significantly higher than the remained mass of the blank samples, 95,5 %. Only on the planed samples, which were extinguished, the blank samples had such a low remained mass and a great difference between the blank and leached samples. The remained mass of the steam treated samples stayed on a higher level than the remained mass of the blank reference samples.

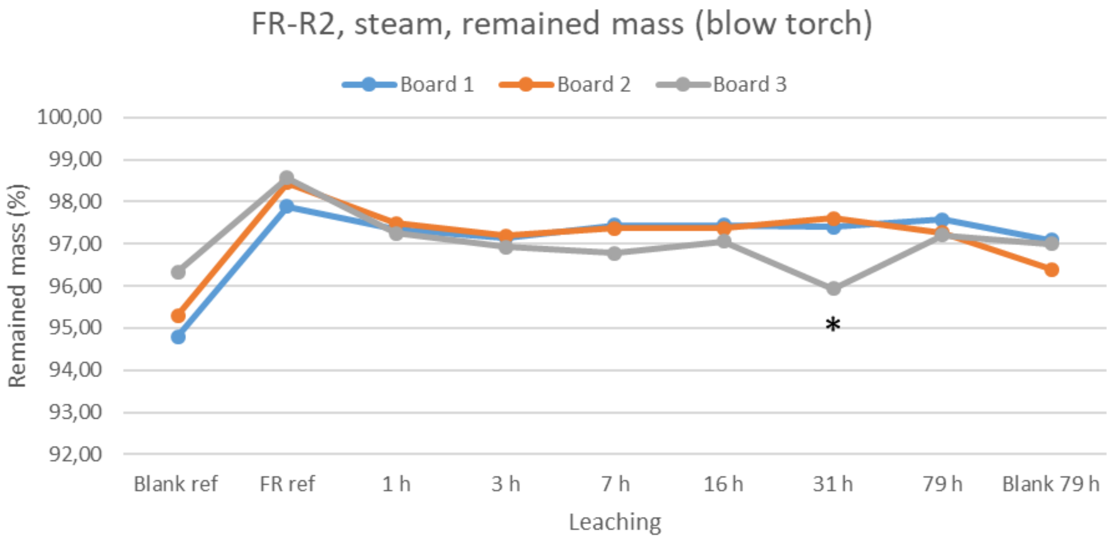


Figure 69. *Leaching results of FR-R2 applied on the steamed surfaces. Asterisk: burning escaped on the other side of sample.*

The steam treatment followed by roasting is the only treatment method where descending trend in the remained mass was observed when the leaching time increased (Figure 70). The remained mass of blank reference samples was 96,3 % while the fire retardant references had the remained mass of 98,3 %. The remained mass of the one hour leached samples was 97,2 % and for the 79 hours leached samples it was 96,6 %. Exception of the three hours leached samples, the other remained mass were between these two. This indicates that the inactivation of surface was successful and the hydrophobicity of the surface was increased and this hindered leaching of the fire retardant.

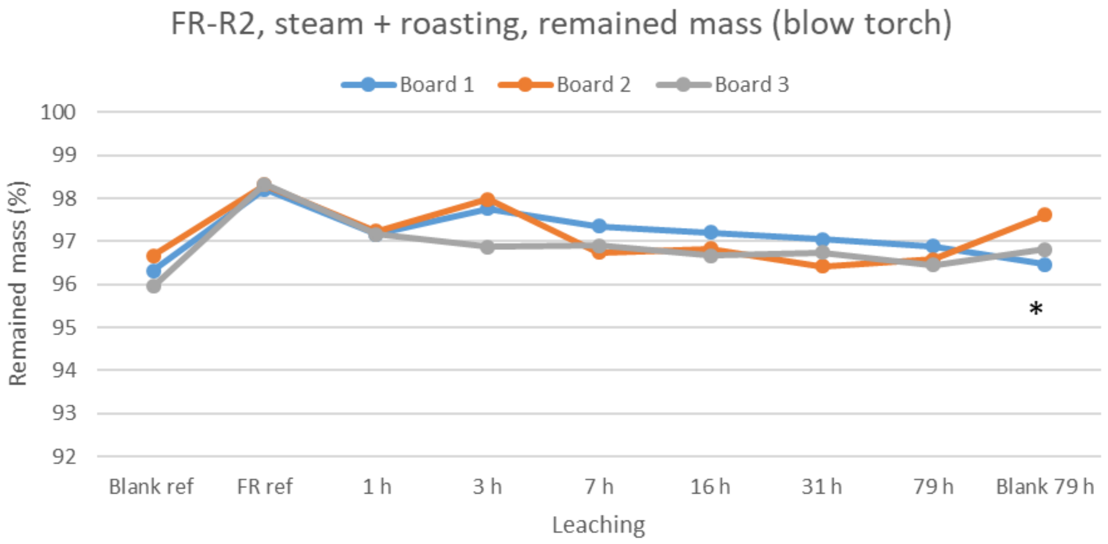


Figure 70. *Leaching results of FR-R2 applied on the steamed surface, the samples roasted at 160 °C for 30 minutes before leaching. Asterisk: gas bottle changed before the blank 79 h samples.*

The remained mass of steam treated samples (Figure 69) stayed on the higher level than the remained mass of the blank reference samples. Steaming also resulted in a deeper penetration that without the pre-treatment was achieved. However, when the results of the steam and roasted samples (Figure 70) are observed, the strong bond between the fire retardant and wood did not appear to be an explanation for the results of steamed samples. Roasting hindered the leaching and still the remained mass returned to the blank reference level.

Extractives have great impact on burning properties of wood. According to Mészaros et al. [163], Poletto [164] and Shebani et al. [165] the removal of extractives improved thermal stability of wood, independent of the specie. In pine woods, extractive amount varies within wood parts, and between trees the total amount of extractives varies significantly [166]. Kilic et al. [167] measured 30,9 mg/g of pine extractives as water soluble. This could explain why the leached blank samples did not have the same percentage of remained mass as the not leached blank samples. Water soluble extractives leached out in the water immersion and the leached samples were thermally more stable than the non-leached samples.

7.7 Impact of wood density on burning properties

According to literature study performed by Friquin [21], it is widely accepted by researchers that density has great impact on burning properties of wood; when the density increases the charring rate decreases. Charring degrades wood mass, with the higher density the mass is greater and thus the charring rate is slower. The slower burning was noticed in this study as well. In Figure 71, the remained mass of the blank samples is grouped by the density. It is seen that the remained mass increased when the density of the samples increased.

According to Friquin [21] also other properties rather than the density alone can affect the burning of wood. One of these is the grain orientation; thermal conductivity and gas permeability is greater along the grain than perpendicular the grain, thus the charring rate is greater in the tangential direction than in the radial direction. In this study, boards were cut in the tangential direction (burning was performed on the radial direction), but still great variation occurred between the boards and even within the board how grains ended on the tested surface. This is the normal case in the commercial boards.

Chemical composition of wood affects burning. Cellulose, hemicellulose and lignin have different thermal degradation characteristics. Lignin content causes the highest differences in burning behaviour. lignin results in a slow pyrolysis rate and a high char yield. Softwoods have higher lignin content than hardwoods which explains higher ignition temperature of softwoods [21]. In this study, only one wood specie was used, thus no great variation in the results should come from the lignin content.

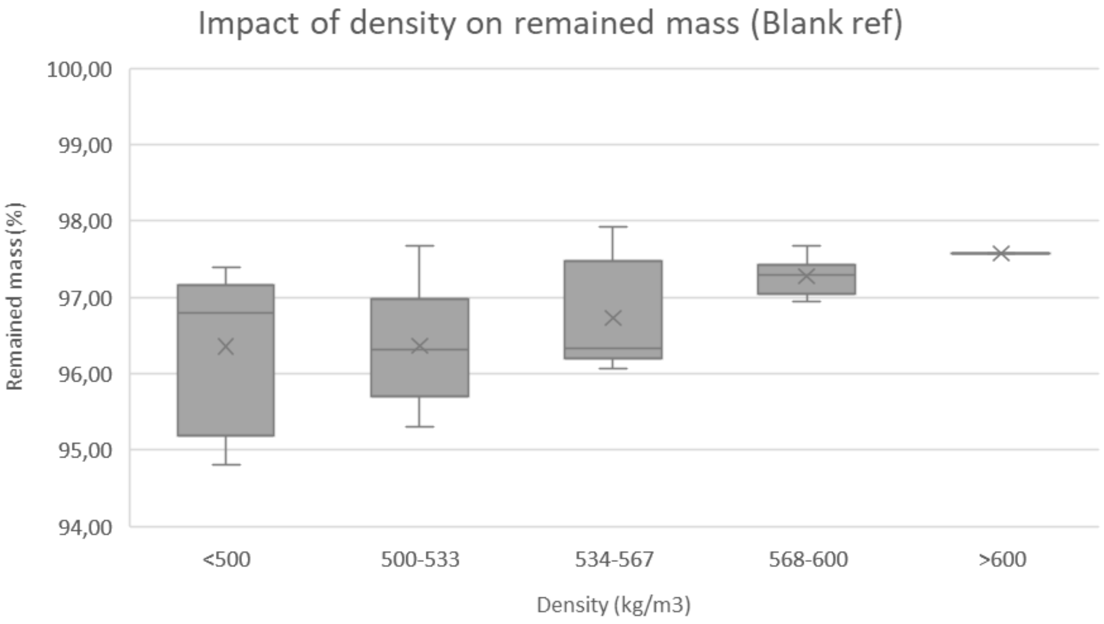


Figure 71. *Impact of density on the remained mass in the blow torch test. Only the blank not leached reference samples. Density group >600 kg/m*^{3} *included only one sample and thus should be concerned with caution.*

Based on results attained in this study, FR-R2 can prevail the burning properties of wood. Figure 72 shows that the remained mass of FR-R2 does not follow the density of wood as did with the blank samples. Thus, the fire retardant treated wood acts predictable in burning.

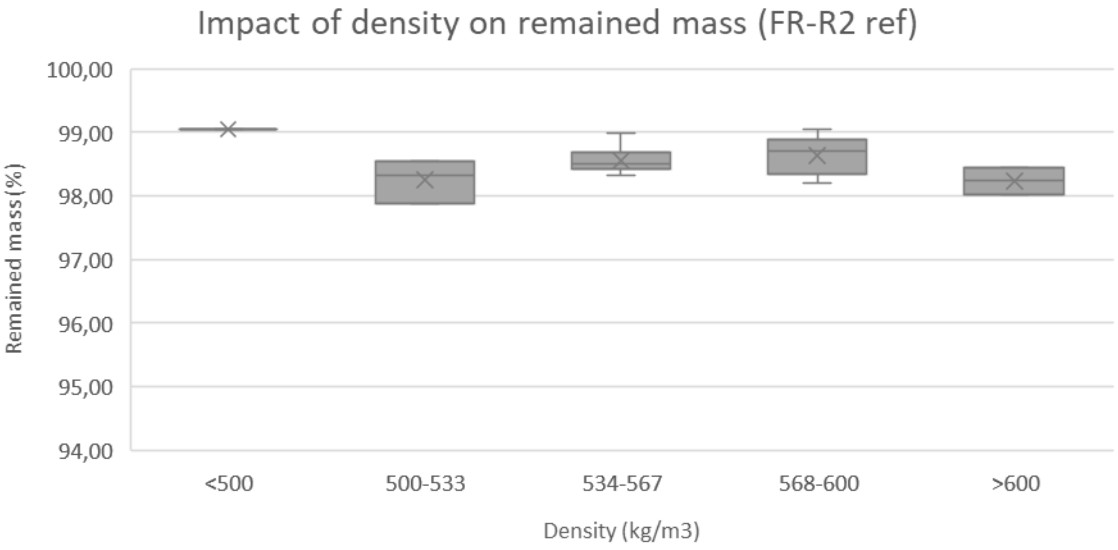


Figure 72. *Impact of density on the remained mass in the blow torch test. FR-R2 treated not leached samples. Density group <500 kg/m*^{3} *included only one sample and thus should be concerned with caution.*

8. CONCLUSIONS

Different surface pre-treatment methods were tested on wood in order to improve the durability and the penetration depth of fire retardant applied on the surface. Planing, sanding, plasma treatment, microwave treatment or steam treatment was performed on the wood surface before the fire retardant application. The impact of treatments was evaluated first by contact angle measurements and then by measuring the penetration depth of fire retardant. Different burning methods, including the small flame test, the in-house UL 94, the blow torch burning, the cone calorimeter test and the radiant panel test were used to compare the burning properties of two fire retardant. Also the leaching of fire retardants in water immersion was tested.

Some improvements on wood wettability were achieved through the surface pre-treatments. Planing decreased the contact angle, but no good penetration or liquid uptake was achieved. Sanding resulted a slightly higher contact angle than planing, but grooves on the surface facilitated liquid spread resulting in deeper penetration and higher liquid uptake. Plasma pre-treatment decreased the contact angle significantly, but variation of the results increased as did with the planing and the sanding. Despite of the hydrophilic surface, no good penetration or durable bond between wood and the fire retardant was achieved. Soaking gave the best penetration depth, but long treatment time and high amount of needed fire retardant did not make it a superior treatment method. Adding surfactants improved the penetration depth and thus made surface applying of the fire retardant more efficient.

Both of the tested fire retardants improved the fire performance of wood; however, the reactive fire retardant was slightly better than the two-component. Problem with FR-TC was salt formation on the surface which prevented the use of any higher concentrations. With FR-R2, the use of higher concentration could be possible at least on the planed surfaces. It should be tested, what is the highest possible concentration, and whether it provides any better fire retardancy. Differences in the fire retardant amounts were so small in this study that they did not correlate directly with the burning properties.

None of the tested fire retardants were leach resistant. No strong bond between FR-R2 and wood were achieved through the pre-treatments. Combining roasting with also other pre-treatments than just steaming could provide interesting information about ability of the surface inactivation to hinder leaching of the fire retardants. Testing higher temperatures and/or longer roasting times could provide more time before all the fire retardant have leached out. Evaluation of the leaching test procedure would require a leach resistant fire retardant, but during these tests, no such thing was available.

Small flame testing was very inefficient with wood even though it is the standard method. With wood it is very easy to pass, but it does not predict anything about performance in the SBI-test. The blow torch burning provided a bigger flame which helped to have differences between the samples. Still there are some parameters that should be considered, for example, the gas amount and a dirt in the nozzle can affect the flame.

Burning behaviour of wood is greatly impacted by its structure and chemical composition. It is very hard to control all aspects. In laboratory conditions, certain parameters can be controlled, like choosing the woods. But in real life, no such thing is possible. Therefore, a fire retardant should be efficient enough to prevail burning properties of wood and thus make it possible to predict events in case of a fire.

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