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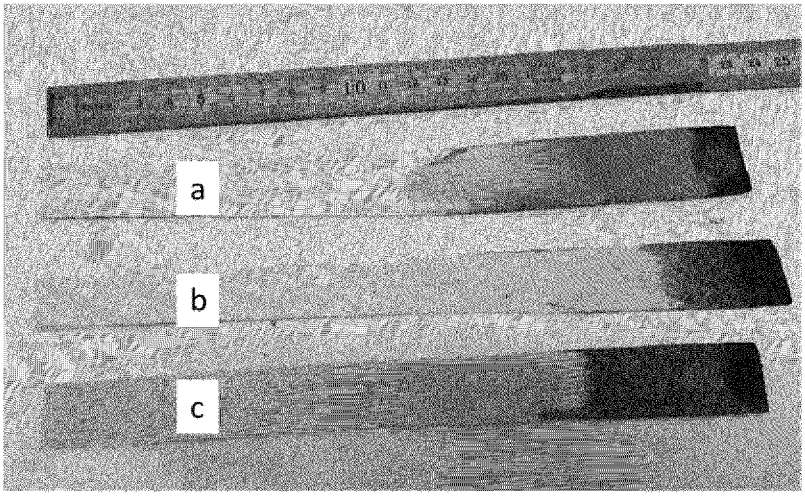
(54) **Title:** Flame retardant composition and its preparation

FIGURE 1



(57) **Abstract:** 53 ABSTRACT The present invention provides a method of producing a flame retardant composition comprising hemicellulose and lignin components; and its use. 5

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TITLE: Flame retardant composition and its preparation

FIELD OF THE INVENTION

The present invention relates to the technical field of flame retardants, in particular to a flame retardant composition comprising lignin and hemicellulose residues and a preparation method of such flame retardant composition.

BACKGROUND OF THE INVENTION

The traditional halogen-based flame retardants have the advantages of good flame retarding effect, but they release a large amount of toxic gases when burned, which causes great harm to human health and the environment

Of halogen-free flame retardant alternatives, phosphorus-based flame retardants are widely used because of their low smoke, low intensity, and no corrosive gas generation. Further, flame retardants containing both phosphorus and nitrogen have low toxicity and better thermal stability, and phosphorus and nitrogen have synergistic flame retardant effect. However, although the current common flame retardants have excellent flame retardant properties, their synthetic raw materials are mainly based on non-biodegradable and increasingly depleted petrochemical resources. Therefore, large-scale production and use will negatively affect the environment.

The preparation of biodegradable, sustainable, and environmentally friendly flame retardants has important social significance and economic value.

SUMMARY OF THE INVENTION

The present invention provides a simple method for manufacturing flame retardants, and provides a flame retardant composition which has great flame retardant effect and at the same time is produced from a sustainable source. Furthermore, the flame retardant components are soluble in water and can therefore be applied as an environmentally benign aqueous preparation for many substrates.

In a first aspect, the present invention provides a **method of preparing a flame retardant composition** comprising hemicellulose components and lignin components from plant material, said method comprising the steps of:

(i) providing plant material,

wherein the plant material is selected from cereal straw and grasses;

(ii) mechanically dry-treating said plant material to reduce its size;

(iii) suspending the plant material in an aqueous solution;

(iv) adjusting the pH to alkaline conditions and increasing the temperature of the suspension, and agitating the suspension, to dissolve and/or disperse hemicellulose components and lignin components in the aqueous solution, wherein said hemicellulose and lignin components originates from the plant material; and

(v) separating the material obtained in step (v) into a solid fibrous fraction and a liquid flame retardant fraction being a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components;

The method optionally further comprises a step of concentrating the liquid flame retardant composition to increase the % dry matter content.

In one preferred embodiment, the method comprises an additional step of adding a flame retardant additive to the liquid flame retardant composition from step (v) or to a concentrated sample of the liquid flame retardant composition from step (v). The flame retardant additive further enhances the flame retardant effectiveness of the composition. In one embodiment the flame retardant additive is a smoke suppressant compound. Preferably, the flame retardant additive is selected from iron oxide, calcium carbonate and expandable graphite.

Hence, in one embodiment, the present invention provides a method of preparing a flame retardant composition comprising hemicellulose components and lignin components from plant material, said method comprising the steps of:

(i) providing plant material,

wherein the plant material is selected from cereal straw and grasses;

(ii) mechanically dry-treating said plant material to reduce its size;

(iii) suspending the plant material in an aqueous solution;

(iv) adjusting the pH to alkaline conditions and increasing the temperature of the suspension, and agitating the suspension, to dissolve and/or disperse hemicellulose components and lignin components in the aqueous solution, wherein said hemicellulose and lignin components originates from the plant material;

(v) separating the material obtained in step (v) into a solid fibrous fraction and a liquid flame retardant fraction being a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components;

(vi) optionally concentrating the liquid flame retardant composition to increase the % dry matter content; and

(vii) adding a flame retardant additive to the liquid flame retardant composition from step (v) or (vi).

In one embodiment, the hemicellulose components and lignin components are dissolve and/or disperse by increasing the temperature in step (iv) to >80 °C and adjusting the pH to between 9-12.

In one embodiment, the average particle size of the plant material resulting from the dry mechanical treatment is less than 1 cm.

In one embodiment, the suspended plant material in step (iii) is enzymatically treated using one or more hemicellulase enzymes, such as xylanases and/or ferulic esterase.

Preferably, the ratio of hemicellulose components and lignin components in the flame retardant composition obtained by the method of the present invention is between 40:60 – 60:40, based on dry matter content.

In one embodiment, the flame retardant composition comprises at least of 60, 70, 80, or 90% hemicellulose components and lignin components, based on total dry matter content.

In one embodiment, the flame retardant composition comprises at least of 90% hemicellulose components and lignin components, based on total dry matter content.

In one embodiment, the plant material suspended in the aqueous solution in step (iii) is dewaxed cereal straw, such as dewaxed cereal straw obtained by a method comprising the steps of: (a) enzymatically treating the cereal straw suspended in an aqueous solution in step (iii) with protease and/or pectinase enzymes, (b) optionally subjecting the mixture obtained in step (a) to wet mechanical treatment, and (c) removing wax from the solution prior to adjusting pH and increasing the temperature in step (v).

In a second aspect, the present invention provides a **flame retardant composition** comprising dissolved and/or dispersed hemicellulose components and lignin components in a ratio of between 40:60 – 60:40, based on dry matter content. This flame retardant composition is obtainable by the method of the present invention, as disclosed herein.

In one embodiment, the hemicellulose components of the flame retardant composition comprise monomers, oligomers and/or polymers of arabinoxylan, and the lignin components of the flame retardant composition comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

In one embodiment, the flame retardant composition comprises at least of 60, 70, 80, or 90% hemicellulose components and lignin components, based on total dry matter content.

In one embodiment, the hemicellulose components and lignin components constitute at least 90% of the total dry matter content of the aqueous composition.

In one embodiment, the flame retardant composition further comprises a flame retardant additive for further enhancing the effectiveness of the flame retardant composition. In one embodiment the flame retardant additive is a smoke suppressant compound. In one preferred embodiment, the flame retardant additive is selected from iron oxide, calcium carbonate and expandable graphite.

In a third aspect, the present invention concerns the use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, as a flame retardant. This aqueous composition is obtainable by the method of the present invention, as disclosed herein.

In one embodiment, the aqueous composition is applied to the item by brushing or spraying the composition on the surface of the item, soaking the item in the composition, and/or impregnating the composition into the item, such as by vacuum pressure impregnation.

In a fourth aspect, the present invention concerns the use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, for enhancing fire resistance of an item, such as solid wood elements, wood composite materials, and/or insulation materials based on wood fibres and other natural fibres such as cotton, flax, hemp, sisal, jute. This aqueous composition is obtainable by the method of the present invention, as disclosed herein.

In one embodiment, the aqueous composition is applied to the item by spraying the composition on the surface of the item, soaking the item in the composition, and/or impregnating the composition into the item, such as by vacuum pressure impregnation.

In a fifth aspect, the present invention provides a **method of enhancing fire resistance of an item**, said method comprising applying a flame retardant composition comprising dissolved and/or dispersed hemicellulose and lignin components, onto the item. This flame retardant composition is obtainable by the method of the present invention, as disclosed herein.

In one embodiment, the flame retardant composition is applied to the item by spraying the composition on the surface of the item, soaking the item in the composition, and/or impregnating the composition into the item, such as by vacuum pressure impregnation.

DESCRIPTION OF THE INVENTION

Brief description of the figures:

Figure 1: Flame retardant test using wood beech strip. Picture of wood beech strip soaked in lignin-based flame retardants and then attempted to light using a cigarette or candle lighter. Lignin-based flame retardants were prepared by mechanical dry treatment, fractionation, protease and pectinase treatment, hemicellulase treatment, alkaline pulping treatment, and concentration by evaporation: (a) 30 % dry solids concentration, (b) 15 % dry solids concentration, (c) 7.5% dry solids concentration.

Figure 2: Flame retardant test using wood beech strip. Picture of wood beech strip soaked in lignin-based flame retardants and then attempted to light using a cigarette or candle lighter. (a) Lignin-based flame retardant prepared by mechanical dry treatment, fractionation, protease and pectinase treatment, hemicellulase treatment, alkaline pulping treatment, and concentration by evaporation. (b) Lignin-based flame retardant prepared as in (a), further oxidized at 80°C, by applying 100 ml of 35% hydrogen peroxide per 2L of flame retardant composition, pH 10.5, temp 80°C, incubation time 2 hours.

Figure 3: Graphical illustrations of data from Mini-SBI test of wooden samples. **(A)** Heat Release Rate, **(B)** Total Heat Release. **(C)** Fire Growth Rate. FIRAX= commercial flame retardant (positive control); Untreated test 417 = negative control. Test 415 and test 416 = samples treated with flame retardant composition of the present invention.

Figure 4: Graphical illustrations of data from Mini-SBI test of wooden samples. **(A)** Scaled Average Heat Release Rate HRRav(t), **(B)** Scaled Total Heat Release THR(t). **(C)** Scaled FIGRA, **(D)** Scaled Total Smoke Production TSP(t). Firax= commercial flame retardant (positive control); Untreated (test 416) = negative control. PFE1, PFE2, PFE3 = samples treated with flame retardant composition of the present invention.

Figure 5: MDF sample triplicates exposed to a small-gas-flame test. The untreated control samples are shown at the top, and the flame retardant composition samples of the present invention are shown at the bottom. **(A)** Front coated face. **(B)** Back uncoated face.

Figure 6: Carbon layer of plywood. **(A)** Sample treated with the flame retardant composition of the present invention, **(B)** Untreated sample.

Figure 7: Wood samples (beechwood sticks -"tongue-depressors") dip-immersed half of the length in test solution and allowing to soak for 20 min followed by wiping off excess liquid with tissue paper, and drying in an convection oven at 70°C for 45 minutes. The sticks were then tested via application of the direct flame of a candle lighter, to the lower face of the stick. Stick 1 = Sample 1B (40/60 ratio lignin/hemicellulose). Stick 2

= Sample 2B (40/60 ratio lignin/hemicellulose + $CaCO_3$ + Fe_3O_4). Stick 3 = Sample 2C (40/60 ratio lignin/hemicellulose + $CaCO_3$ + expandable graphite). Stick 4 = untreated.

Abbreviations, terms, and definitions:

The term "flame retardants" refers to chemicals and compositions which prevent or slow the further development of ignition. They may be added to manufactured materials, such as wood, plastics, and textile materials, preferably wood, wood based panels, wood and/or other plant derived natural fibres, such as those used for insulation for buildings. As further disclosed herein flame retardants may be added to the materials as a surface coating or be added by means of soaking and/or impregnation. Flame retardants of the present invention also

"Plant or lignocellulosic material" or "plant or lignocellulosic biomass" means a wide and varied group of plant parts from many species. The terms plant and lignocellulosic material and biomass are used interchangeably. Plant material that may be used as starting material in the present invention comes from multicellular, macroscopic plants comprising stem and leaves which might be (at least one of them) sheathed by a natural outer layer or epidermis that is coated with a waxy waterproof protective layer.

"Cereal straws" means the stems, leaves and husks of the cereal plant remaining after harvest of the cereal grains.

"Grasses" means late season (partially) lignified grass material.

"Cellulose" means a polysaccharide built up from ß-D-glucose units. D-glucose ($C_6H_{12}O_6$) is a saccharide containing five hydroxyl functional groups and an aldehyde group on carbon-1. Cellulose is a straight chain polymer; hydroxyl (-OH) groups form hydrogen bonds with atoms on neighboring chains to connect them, forming microfibrils. Cellulose exhibits both crystalline and amorphous regions. Many properties of cellulose depend on its degree of polymerization, i.e. the number of glucose units that make up one polymer molecule.

"Hemicellulose" means an often branched type of polysaccharide, derived from several sugars including xylose, mannose, glucose, galactose, rhamnose, and arabinose. Cereal straw hemicellulose primarily consists of arabinoxylan. In the present invention, the definition of hemicellulose further means hemicellulose derived products such as oligosaccharides and sugar monomers derived by hydrolysis of the hemicellulose.

"Hemicellulose residue" or "Hemicellulose component" means fractions of different degree of polymerization derived from plant hemicellulose, released from the plant cell walls via chemical, physical and/or enzyme aided processing of said plants or parts of plants, and can be identified as having been derived from said hemicelluloses. Cereal

straw hemicellulose components primarily comprise oligomers and/or polymers of different degree of polymerization originating from arabonixylan hemicellulose.

"Lignin" is a complex cross-linked racemic polymer comprising various phenyl propane units. It is relatively hydrophobic and aromatic in nature. There are three monolignol monomers, methoxylated to various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These lignols are incorporated into lignin in the form of the phenylpropanoids p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively.

"Lignin residue" or "Lignin component" means fractions derived from plant lignin released from the plant cell walls via chemical, physical and/or enzyme aided processing of said plants, and can be identified as having been derived from said lignin. Cereal straw lignin components primarily comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

"Wax" or "wax components" means all various forms of wax coated on the surface of the plant material. It is collectively used to describe the waxy components of cuticles (cuticular wax) covering the areal parts of plants, including wax at the surface of the plant (epicuticular wax) as well as wax just below the surface of the plant (intracuticular wax). Wax comprises linear very-long chain (VLC) compounds, including varying ratios of fatty acids, primary and secondary alcohols, esters, aldehydes, free fatty acids, alkanes, and ketones. In addition, cyclic compounds such as pentacyclic triterpenoids, alkylresorcinols, sterols, and steryl esters occur in the wax of many species. Lipids making up plant cell walls in macroscopic or in microscopic (unicellular) plants are not considered "wax" as such in the present context.

"Dewaxed plant material" means plant material which has been treated in a way that removes/disassociates cuticular wax from the plant material, such as more than 50, 55, 60, 65, 70, 75, 80, 85, 90%, or even more than 95% of all plant wax has been removed, wherein the wax content is determined by the method provided in section IV of this application.

"Dry mechanical pretreatment" relates to mechanically processing the plant material in a dry process by cutting, chopping, crushing, milling, or a similar process, such that the plant material is reduced in size. It may involve the wax coating being cracked and released from the remaining, partly de-waxed plant material.

"Wet mechanical pretreatment" is in the present context a mechanical treatment of the plant material suspended in aqueous phase. It may be performed using a refiner, such as a refiner known from the standard paper pulping industry, including e.g. conical refiners and disc type refiners, operated at ambient or atmospheric pressure: so-called "atmospheric refining". Alternatively, wet mechanical treatment may be performed by

wet milling to shear or crush solids suspended in a liquid (slurry), such as using e.g. a toothed colloid mill.

The term "pulping" traditionally refers to a process that extracts fibrous material, cellulose, from wood or other raw material as a prelude to papermaking. The purpose of pulping is to liberate cellulose fibers from other chemicals and impurities in the wood (or other fibrous source). Chemical pulping results in extensive removal of lignin and other non-fiber constituents of wood; alkaline pulping being the dominant method used. In the present invention, alkaline pulping is used for solubilizing hemicellulose and lignin components from plant material, specifically from non-woody biomass, preferably from cereal straw and/or grasses, most preferably cereal straw.

"Protease" (EC 3.4) is any enzyme which digests long protein chains into shorter fragments by splitting the peptide bonds that link amino acid residues.

"Pectinase" (EC 3.2) is any enzyme which is directly involved in breaking down pectin.

"Hemicellulase" belongs to the group carboxyl ester hydrolases (EC 3.1.1) and comprises any enzyme which is involved in breaking down hemicellulose. Feruloyl esterase (EC 3.1.1.73) is a further example of a "hemicellulase".

"Ligninase" is any enzyme which is involved in the breakdown of lignin, also referred to as lignolytic enzymes, such as peroxidases and laccases.

"Alkaline conditions" (or "alkaline pH") means pH above 7, measured by techniques trivial to a person skilled in the art.

"Flame retardant additive" refers to a compound that further enhances the effectiveness of a flame retardant composition. In general, such additives are substances added to delay or suppress ignition and reduce the rate of flame spread when exposed to flame impingement. Several flame retardant additives are known in the art. The flame retardant additive may enhances the effectiveness of the flame retardant composition in different ways, such as by acting as a smoke suppressant."Smoke suppressant compound" refers to a flame retardant additive which imparts smoke suppressant properties to a composition.

Detailed description of the invention:

The present invention concerns flame retardant compositions and methods of preparing flame retardant compositions.

Lignocellulosic plant biomasses comprise the most abundantly available raw material on the Earth for the production of bioproducts. It is composed of cellulose, hemicellulose and lignin together with small amounts of protein, pectin, wax and different inorganic compounds.

Cellulose is an important structural component of the primary cell wall of plants. It is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units.

Hemicellulose is any of several heteropolymers, such as xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan, present along with cellulose in almost all plant cell walls. Hemicellulose typically (but not exclusively) has a random, amorphous structure with little strength and can be hydrolyzed by dilute acid or base as well as by myriads of hemicellulase enzymes. The hemicellulose polysaccharides contain many different sugar monomers. For instance, sugar monomers in hemicellulose can include xylose, mannose, glucose, galactose, rhamnose, and arabinose. Xylose is in most cases the sugar monomer present in the largest amount, although in some plant material mannose can be the most abundant sugar. Not only regular sugars can be found in hemicellulose, but also their acidified form, for instance glucuronic acid and galacturonic acid can be present. Cereal straw hemicellulose primarily consists of arabinoxylan.

Lignin is a cross-linked racemic macromolecule; it is relatively hydrophobic and aromatic in nature. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures that appear to repeat in a haphazard manner. There are three monolignol monomers, methoxylated to various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. It is often covalently linked to hemicellulose and therefore cross-links different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole.

The present inventors have surprisingly found that a composition comprising lignin and hemicellulose residues obtained by alkaline pulping treatment of plant material, specifically cereal straw or grasses, has effective flame retardant properties.

The present inventors have surprisingly found that a composition comprising lignin components, hemicellulose components, and minerals obtained by alkaline pulping treatment of plant material, specifically cereal straw or grasses, has effective flame retardant properties.

Several prior art publications disclose traditional pulping of plant material for obtaining cellulose fibre factions, especially from woody biomasses, but also from cereal straw, such as described in WO 2020/152178. However, none of the prior art suggest that an aqueous fraction comprising dissolved/dispersed hemicellulose and lignin components, obtained from such pulping processes, is suitable for use as an effective flame retardant.

Without wishing to be bound by theory, it is suspected that when a flame is applied the hemicellulose oligomers generate energy fast, which rapidly chars the lignin component,

which suppresses the flammable gases and the flame / burning, as the char layer is much harder to burn and prevents further burning. In addition, residual NaOH or KOH and silicate salts from the pulping reaction may further contribute with the overall fire resistance, such as by absorbing heat or catalyzing char formation. As demonstrated herein, the lignin when isolated exhibits some flame retarding effect, but the addition of hemicellulose oligomers and component sugars markedly increases the formation of char. The precise mechanism of the synergistic relationship is not known, but it is speculated that the hemicellulose components help synergize the major effects, especially charring, by virtue of them acting as a supply of active hydroxyl groups.

In addition, the composition acts as a binder that can be applied to cellulose-containing materials such as paper, cardboard, MDF, textiles, and wood, because these materials readily take up the composition. This property is advantageous for further incorporating compatible additives, such as smoke suppressors, which help to maintain consistency within the composition and enhance its effectiveness in retarding fire.

The present invention provides the benefit of being non-disruptive, hence facilitating the option of additionally purifying cellulose and even wax from the lignocellulosic material for other uses.

I. Method of preparing a flame retardant composition

As disclosed herein, the present inventors have surprisingly found that an aqueous composition obtained by an alkaline pulping treatment of plant material, preferably cereal straw or grasses, has effective flame retardant properties.

One aspect of the present invention provides a method of preparing a flame retardant composition, comprising the steps of:

1. providing plant material, preferably cereal straw and grasses;
2. mechanically dry-treating said plant material to reduce its size;
3. suspending the plant material in an aqueous solution;
4. pulping the suspended plant material by adjusting the pH to alkaline conditions and increasing the temperature of the suspension, and agitating the suspension, to dissolve and/or disperse hemicellulose components and lignin components in the aqueous solution, wherein said hemicellulose and lignin components originates from the plant material; and
5. separating the pulped material into a solid fibrous fraction and a liquid flame retardant fraction being a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components;

6. optionally concentrating the liquid flame retardant composition to increase the % dry matter content.

I.i Plant material

In one embodiment, the plant material provided and used in the method of preparing a flame retardant composition is selected from cereal straw and grasses. Preferably, the plant material is cereal straw. As evidenced in the examples section, an efficient flame retardant composition can be obtained from such plant material. Preferably, the cereal straw material of the invention originates from straws, husks and/or brans from cereal, selected from the group consisting of wheat, rye, barley, oats, sorghum, rice, triticale, etc. and combinations thereof. In one preferred embodiment, the plant material is straw, husk, and/or bran from wheat.

In another embodiment, the present invention of preparing a flame retardant composition may be applied to lignocellulosic material originating from lignocellulosic biomass, preferably a non-woody biomass, such as an annual plant, such as grasses, sugar cane, palm leaves, bagasse, high energy grasses, or other plants.

The plant material used in the present invention for preparing a flame retardant composition is preferably a non-woody biomass. As seen in Example 2, using a woody biomass as starting material, good flame retardant properties are not obtained.

In one embodiment, the cereal straw material used in the method of preparing a flame retardant is pretreated straw material, preferably dewaxed straw material.

Dewaxed biomass material may be obtained by any known method in the art, such as pretreating lignocellulosic biomass by mechanically stripping the wax from the surface; organic solvents extraction such as using chloroform, benzene and hexane; and use of supercritical CO2; or even by hydrothermal and wet oxidation pretreatment. Based on the pretreatment method applied, the resulting dewaxed material may be in different form, such as pellets or even partly of fully suspended as a result of a previous treatment.

In one embodiment, the straw material has been treated in a way whereby more than 50% of the wax has been removed, such as treated in a way whereby more than 55, 60, 65, 70, 75, 80, 85, 90%, or even more than 95% of all plant wax covering the surface of the plant material has been removed, thereby obtained dewaxed straw material.

I.ii Dry mechanical treatment

As a first step, the plant material is mechanically dry treated to reduce the size of the plant material. In one embodiment of the present invention, this dry mechanical pretreatment of the plant material comprises cutting, chopping, and/or crushing, such as a mechanical treatment selected from the group consisting of shredding, hammer milling, disc milling grinding and combinations thereof. WO2015/185688 discloses an example of a dry mechanical pretreatment of plant material.

The cereal straw material may be cut in lengths suitable for a subsequent treatment in a suitable mill for deforming the plant material. The primary chopping may result in cuts between about 5 and 20 cm in length, between 5 and 15 cm, or between 5 and 10 cm in length. The milling further minces the plant material to pieces of less than 5 cm in length, less than 3 cm, less than 2 cm, or less than 1 cm. The processes can be optimized to adjust the sizes according to the downstream use of the mechanically treated plant material. In one embodiment, the dry mechanical pretreatment may further serve to deform the outer surface of the plant material so that the wax coating is cracked and released, obtaining a partly dewaxed plant material.

In one embodiment, the material obtained from the dry mechanical pretreatment is fractionated according to size. In a preferred embodiment, the dry mechanically pretreated material is subjected to a sieving treatment in order to obtain two fractions, the first fraction passing through the sieve mesh and the second fraction being retained by the sieve mesh. In an embodiment of the present invention, the mesh size of the sieve is in the range of 0.1-5 mm, such as in the range from 0.15-2 mm, e.g. in the range from 0.2 – 0.5 mm. In a preferred embodiment, the mesh size is 0.3 mm. The sieving treatment may comprise one or more sieves having the same or different mesh sizes. The sieving treatment may be performed in order to separate partly dewaxed plant material (the second fraction retained by the sieve) from a fraction enriched in cracked and released wax (the first fraction passing through the sieve), such as to preferably remove at least 65%, such as at least 75%, such as at least 80% of the total wax in the lignocellulosic biomass by sieving.

In one embodiment, the plant material is cereal straw, which is pretreated by first a mechanical dry treatment followed by fractionation. The fractionation may be performed in order to remove wax components from the remaining plant material.

In another preferred embodiment, fractionation may be omitted and thus directly suspending the dry mechanically pretreated material in an aqueous solution. Following the dry treatment, the plant material – all or a selected fraction thereof – is suspended in an aqueous solution to facilitate the pulping and optionally enzyme treatments steps, as further disclosed herein.

In one embodiment, the plant material is cereal straw, which is pretreated by first a mechanical dry treatment optionally followed by fractionation. The plant material is then suspended in an aqueous solution, wherein the average particle size of the plant material is less than 5cm, less than 4cm, less than 3cm, less than 2cm, or preferably less than 1cm, to facilitate efficient the pulping and optionally enzyme treatments steps, as further disclosed herein.

I.iii Enzyme assisted dewaxing pretreatment

In one embodiment of the invention, after the dry mechanical pretreatment of the plant material – all or a selected fraction thereof – is enzymatically pretreated to facilitate release and/or removal of wax from the plant material. In such embodiment, the dry mechanically pretreated material is suspended in an aqueous liquid together with one or more protease and/or pectinase enzymes, and the temperature and pH are adjusted to optimize the activity of the enzyme(s) added.

Proteases are involved in digesting long protein chains into shorter fragments by splitting the peptide bonds that link amino acid residues. In one embodiment, proteases applied in the enzymatic pretreatment may be selected among proteases which detach the terminal amino acids from the protein chain (exopeptidases, such as aminopeptidases, carboxypeptidase A). In another embodiment, proteases may be selected among proteases which attack internal peptide bonds of a protein (endopeptidases, such as trypsin, chymotrypsin, pepsin, papain, elastase); or from the group consisting of serine proteases, threonine proteases, cysteine proteases, aspartate proteases, glutamic acid proteases and metalloproteases. In yet another embodiment the proteases may be selected from commercially available proteases, such as selected from the group consisting of Alcalase®, (a protease from Bacillus licheniformis) Neutrase® (a protease from Bacillus amyloliquefaciens, both being available from Novozymes, Denmark) and Promod® (a protease from Ananas comosus, available from BioCatalysts, UK). In yet another embodiment, a combination of two or more protease enzymes or commercial protease enzyme products may be used for degrading the plant proteins.

Pectinases are involved in breaking down pectin, a polysaccharide found in plant cell walls, wherein e.g. cellulose fibrils are often embedded. In one embodiment, pectinases applied in the enzymatic pretreatment may be selected from a group consisting of (i) pectin hydrolases which hydrolyse the pectic acid backbone in pectins (endopolygalacturonase, EC 3.2.1.15; exopolygalacturonase, EC 3.2.1.67), (ii) pectin lyases which degrade pectic acid via elimination rections (endopolygalacturonase lyase, EC 4.2.2.2; exopolygalacturonase lyase, EC 4.2.2.9; endopolymethyl-d-galactosiduronate lyase, EC 4.2.2.10), and (iii) pectin esterase, which cleave the methyl

ester bond (pectin methyl esterase, EC 3.1.1.11). Pectinases are widely available commercially and most are blends which incorporate all three mentioned enzyme types. In another embodiment, the pectinases may be selected from a group consisting of Pectinex® (a mix of pectinases from Aspergillus Niger, available from Novozymes, Denmark) and Pectinase 947 L® (a pectinase mix available from BioCatalysts, UK; Pektozyme, a range of Pectin active enzyme blends supplied by DuPont). In yet another embodiment, a combination of two or more pectinase enzymes or commercial pectinase enzyme products may be used for degrading the plant pectins.

A combination of two or more protease(s) and/or pectinase(s) and/or commercial protease product(s) and/or commercial pectinase product(s) may be applied for degrading the plant proteins and / or pectins.

In an embodiment the one or more enzymes may be added to obtain an enzyme concentration in the range from 0.01-2% w/w, such as in the range of 0.03-1.8% w/w, e.g. in the range of 0.05-1.6% w/w, such as in the range of 0.07-1.4% w/w, e.g. in the range of 0.09-1.2% w/w. The enzyme concentration depends on the enzyme activity however, it may be preferred that the enzyme concentration is 1-2% w/w. In one embodiment, it may be preferred that the enzyme activity is in the range from 1000-12000 U/g, such as in the range of 2000-10000 U/g, e.g. in the range of 3000-9000 U/g, such as in the range of 4000-8000 U/g, e.g. in the range of 5000-7000 U/g.

In order to benefit as much as possible from the enzyme treatment, the conditions for enzyme activity, such as temperature, pH, salt concentration, etc., should be optimized with respect to the enzyme(s) used. Addition of acid or base to the slurry/mixture may be necessary to reach optimal pH conditions.

Optimal temperature during enzyme treatment is selected to suit the enzyme(s) used. The temperature may be 25, 30, 35, 40, 45, 50 °C or even higher if thermostable enzymes are used. In one embodiment, the temperature of the mixture in step (d) is adjusted in the range of 30-70°C, such as in the range of 35-65°C, e.g. in the range of 40-60°C, e.g. in the range of 45-55°C, preferably in the range of 45-65 °c, most preferably in the range of 50-60 °C to optimize the activity of the enzymes used in performing targeted hydrolysis of cell wall components.

Optimal pH during enzyme treatment is selected to suit the enzyme(s) used. In one embodiment, the pH maintained during the enzyme treatment is in the range of 3.5-7.0, such as in the range of 4.0-7.0, e.g. in the range of 4.0-6.0, preferably in the range 4.5-5.5 to optimize the activity of the enzymes used in performing targeted hydrolysis of cell wall components. The pH may be adjusted by adding at least one acid and/or buffer selected from the group consisting of phosphoric acid, hydrochloric acid, sulfuric

acid, phosphate buffers, acetate buffers, and combinations thereof. In a preferred embodiment the acid is phosphoric acid.

In order to obtain an optimal exposure of the biomass components to the enzymes, agitation is preferably applied and may be selected from the group consisting of stirring and/or compressed air or gas bubbling agitation and/or vessel-shaking. Applicable stirrers may be selected from the group consisting of anchor stirrers, blade stirrers, K-stirrers, paddle stirrers or any combinations thereof.

In a further embodiment, the protease and/or pectinase pretreatment of the plant material further comprises a wet mechanical treatment during the enzymatic treatment. The wet mechanical treatment may be simultaneous with the enzyme treatment or a subsequent mechanical treatment. A limited wet mechanical treatment is preferred, such as for a selected, optimized, intermittent, time period during enzyme treatment. In an embodiment of the invention, the wet mechanical treatment is selected from the group consisting of conical refiners, disc type refiners, carried out at ambient pressure (so-called atmospheric refining) and combinations thereof; or wet milling such as toothed colloid mill. Such wet refining or milling may be repeated as many times as desired: 1, 2, 3 or 4 repetitions will normally suffice. Alternatively, or additionally, very powerful stirring may be applied.

In a preferred embodiment the hydrolysis and wet mechanical treatment under agitation in the pretreatment is performed for 0.5-5.0 hours such as in the range of 0.5-4.0 hours, e.g. in the range of 0.5-3.0 hours, e.g. in the range of 1.0-2.5 hours, e.g. in the range of 1.0-2.0 hours, e.g. preferably in the range of 1.0-1.5 hours, preferably for 1.5 hours.

As disclosed herein, the protease and/or pectinase treatment facilitates release of wax from the plant material. Once the enzymatic treatment is considered to be sufficient, the wax may then be removed, thereby recovering dewaxed lignocellulosic material. In one embodiment, the released wax components remain in the composition when carrying on the with following steps for the method disclosed herein. In another embodiment the wax components are partly or fully removed from the remaining dewaxed material.

In one embodiment, the dewaxed lignocellulosic material may be recovered by raising the temperature of the mixture to melt and liquefy the liberated wax, such that the dewaxed lignocellulosic material can be separated from a liquid part comprising the melted waxes. The wax may be fully or partly liquefied dependent on the composition of the wax and the temperature. When the temperature is raised in order to melt the liberated wax, it is desirable to minimum reach a temperature at which the enzymes are inactivated. In one embodiment, the temperature of the dry mechanically and

enzymatically pretreated material is increased to 65-95°C, such as in the range from 70-90°C, e.g. in the range from 75-85°C, such as in the range from 80-85°C and preferably to 80°C in order to melt and liquefy the liberated wax. In one embodiment, the temperature is increased to above 70°C, preferably above 80, 90 or 95°C.

In one embodiment, the removal of wax and recovery of dewaxed material is performed by a method selected from the group consisting of decanting, centrifugation, and filtration. In principle, any known method which can be applied to remove an insoluble fiber fraction from a bulk aqueous suspension may be applied. Preferably, the separation is performed by any form of sieving/filtration, using any molecular size as desired. In respect of filtration such filtration may be selected from small mesh filter, pressurized filter, belt filter, filter press and combinations thereof.

In a preferred embodiment pretreatment of the plant material by enzyme assisted dewaxing comprises the step of:

(a) providing plant material, preferably cereal straw,

(b) subjecting the cereal straw to a dry mechanical treatment,

(c) subjecting the material obtained in step (b) to a sieving treatment and obtaining at least two fractions, the first fraction passing through the sieve mesh and the second fraction being retained by the sieve mesh,

(d) suspending the second fraction obtained in step (c) in an aqueous liquid together with one or more protease and/or pectinase enzymes,

(e) optionally subjecting the mixture obtained in step (d) to wet mechanical treatment,

(f) removing wax from the solution, thereby obtaining a dewaxed plant material.

I.iii Pulping treatment for solubilizing hemicellulose and lignin components

As an essential step of the present invention, a pulping treatment is performed to solubilize hemicellulose and lignin components; specifically, the temperature is increased and the pH is adjusted to alkaline conditions in order to solubilize hemicellulose and lignin components in the solution. Such process is traditionally referred to as pulping, where the cellulose fibrous pulp is recovered. In the present invention, it is on the contrary the liquid fraction that is of particular interest, as the inventors have surprisingly discovered that it can be used as an efficient flame retardant.

Hence, in one embodiment, the present invention provides a method for providing a flame retardant composition, said method comprising the steps of obtaining a plant

material as disclosed herein, subjecting said plant material to a pulping treatment, and recovering the liquid fraction comprising hemicellulose and lignin components for use as a flame retardant composition.

In one embodiment, the temperature in the pulping step is increased to between 65-120°C, such as to the between 65-95°C, e.g. to the between 75-85°C, such as to the range 80-85°C and preferably to 80°C. In one embodiment, the temperature is increased to above 65°C, preferably above 70, 80, 90 or 95°C, more preferably above 100, 110, or 120°C. In some embodiments, the pulping temperature may be even higher, such as above 130, 140, 150, 160, 170°C or even up to around 180°C.

The alkaline pH conditions in the pulping step refer to a pH above 7. In one embodiment, the pH is above 7.5, 8.0, or 8.5, preferably above 9.0, 9.5, or 10.0, or most preferably above 10.5. In one embodiment, the pH is between 7.0-12.0, such as between 8.0-12.0, such as between 9.0-12.0, preferably between 10.0-12.0, most preferably between 10.5-12.0. The pH adjustment to obtain alkaline conditions may be performed by adding a base composition selected from the group consisting of sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, sodium carbonate, and combinations thereof. It may be preferred that the solution is agitated at such pH and temperature for 5-120 minutes, preferably 10-90 minutes, most preferred 20-75 mins.

In a most preferred embodiment, the pulping step is performed at a temperature of around 120°C and at a pH between 10.5-12.0, to ensure hemicellulose and lignin are solubilized.

In another preferred embodiment, the temperature is increased to between 80-90°C and pH to 9-11.0 to ensure hemicellulose and lignin are solubilized, while the cellulose remains insoluble. This embodiment is particularly preferred when the enzyme (hemicellulase) assisted pulping is performed, as disclosed in the following section. Generally, the pH of the pulping step is not increased above pH 11, if enzyme assisted pulping is performed, and the temperature is kept below 120°C, preferably between 80-90°C.

Meanwhile, if the method of the present invention is performed wherein the pulping is not enzyme-assisted (i.e. no hemicellulase treatment), then the pulping step may be performed at temperatures as high as 180°C.

In order to obtain an optimal exposure of the biomass components, agitation is preferably applied and may be selected from the group consisting of stirring and/or compressed air or gas bubbling agitation and/or vessel-shaking. Applicable stirrers may be selected from the group consisting of anchor stirrers, blade stirrers, K-stirrers, paddle stirrers or any combinations thereof.

In a further embodiment, the pulping treatment further comprises a wet mechanical treatment. The wet mechanical treatment may be prior to and/or simultaneous with the alkaline treatment. A limited wet mechanical treatment is preferred, such as for a selected, optimized, intermittent, time period. In an embodiment of the invention, the wet mechanical treatment is selected from the group consisting of conical refiners, disc type refiners, carried out at ambient pressure (so-called atmospheric refining) and combinations thereof; or wet milling such as toothed colloid mill. Such wet refining or milling may be repeated as many times as desired: 1, 2, 3 or 4 repetitions will normally suffice. Alternatively, or additionally, very powerful stirring may be applied. As a further alternative, the use of a screw, twin screw or transport screw within a vessel can be a suitable method of agitation.

I.iv Enzyme assisted pulping

In one embodiment, the biomass is enzymatically treated prior to the pulping treatment using one or more hemicellulase enzymes suitable for degrading hemicellulose components. The side chains of hemicellulose interlink with lignin in the complex lignocellulosic plant biomass structure. Disruption of the hemicellulose is an essential step in separating the different lignocellulosic components.

If a protease and/or pectinase enzyme treatment is performed as part of the method of the present invention, as optionally disclosed herein, the hemicellulase enzyme treatment step may be applied (i) in combination with the protease and/or pectinase treatment described above, (ii) as a separate treatment prior to protease and/or pectinase treatment, (iii) as a separate treatment after protease and/or pectinase treatment, or (iii) as a separate treatment of dewaxed lignocellulosic after wax has been removed.

Most preferably, the hemicellulose treatment is performed prior to the pulping step to facilitate disruption the hemicellulose side chain interlinking with the lignin in the plant material.

In one embodiment, the hemicellulase enzymes applied are xylanases (EC 3.2.1.8) which randomly break the internal linkages of the linear polysaccharide beta-1,4-xylan (back bone of most hemicelluloses), yielding different lengths of xylo-oligosaccharides or if the reaction is run to its completion, yielding xylose monomers. However, hemicellulose is not merely a linear polysaccharide of beta-1,4-xylan; it further comprises numerous side chains, requiring separate enzyme action for their degradation. The high degree of substitution in hemicellulose polymers thus requires the action of various accessory enzymes, therefore in another embodiment, the hemicellulase enzymes include different glycoside hydrolases and carbohydrate

esterases, to completely degrade the hemicellulose substituents. In a preferred embodiment, ferulic esterase is such accessory enzyme of the invention, which hydrolyzes feruloyl-polysaccharides, releasing ferulate by acting on the carboxylic ester bond. Ferulic esterase may be added to aid in the release of lignin moieties bound to hemicellulose.

In one embodiment, enzymes for degradation of hemicellulose (hemicellulases) may be selected from a group consisting of glycoside hydrolases and/or carbohydrate esternases, such as selected from the list of endo-xylanase, beta-xylosidase, alpha-L-arabinofuranosidase, alpha-glucurondiase, alpha-galatosidase, acetylxylan esterase, feruloyl esterase, etc. Beta-glucanases, which can act on bonds in non-crystalline cellulose in the plant cell wall, are further optionally utilized.

Hemicellulose preparations are widely available commercially. In one embodiment, the hemicellulase may be selected from a group consisting of Depol 333P (xylanase rich enzyme preparation from BioCatalysts Ltd, UK) and Depol 740L (a ferulic esterase rich enzyme preparation from BioCatalysts Ltd, UK). In a preferred embodiment, a combination of two or more hemicellulase enzymes or commercial hemicellulase enzyme products may be used for degrading the plant hemicellulose.

In an embodiment the one or more hemicellulase enzymes may be added to obtain an enzyme concentration in the range from 0.01-2% w/w, such as in the range of 0.03-1.8% w/w, e.g. in the range of 0.05-1.6% w/w, such as in the range of 0.07-1.4% w/w, e.g. in the range of 0.09-1.2% w/w. The enzyme concentration depend on the enzyme activity however, it may be preferred that the enzyme concentration is 1-2% w/w.

In one embodiment of the present invention it may be preferred that the hemicellulase enzyme activity is in the range from 1000-12000 U/g, such as in the range of 2000-10000 U/g, e.g. in the range of 3000-9000 U/g, such as in the range of 4000-8000 U/g, e.g. in the range of 5000-7000 U/g.

In order to benefit as much as possible from the enzyme treatment, the conditions for enzyme activity, such as temperature, pH, salt concentration, etc., should be optimized with respect to the enzyme(s) used. Addition of acid or base to the slurry/mixture may be necessary to reach optimal pH conditions.

Optimal temperature during hemicellulase treatment is selected to suit the enzyme(s) used. The temperature may be 25, 30, 35, 40, 45, 50 °C or even higher if thermostable enzymes are used. In one embodiment, the temperature is adjusted in the range of 30-70°C, such as in the range of 35-65°C, e.g. in the range of 40-60°C, e.g. in the range of 45-55°C, preferably in the range of 45-65 °c, most preferably in the range of 50-60 °C to optimize the activity of the enzymes used in performing targeted hydrolysis of cell wall components.

In a further embodiment, the pH during hemicellulase treatment is adjusted in the range of 3.5-7.0, such as in the range of 4.0-7.0, e.g. in the range of 4.0-6.0, preferably in the range 4.5-6.0 to optimize the activity of the enzymes used in performing targeted hydrolysis of cell wall components. The pH may be adjusted by adding at least one acid and/or buffer selected from the group consisting of phosphoric acid, hydrochloric acid, sulfuric acid, phosphate buffers, acetate buffers, and combinations thereof. In a preferred embodiment the acid is phosphoric acid.

In a preferred embodiment, the temperature and pH during hemicellulase treatment are in the range 45-65°C and pH 4.5-6.0.

In order to obtain an optimal exposure of the biomass components to the enzymes, agitation is preferably applied and may be selected from the group consisting of stirring and/or compressed air or gas bubbling agitation and/or vessel-shaking. Applicable stirrers may be selected from the group consisting of anchor stirrers, blade stirrers, K-stirrers, paddle stirrers or any combinations thereof.

In a further embodiment, the hemicellulase treatment may comprise a wet mechanical treatment during the enzymatic treatment. The wet mechanical treatment may be simultaneous with the hemicellulase treatment or a subsequent mechanical treatment. A limited wet mechanical treatment is preferred, such as for a selected, optimized, intermittent, time period during hemicellulase treatment. In an embodiment of the invention, the wet mechanical treatment is selected from the group consisting of conical refiners, disc type refiners, carried out at ambient pressure (so-called atmospheric refining) and combinations thereof; or wet milling such as toothed colloid mill. Such wet refining or milling may be repeated as many times as desired: 1, 2, 3 or 4 repetitions will normally suffice. Alternatively, or additionally, very powerful stirring may be applied.

The hemicellulase treatment is considered to be sufficient, e.g. a desired degree of hydrolysis is obtained, after 0.5, 1.0, 1,5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 or 5.0 hours of hydrolysis, or even after 6, 8, or 12 hours of hydrolysis. In a preferred embodiment, hydrolysis is performed for 0.5-5.0 hours such as in the range of 0.5-4.0 hours, e.g. in the range of 1.0-3.5 hours, e.g. in the range of 1.5-3.0 hours, e.g. preferably in the range of 1.5-2.5 hours, preferably for 2 hours.

In another embodiment, the biomass may also be enzymatically pretreated using one or more enzymes suitable for degrading lignin components. The ligninases, such as peroxidases and laccases, may be applied in combination with any of the other enzyme treatments described above or as a separate step. In one embodiment, the ligninases are selected from the group consisting of peroxidases and laccases.

As disclosed herein, the enzymatic hemicellulose and/or ligninase treatment may be performed prior to the pulping treatment. As disclosed previous, if such enzyme assisted

pulping is performed, it is followed by an alkaline extraction, but at less harsh conditions, such as keeping the pH at maximum pH 12, preferably a pH between 9-12, and temperature at maximum 120°C, preferably a temperature in the range 80-100°C.

In one embodiment of the invention, prior to the pulping treatment, plant material is treated by the following steps:

(a) a first enzymatic treatment of the dry mechanically treated lignocellulosic biomass in an aqueous suspension using one or more enzymes selected from a proteases and pectinases to liberate wax; and

(b) a second enzymatic treatment using one or more enzymes selected from hemicellulases and ligninases to liberate cellulose from hemicellulose and lignin.

The first and second enzymatic treatment may be performed separately or concurrently. In one embodiment, the first enzymatic treatment is performed on dry mechanically treated plant material, followed by removal of liberated wax, followed by the second enzymatic treatment performed on the remaining dewaxed biomass.

In another embodiment, the first and second enzymatic treatment are one combined enzyme treatment step prior to pulping, not requiring wax removal.

I.v Separation of solid fiber fraction and a liquid fraction comprising hemicellulose and lignin components

The material obtained after the pulping treatment is separated into a solid cellulose fiber fraction and a liquid fraction comprising hemicellulose and lignin components. The liquid fraction may further comprise minerals. The cellulose fiber product may be separated from the solution by any known method of separating an insoluble fraction from a bulk aqueous suspension.

In one embodiment, the separation is selected from the group consisting of decanting, centrifugation, and filtration. Separation may be performed by any form of sieving/filtration, using any molecular size as desired. In respect of filtration such filtration may be selected from small mesh filter, pressurized filter, belt filter, filter press, filter band and combinations thereof. Preferably the separation is performed by a decanter centrifuge.

I.vi Upconcentrating the liquid fraction comprising hemicellulose and lignin components

The liquid fraction obtained after pulping may optionally be concentrated. This may for example be done by evaporation. Depending on the application of the fire retardant composition – i.e. the liquid fraction obtained from the method of the present invention, the preferred dry matter percentage may vary. For example, for treatment of wood

strips, the preferred %DM is around 30%, while for spaying onto insulation mats and fibres, the preferred %DM is around 15-20%. In one embodiment, the liquid fraction is concentrated to between 2-50 %DM, preferably between 5-40 %DM, most preferably 10-30 %DM. In one embodiment, the liquid fraction is concentrated to around 10, 15, 20, 25, 30, 35, 40, 45, or 50 %DM, preferably around 20, 25, 30, 35 or 40 %DM, most preferably around 30 %DM. In one embodiment, the liquid fraction is concentrated to at least 10, 15, 20, 25, or 30 %DM

As disclosed herein, and as evident from the experimental section, the method of the present invention of preparing a flame retardant composition comprises several optional steps. Table 1 provides a non-limiting overview of different options of performing the method – i.e. different options of which steps to include or omit in preparing a flame retardant composition.

Table 1. The method of the present invention of preparing a flame retardant composition comprises several optional steps. This table provides a non-limiting overview of different options of performing the method – i.e. different options of which steps to include or omit in preparing a flame retardant composition.

	Options for combining the method steps											
Method step	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10	# 11	# 12
Providing plant material	+	+	+	+	+	+	+	+	+	+	+	+
Mechanical dry treatment (reduce size)	+	+	+	+	+	+	+	+	+	+	+	+
Fractionation	+	+	+	+	+	+	-	-	-	-	-	-
Suspending the plant material in an aqueous solution	+	+	+	+	+	+	+	+	+	+	+	+
Protease/pectinase enzyme treatment	-	+	-	+	+	+	-	+	-	+	+	+
Removal of wax	-	-	-	+	-	+	-	-	-	+	-	+
Hemicellulase enzyme treatment	-	-	+	-	+	+	-	-	+	-	+	+
Pulping treatment	+	+	+	+	+	+	+	+	+	+	+	+
Separating the liquid phase of the pulped material from the solid fibres	+	+	+	+	+	+	+	+	+	+	+	+

+ means the step is performed in the method

- means the step is omitted in the method

All options listed in Table 1 may optionally be followed by the step of concentrating the liquid flame retardant fraction, as disclosed above.

I.vii Addition of flame retardant additives

In one preferred embodiment, the method further comprises an additional step of adding a flame retardant additive to the liquid flame retardant composition from step (v) or to a concentrated sample of the liquid flame retardant composition from step (v). The flame retardant additive further enhances the flame retardant effectiveness of the composition.

The flame retardant additive may be selected from compounds known in the art to have flame retardant effect, such as various inorganic and mineral compounds. The inorganic compounds may include those based on nitrogen, graphite, silica, and inorganic phosphates such as ammonium phosphate and polyphosphate. Mineral compounds may include certain phosphates, metal oxides, hydroxides, and other metal products such as aluminum, zinc and magnesium. Inorganic and mineral compounds used with other elements can help to achieve fire safety in many types of material, including plastics, foams, textiles and wood products. In one embodiment, the flame retardant additive is a compound based on nitrogen, graphite, silica, or inorganic phosphates such as ammonium phosphate and polyphosphate; or a phosphate, metal oxide, hydroxide, or other metal product such as aluminum, zinc and magnesium.

In one embodiment, the flame retardant additive is selected from titanium dioxide, fiber glass, mineral fibers, kaolin, talc, aluminum oxide, aluminum hydroxide, magnesium hydroxide, precipitated silica, silicates, hollow microspheres, crushed cellulose.

Most preferably, the flame retardant additive is selected from iron oxide, calcium carbonate, and expandable graphite.

In one embodiment, the flame retardant additive is a smoke suppressant compound. Examples of smoke suppressants include zinc borate, aluminum trihydrate, zinc hydroxystannate, low-melting sulfate glasses, iron oxide, zinc oxide, ferrites, bromide-intercalated hydrotalcite, borate-intercalated layered double hydroxide, hot melt adhesive composition, functionalized graphene oxide, expandable graphene, modified ammonium poly(phosphate), glass microspheres, phosphorus-containing polyol, porous silicon dioxide PU foams, sepiolite-based nanocoating, abandoned molecular sieve, melamine octamolybdate, cardanol-derived zirconium phosphate, montmorillonite nanocomposites, and waste printed circuit boards. In one preferred embodiment, the smoke suppressant is selected from: calcium carbonate, iron oxide, and expandable graphite.

II. A flame retardant composition

The flame retardant composition of the present invention has excellent water solubility which is an advantage with respect to its envisaged usages, such as when applied onto surfaces as a liquid solution. The water solubility is of particular advantage for treating wood, wood fibres, cellulose fibres, veneers and the like as good penetration and distribution of the flame retardant compounds in the substrate is easily achieved in these water-swellable matrices, with subsequent drying finishing the treatment of the substrate. A further advantage of the flame retardant composition of the present invention is that it does not easily wash out of the material and thereby provide improved long term advantages of flame retardancy – i.e. after the water is evaporated, the remaining components do not easily wash out.

In one embodiment, the present invention provides a flame retardant composition comprising lignin components and hemicellulose components. The dry solids component in the liquid flame retardant product of the present invention is made up of lignin components and hemicellulose components, potentially further comprising small amounts of salt and silica, and potentially some residues from cuticular wax if dewaxing is not performed as one of the preparation steps.

In one embodiment, the present invention provides a flame retardant composition prepared by the method as disclosed herein. In one embodiment, the present invention provides a flame retardant composition obtainable by the method as disclosed herein.

The flame retardant composition of the present invention is an aqueous composition comprising hemicellulose and lignin components. In the plant cell wall, there is a lignin-hemicellulose complex, in which lignin subunits are bonded to hemicellulose (mainly arabinoxylan) polymer chains. Breakage of these bonds (ester and ether types) disrupts this and releases lignin and hemicellulose fragments from the complex. The process conditions applied during the method of preparing the flame retardant results in such ester bonds between the hemicellulose and lignin of the plant material being broken, and also bonds within the hemicellulose. Depending on the temperature and pH applied, even ether bonds in the lignin, and between lignin and hemicellulose, may also be affected.

The plant lignin and hemicellulose have therefore been degraded to lignin component and hemicellulose components by virtue of the method of preparing the flame retardant composition. More specifically, the degree of polymerization of the hemicellulose has decreased due to the alkaline pulping conditions and enzymatic treatment, such as arabinoxylan being degraded to oligosaccharides having a degree of polymerization (DP) ranging from 2-20, based on xylan backbone cleavage; and additionally some proportion of soluble, more polymeric arabinoxylan fragments (>20 DP) may be present. The plant

lignin has been degraded to fragments of molecular weights ranging from approx. 500-9000 daltons. Ways of measuring/identifying these hemicellulose and lignin components are disclosed on section IV. The hemicellulose and lignin components are soluble and/or dispersed in the aqueous solution, hence the flame retardant composition of the present invention has excellent water solubility properties.

As mentioned, the main constituents of the flame retardant composition of the present invention are lignin components and hemicellulose components. In one embodiment, the flame retardant composition comprises at least of 60, 70, 80, or 90% hemicellulose components and lignin components, based on total dry matter content.

Other extractives and degradation products may also be present in the composition, such as acetic acid from degradation of hemicelluses. Such other extractives may vary in amounts, but could typically comprise around 2-5% of the composition, based on total dry matter. Further, cereal straw and grasses contain silicates that may react with the alkali to form salts, such as sodium or potassium salts, which therefore may also be comprised in the composition. Such silicate salts may be beneficial in fire retardant formulations due to their ability to form protective layers, promote char formation, undergo endothermic reactions, and suppress smoke. Their contribution enhances the overall fire resistance of materials and contributes to safer fire management. Finally, residual NaOH or KOH from the alkaline pulping may constitute around 1-5%, depending on the pulping conditions and the initial concentration applied.

In one embodiment, the ratio of lignin components to hemicellulose components (L:H ratio, based on dry matter(DM), (w/w)) in the flame retardant composition is between 80:20 – 20:80, between 75:25 – 25:75, between 70:30 – 30:70, between 65:35 – 35:65, between 60:40 – 40:60, between 55:45 – 45:55, or even 50:50. In a preferred embodiment, the ratio of lignin components to hemicellulose components in the flame retardant composition is between 60:40 – 40:60.

In one embodiment, the total dry matter content of the flame retardant composition essentially consists of only lignin components and hemicellulose components. In one embodiment, the flame retardant composition comprises 20-80 %DM dissolved and/or dispersed lignin components and 20-80 %DM dissolved and/or dispersed hemicellulose components. In one embodiment, the flame retardant composition comprises 30-70 %DM dissolved and/or dispersed lignin components and 30-70 %DM dissolved and/or dispersed hemicellulose components. In one preferred embodiment, the flame retardant composition comprises 40-60 %DM dissolved and/or dispersed lignin components and 40-60 %DM dissolved and/or dispersed hemicellulose components. In one embodiment, the flame retardant composition comprises approximately 50 %DM dissolved and/or dispersed lignin components and approximately 50 %DM dissolved and/or dispersed hemicellulose components.

In a further embodiment, the flame retardant composition comprises other components in addition to the lignin components and hemicellulose components. Hence, in such embodiments, lignin components and hemicellulose components may constitute at least 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95% (based on total dry matter content) of the flame retardant composition, wherein the ratio of the lignin components and hemicellulose components is as disclosed above. These other components may be selected from calcium carbonate and/or iron oxide. In one embodiment, the flame retardant composition comprises between 0.1-2% of calcium carbonate and/or between 0.1-2 % of iron oxide (% based on total dry matter content). These components, and other additives such as TiO2 or expandable graphite, as well as diatomaceous earth, may provide thermal insulation, improve the operational characteristics of the carbon layer during a fire suppress smoke, and/or any other synergetic function. Inclusion of these compounds in the flame retardant composition enhances the effectiveness of the composition as a fire retardant. The final combined flame retardant composition – i.e. comprising the liquid flame retardant fraction obtainable by the method of disclosed herein and one or more additional components as disclosed herein - acts as a binder and when applied to e.g. woody materials provides high flame resistant and thermal isolation properties.

In one preferred embodiment, the flame retardant composition comprise a flame retardant additive as disclosed herein. The flame retardant additive further enhances the flame retardant effectiveness of the composition. In one embodiment, the flame retardant additive is a smoke suppressant compound. In one preferred embodiment, the flame retardant additive is selected from calcium carbonate, iron oxide, and expandable graphite.In one embodiment, the present invention provides an aqueous composition comprising dissolved and/or dispersed hemicellulose and lignin components, obtainable by the method disclosed herein, for use as a flame retardant. Specifically, the aqueous composition comprises dissolved and/or dispersed hemicellulose and lignin components in ratios and amounts as disclosed above.

III. Potential uses of the flame retardant composition

The liquid composition comprising lignin components and hemicellulose components, produced from the pulping process as disclosed herein, is a very effective flame-retardant treatment for wood products when applied via soaking. Another means of applying the flame retardant composition is pressure and/or vacuum impregnation treatments, such as the types routinely used in the wood industry. Yet another means of applying the flame retardant composition is by spraying onto fibres and optionally followed by flash drying.

The flame retardant composition of the present invention is very useful in application to especially wood and cellulose / lignocellulose products, including fibres, fibre mats, veneers as well as wood based composites, and even solid wood products especially due to its excellent water solubility.

In one embodiment, the flame retardant composition is applied to solid wood elements, such as for use in furniture, building products and the like; wood composite materials and wooden elements thereof; or insulation materials (e.g. loose fibre fill, preformed panels and batts) based on wood fibres and other natural fibres such as cotton, flax, hemp, sisal, jute. An example of use is in fiber cement boards where the fibers, e.g. cellulose fibers or synthetic fibers) may be impregnated before incorporated in the board.

In one embodiment, the present invention concerns the use of the liquid composition obtainable by the method disclosed herein as a flame retardant, such as by applying the composition onto the surface of an item, soaking the item in the composition, and/or impregnating the item with the composition.

In one embodiment, the present invention provides a method of making an item more resistant to catching fire by applying to the item the liquid composition obtainable by the method disclosed herein, such as by applying the composition onto the surface of an item, soaking the item in the composition, and/or impregnating the item with the composition.

In one embodiment, the present invention provides a method of making an item more resistant to catching fire by treating the item with the liquid composition obtainable by the method disclosed herein, such as by applying the composition onto the surface of an item, soaking the item in the composition, and/or impregnating the item with the composition, compared to a non-treated sample.

In one embodiment, the present invention provides cellulose- or lignocellulose-based products comprising the liquid fire retardant composition obtainable by the method disclosed herein; such as a product selected from solid wood elements, wood composite materials, paper, cardboard, MDF, insulation materials based on wood fibres and/or other natural fibres (such as cotton, flax, hemp, sisal, jute), and textiles.

IV. Methods of analyzing/characterizing the flame retardant composition

Methods for characterizing the flame retardant composition are provided herein – i.e. identifying the amounts and structure of specifically lignin and hemicellulose components.

II.i Lignin content

Lignin content may be determined as follows:

Lignin is precipitated from the flame retardant composition by lowering pH gradually to 4.5, using sulfuric acid. The lignin rich precipitate is then isolated by filtration, using a fine nylon cloth, then washed with fresh acidified water (pH 4.5), after which it is dried in a 65C oven, and weighed. The mass of dried lignin precipitate is taken as the lignin content of the material, proportional to the initial dry solids content and volume treated. The lignin fraction can then be further characterized by HPLC analysis, after nitrobenzene oxidation of the dried material, and analysis of the resultant fragments as oxidation products. This yields information such as the G:S:H ratio of the component aromatic units within the lignin (G=Guaiacyl, S=syringyl, and H=p-hydroxyphenyl phenylpropanoid).

II.ii Hemicellulose content

Hemicellulose content may be determined as follows: The residual liquid (from which the lignin has been precipitated) is analyzed by HPLC and is used to identify and quantify the sugar composition of especially the hemicellulose component, i.e. identifying different hemicellulose oligomers.

A portion (normally 25 ml of the 32% concentrate, for example) is mixed with concentrated sulfuric acid to reach an acid concentration of 72-74 % H2S04. The mix is heated to 120 C (in an autoclave) for 20 mins, allowed to cool, and water is then added to reach a final H2SO4 content of 4%. The subsequent liquid is then filtered through a fine nylon mesh cloth and a 25 ml portion neutralised by adding NaOH (50% solution) dropwise. The neutralized liquid is then directly introduced to a suitable HPLC set up for sugar analysis. For example, a Waters system using a Shodex SP 0810 column, isocratically (flow rate 0.5 mls per minute) with water as the eluent, using a differential refractometer as detector and suitable monosaccharide sugar standards for calibration.

II iii Residual ash and salt content

The residual ash and salt content is determined on a dried sample of the material using a muffle furnace and heating / ashing for 12 hours at a temperature of 600 C. The residual mass is used to determine the ash content.

II.iv Wax content

The total wax content of plant materials can be determined gravimetrically as total extractable lipophilic compounds. Dried plant material is milled and then extracted with hot / boiling chloroform. This is performed by either of two basic methods, where method 2 is preferred over method 1 if the bulk density of the plant material is high.

1. An accurately weighed portion of milled biomass (oven dry) is placed in a soxhlet thimble and then subjected to 12 hour extraction in a soxhlet extraction system, using the standard soxhlet methodology. After extraction, the thimble and remaining solid material are dried at 103°C, and the extracted wax is determined by mass difference compared to the start material. Or,

2. A portion of (accurately weighed) approximately 30g of dried, milled straw or other plant material is placed into a 2L round bottomed flask and to this is added 1 Liter of chloroform. The flask is fitted with a reflux condenser and the material is refluxed in Chloroform for a minimum of 3 hours. After this time, the remaining solids are collected quantitatively, then dried (103°C) and weighed. The wax content is determined via the mass difference with respect to the input material.

II.v Characteristics of the liquid frame retardant composition

The flame retardant composition of the present invention is characterized by the proportions of lignin derived material (i.e. lignin component) and hemicellulose derived material (i.e. hemicellulose components), and the chemical speciation within.

Straw hemicellulose is mainly arabinoxylan and the ratio of arabinose to xylose in this hemicellulose is well known. The hemicellulose components (oligomers and possibly longer polymers) in the flame retardant composition will directly reflect this. By HPLC analysis, the constituent sugars of the hemicellulose can be identified and measured. Based on this, the hemicellulose source can be identified. Specifically, for arabinoxylan, the amounts and ratio of arabinose to xylose is 1:4. By ion chromatography (DIONEX) and PAD detection, oligosaccharides DP between approx.1-20 can be separated and detected. Further, by size exclusion chromatography analysis and/or mass spec, oligo/polysaccharides can be separated and the mass distribution profile can be determined.

The lignin in cereal straw differs significantly from that in softwoods. Cereal straw lignin comprises mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid, whereas softwood lignin mostly comprises Guaiacyl and 4- hydroxyphenyl propane residues. These compounds can be detected via HPLC analysis of the lignin component in the flame retardant composition. Specifically, for cereal straw lignin, the G:S:H ratio (G=Guaiacyl, S=syringyl, and H=p-hydroxyphenyl phenylpropanoid) is approx. 45:45:10 (based on %DM).

Preferred embodiments of the invention

Preferred embodiment 1. A method of preparing a flame retardant composition comprising hemicellulose components and lignin components from plant material, said method comprising the steps of:

(i) providing plant material,

wherein the plant material is selected from cereal straw and grasses;

(ii) mechanically dry-treating said plant material to reduce its size;

(iii) suspending the plant material in an aqueous solution;

(iv) adjusting the pH to alkaline conditions and increasing the temperature of the suspension, and agitating the suspension, to dissolve and/or disperse hemicellulose components and lignin components in the aqueous solution, wherein said hemicellulose and lignin components originates from the plant material; and

(v) separating the material obtained in step (iv) into a solid fibrous fraction and a liquid flame retardant fraction being a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components;

(vi) optionally concentrating the liquid flame retardant composition to increase the % dry matter content.

Preferred embodiment 2. The method according to Preferred embodiment 1, wherein the temperature in step (iv) is increased to >80 °C and the pH is between 9-12.

Preferred embodiment 3. The method according to Preferred embodiment 1 or 2, wherein the average particle size of the plant material in step (iii) is less than 1 cm.

Preferred embodiment 4. The method according to any one of Preferred embodiments 1-3, wherein the suspended plant material in step (iii) is enzymatically treated using one or more hemicellulase enzymes, such as xylanases and/or ferulic esterase.

Preferred embodiment 5. The method according to any one of Preferred embodiments 1-4, wherein the ratio of hemicellulose components and lignin components in the flame retardant composition is between 40:60 – 60:40, based on dry matter content.

Preferred embodiment 6. The method according to any one of Preferred embodiments 1-5, wherein the flame retardant composition comprises at least of 90% hemicellulose components and lignin components, based on total dry matter content.

Preferred embodiment 7. The method according to any one of Preferred embodiments 1-6, wherein the plant material suspended in the aqueous solution in step (iii) is dewaxed cereal straw, such as dewaxed cereal straw obtained by a method comprising the steps of:

(a) enzymatically treating the cereal straw suspended in an aqueous solution in step (iii) with protease and/or pectinase enzymes,

(b) optionally subjecting the mixture obtained in step (a) to wet mechanical treatment, and

(c) removing wax from the solution prior to adjusting pH and increasing the temperature in step (v).

Preferred embodiment 8. A flame retardant composition obtainable by the method according to any one of Preferred embodiment 1-7, wherein the composition comprises dissolved and/or dispersed hemicellulose components and lignin components in a ratio of between 40:60 – 60:40, based on dry matter content.

Preferred embodiment 9. A flame retardant composition according to Preferred embodiment 8, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

Preferred embodiment 10. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, obtainable by the method according to any one of Preferred embodiments 1-7, as a flame retardant.

Preferred embodiment 11. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, obtainable by the method according to any one of Preferred embodiments 1-7, for enhancing fire resistance of an item, such as solid wood elements, wood composite materials, and/or insulation materials based on wood fibres and other natural fibres such as cotton, flax, hemp, sisal, jute.

Preferred embodiment 12. Use according to Preferred embodiment 10 or 11, wherein the ratio of hemicellulose components and lignin components in the aqueous composition is between 40:60 – 60:40, based on dry matter content.

Preferred embodiment 13. Use according to any one of Preferred embodiments 10-12, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

Preferred embodiment 14. Use according to any one of Preferred embodiments 10-13, wherein the hemicellulose components and lignin components constitute at least 90% of the total try matter content of the aqueous composition.

Preferred embodiment 15. Use according to any one of Preferred embodiments 10-14, wherein the aqueous composition is applied to the item by spraying the composition on the surface of the item, soaking the item in the composition, and/or impregnating the composition into the item, such as by vacuum pressure impregnation.

Preferred embodiment 16. A method of enhancing fire resistance of an item, said method comprising applying a flame retardant composition comprising dissolved and/or dispersed hemicellulose and lignin components, obtainable by the method according to any one of Preferred embodiments 1-8, onto the item.

Preferred embodiment 17. Method according to Preferred embodiment 16, wherein the ratio of hemicellulose components and lignin components in the aqueous composition is between 40:60 – 60:40, based on dry matter content.

Preferred embodiment 18. Method according to Preferred embodiments 16 or 17, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

EXAMPLES

Example 1A: Lignin-based flame retardants - initial tests

1A.1 Sample preparation

Mechanical dry treatment and fractionation: Wheat straw was dry mechanically treated by hammer-milling. The hammer-milled straw was fractionated using an 8 mm sieve. The fraction passing the sieve was then processed in a dust separator for removal of fines material (15-20% of the straw mass was removed as fines material). The longer fraction generated after having removed the fines was then further cleaned of dust by gentle disc-milling (1 mm plate gap in disc mill) and a further circa 5% dust fraction was removed using 0.3 mm sieve. The longer fraction was now mainly straw pieces of length 2-3 mm.

Protease and pectinase treatment: This longer fraction was suspended in 55 °C water, in a jacketed steel tank, at a loading of 85 kilograms minced straw (corresponding to circa 75 kg straw dry matter) per 1400 liters of water. pH of the resultant slurry was

adjusted to pH 5.3 using phosphoric acid and the temperature maintained at circa 55°C. The slurry was stirred using a Myers type dispersion mixer, to ensure good dispersion. 200 ml protease rich preparation (Promod 24L, BioCatalysts Ltd, UK) and 100 ml pectinase rich enzyme preparation (Pectinase 974L, BioCatalysts Ltd, UK) were added to disrupt the straw cuticle and help release constituent wax. The slurry was circulated through a Fryma type wet-mill (fitted with a toothed colloid milling head) with a wide mill (> 2mm) head gap, meaning that the mill is acting as an effective pump mixer, rather than a true grinding mill, helping ensure access of the enzymes to the straw cuticular surface. The wet-milling and stirring was applied during enzymatic treatment while maintaining pH and temperature profile specified above. After 1 hour, the temperature of the slurry was raised to 80°C to ensure all waxy components are in a molten state; and the mixture was further stirred for 10 minutes. The insoluble fibrous fraction was then separated from the bulk process liquor via decanter centrifuge using a GEA UCD 2015 2-phase decanter, running with a feed rate of 1800 liter slurry per hour, with a barrel speed of 5500 rpm. This product is referred to as dewaxed material.

Hemicellulase treatment: For the hemicellulose treatment, the temperature was brought to 55°C and pH was adjusted to pH 5.3, using phosphoric acid. A xylanase rich enzyme preparation (mainly endoxylanase activity; Depol 333P, BioCatalysts Ltd, UK) and a ferulic esterase rich enzyme preparation (Depol 740L, BioCatalysts Ltd, UK) were added. Enzymatic hydrolysis was performed for 2 hours, with mechanical stirring, while maintaining pH and temperature profile specified above. The straw was continuously refined during enzymatic hydrolysis (enough to vigorously stir the mix) by circulation through a Fryma type, toothed colloid, wet-mill, with head gap set at 1.5 mm.

Alkaline pulping treatment: The enzymatic hydrolysis was terminated by raising the pH to 11 via addition of NaOH as well as raising the temperature to 80°C. Stirring was continued for a further 90 minutes. The released lignin and hemicellulose fragments are thereby dissolved.

The insoluble fibers were separated from the aqueous liquid phase by decanter centrifuging using a GEA UCD 205 2-phase decanter, running 1800 liter slurry per hour with a speed of 5500 rpm.

Concentration by evaporation: The aqueous liquid phase comprising the dissolved and dispersed lignin and hemicellulose fragments (approx. 4-5% dry solid content) was then concentrated by evaporative removal of water, reaching a dry solids content of sample (a) 30%, sample (b) 15%, or sample (c) 7.5%.

1A.2 Flame retardant tests - wood beech strip test

Sample (a), (b), and (c) obtained as disclosed above were tested for their flame retardant properties as follows: Wood beech strips (200mm long, circa 20mm wide,

veneer strip, ca 1.5mm thick) were dipped into the samples, left for 20 minutes to soak in the samples, then drained and dried in an oven at 70°C for 45 minutes.

Using a cigarette or candle lighter, it was then attempted to light the treated strips. The results were as follows:

Sample (a) 30 % dry solids concentration: The flame barely took and any slight flame went out about 1 cm up the strip. See Figure 1.

Sample (b) 15 % dry solids concentration: Same flame suppression effect as sample (a). See Figure 1.

Sample (c) 7.5% dry solids concentration: Same flame suppression effect as sample (a). See Figure 1.

As a control, a non-treated wood beech strip was also tested. This untreated wood burned freely until the strip was consumed.

Example 1B: Lignin-based flame retardants - additional tests

All samples tested in Example 1 had been treated in the same way by dry-mechanical treatment, fractionation, protease and pectinase treatment, hemicellulose treatment, and alkaline pulping treatment; the only difference being the concentration step (i.e. the final %DM). The present example demonstrates that a good flame retardant product can also be obtained from plant material by simplifying the method - i.e. that only the dry-mechanical treatment (size reduction) and alkaline treatment are essential steps of the method.

1B.1 Sample preparation

Sample 1 was prepared by a combination of dry-mechanical treatment, fractionation, and alkaline pulping of straw:

1. Mechanical dry treatment of straw: Wheat straw was dry mechanically treated by hammer-milling.
2. Fractionation: The hammer-milled straw was fractionated using an 8 mm sieve. The fraction passing the sieve was then processed in a dust separator for removal of fines material (15-20% of the straw mass was removed as fines material). The longer fraction generated after having removed the fines was then further cleaned of dust by gentle disc-milling (1 mm plate gap in disc mill) and a further circa 5% dust fraction was removed using 0.3 mm sieve. The longer fraction was now mainly straw pieces of length 2-3 mm.

3. Aqueous suspension: This longer fraction was suspended in 55°C water, in a jacketed steel tank, at a loading of 85 kilograms minced straw (corresponding to circa 75 kgs straw dry matter) per 1400 liters of water.
4. Alkaline pulping of straw: The pH in the tank was raised to 11 via addition of NaOH as well as raising the temperature to 80°C. Stirring using these conditions was performed for 120 minutes. Thereby an alkaline lignin and hemicellulose mix is released from the straw substrate and lignin and hemicellulose fragments are thereby dissolved.
5. The insoluble fibers were separated from the aqueous liquid phase by decanter centrifuging using a GEA UCD 205 2-phase decanter, running 1800 liter slurry per hour with a speed of 5500 rpm. The aqueous liquid phase comprising the dissolved and dispersed lignin and hemicellulose fragments (approx. 4-5% dry solid content) was then optionally concentrated by evaporative removal of water, reaching a dry solids content of 32%.

Sample 2 was prepared by a combination of dry-mechanical treatment and alkaline pulping of straw:

1. Mechanical dry treatment of straw: Wheat straw was dry mechanically treated by hammer-milling.
2. Aqueous suspension: This hammer-milled straw was suspended in 80°C water, in a jacketed steel tank, at a loading of 85 kilograms minced straw (corresponding to circa 75 kgs straw dry matter) per 1400 liters of water.
3. Alkaline pulping of straw: The pH in the tank was raised to 11 via addition of NaOH as well as maintaining the temperature to 80°C. Stirring using these conditions was performed for 120 minutes. Thereby an alkaline lignin and hemicellulose mix is released from the straw substrate and lignin and hemicellulose fragments are thereby dissolved.
4. The insoluble fibers were separated from the aqueous liquid phase by decanter centrifuging using a GEA UCD 205 2-phase decanter, running 1800 liter slurry per hour with a speed of 5500 rpm. The aqueous liquid phase comprising the dissolved and dispersed lignin and hemicellulose fragments (approx. 4-5% dry solid content) was then optionally concentrated by evaporative removal of water, reaching a dry solids content of 32%.

Sample 3 was prepared by a combination of dry-mechanical treatment, fractionation, and alkaline pulping of straw:

1. Mechanical dry treatment of straw: Wheat straw was dry mechanically treated by hammer-milling.
2. Removal of 'dust': dust particles 0.2 mm and lower were removed.

3. Aqueous suspension: 109 g of the remaining straw was suspended in 2 L water (consistency close to 5%).
4. Alkaline pulping: pH was adjusted to 10.5 using 27% NaOH solution. Temperature raised to 95°C, and the mix stirred for 2 hours at this temperature, with mill-blending every 20 mins. The pH was maintained between 10 and 10.5 throughout the reaction time.
5. The liquid phase was separated from the fibres via filtration using a filter bag with 125 micron mesh size. The liquid phase was then rotary evaporated to a dissolved solids content of 35.8%.

Sample 4 was prepared by a combination of dry-mechanical treatment, fractionation, and alkaline pulping (higher pH) of straw:

1. Mechanical dry treatment of straw: Wheat straw was dry mechanically treated by hammer-milling.
2. Removal of 'dust': dust particles 0.2 mm and lower were removed.
3. Aqueous suspension: 109 g of the remaining straw was suspended in 2 L water (consistency close to 5%).
4. Alkaline pulping: pH adjusted to 12.5 using 27% NaOH solution. Temperature raised to 95°C, and the mix stirred for 2 hours at this temperature, with mill-blending every 20 mins. The pH was maintained between 12-12.5 throughout the reaction time.
5. The liquid phase was separated from the fibres via filtration using a filter bag with 125 micron mesh size,. The liquid phase was then rotary evaporated to a dissolved solids content of 30%

Sample 5 was prepared by a combination of dry-mechanical treatment, fractionation, and alkaline pulping (higher pH) of wood fibres:

1. Wood fibres, TMP type (ie non-delignified).
2. Aqueous suspension: 113g of wood fibres were blended with 3 L of water and temperature raised to 95°C, pH to 11 using 27% NaOH solution. The mix was stirred at this temperature for 2 hours, with mill-blending every 20 mins. pH was maintained between 10.5 and 11 for the duration of the extraction.
3. The liquid phase was separated from the fibres via filtration using a filter bag with 125 micron mesh size,. The liquid phase was then rotary evaporated to a dissolved solids content of 30%

1B.1 Flame retardant tests - wood beech strip test

The samples obtained as disclosed above were tested for their flame retardant properties as follows:

The liquid phases were separately used to treat wood samples (beechwood sticks - "tongue-depressors") of dimension 115mm x 20mm x 1.5mm thick, via dip-immersing half of the length in the relevant solution and allowing to soak for 15 mins., followed by wiping off excess liquid with tissue paper, and drying the treated sticks in an 80C oven for 30 mins.

The treated sticks were then tested via application of a candle lighter flame, from a 2 cm distance, to the lower face of the stick, 1cm from its end, for 15 seconds.

Results:

Samples 1-4 hardly ignited, and burned for maximum 2 seconds, before a char formed and the flame extinguished. Sample 5 (wood fibre extract) ignited and burned for more than 20 seconds, burning at least 8 cms along the stick, before charring and the flame going out. This demonstrates that the liquid from pulped straw is an efficient flame retardant, while the liquid from pulped wood fibres is not ideal as a flame retardant.

Example 2: Insulation materials

In addition, wood fibres produced for insulation materials have been treated, and wood fibre insulation mats (similar to rockwool mats, but using wood fibres instead) with the flame retardant product of the present invention.

Specifically, preformed insulation mat sections (65mm x 60mm x 400mm) were soaked overnight in a 32% dissolved solids flame retardant composition of the present invention (prepared as disclosed in example 1), then drained and subsequently dried at 75C for 12 hours. It was found that it works very well as a flame retardant in such application.

Example 3: Effect of oxidation

In a further experiment set, the flame retardant composition (prepared as disclosed in example 1) was oxidized using hydrogen peroxide. Theoretically, the sample would thereby better resemble an "oxidized product" and therefore it should char and suppress flame better.

Specifically, the composition was oxidized at 80C, applying 100 ml of 35% Hydrogen peroxide per 2L of flame retardant composition, pH 10.5, temp 80C, incubation time 2 hours.

This oxidized composition was applied to the wood strips at both 30% and 15% dry solids preparations, in the same way as above (wood beech strip tests). In both cases flame retardant effect as above was observed – see figure 2. Hence oxidation is an option, and could be beneficial (also see example 6 below).

Soaking the wood sample in the flame-retardant composition was shown to be a sufficient way to achieve best results – i.e. improvement in thermal stability, increased charring, self-extinguishment, and the reduction of smoke production - and thereby prove that the composition is a good flame retardant.

Example 4: Comparison with commercial water-based flame-retardant formulations

Phosphoric acid is a known flame suppressant (phosphate salts). Wood strips were treated with the Phosphoric acid alone. This treatment was found to be only a little flame retarded compared to the control (non-treated wood strips), but slowly burned. Meanwhile, when phosphoric acid (circa 1% w/v) was added to the flame retardant composition of the present invention, and the wood strip test was performed using both 30 % and 15% dry solids lignin preparations, the flame inevitably goes out after maybe 1 cm of burning along the strip. Hence, same effect as in sample (a) above, but no particular further enhancement.

A commercial flame retardant formulations comprising a blend of diammonium hydrogen phosphate and monoammonium dihydrogen phosphate has been tested, and compared to the flame retardant composition of the present invention (prepared as disclosed in example 1). It was found that the flame retardant composition of the present invention performs best.

Example 5: Combined effect of lignin and hemicellulose fragments in wood strip test

5.1 Composition analysis

The flame retardant product of the present invention as prepared in example 1 is a blend between lignin and hemicellulose oligomers extracted from straw after alkaline treatment. The hemicellulose and lignin content was determined as described in section IV, finding that the dry solids in the mix are composed of approximately 60-65% lignin derived material, the remainder being oligosaccharidic fragments of hemicelluloses (mainly arabinoxylan type).

5.2 Mixture is better than the lignin and hemicellulose fragments individually

The lignin fraction of the flame retardant composition was precipitated, resuspended in water at 32% dry solids, and tested for its flame retardance, using birch veneer wood strips, as disclosed herein. Some suppression was observed, but inferior to the "mixed" flamed retardant composition (i.e. the composition comprising lignin and hemicellulose components).

Further, the isolated "hemicellulose rich" fraction from above was also used to treat wood strips in the same way. Here, no evidence of flame retardance was observed.

It is therefore concluded that both the hemicellulose and lignin components should be present for the composition to have good flame retardance properties, preferably in proportions close to the original mix.

Example 6: Additional char formation studies

Studies were performed which indicate that the flame retardant product of the present invention produces a lot of char compared to lignin alone (i.e. lignin separated as a "pure" component, originating from the flame retardant composition of the present invention).

TGA/DSC analysis (in nitrogen) was performed on a METTLER TOLEDO TGA/DSC 1 STAR^e System instrument using Al_2O_3 crucibles between 50 and 800°C with a temperature ramp-rate of 10°Cmin^{-1}. The samples analysed were: a pure lignin sample, a mixture of hemicellulose and lignin sample (i.e. the flame retardant composition of the present invention), and an oxidised mixture of hemicellulose and lignin sample (i.e. oxidized flame retardant composition of the present invention). Around 15mg of each of the samples were weighed out prior to the analysis.

Examination of the data was done via the STAR^e software. Key results extracted from the data include (i) the remaining mass and the corresponding percentage, and (ii) the onset temperature, which is the temperature at which the sample starts to decompose; this is defined as 2% weight decrease (water weight subtracted).

The results of the TGA studies are summarized in Table 2

Table 2. results of the TGA studies

Lignin+ Hemicellulose 50-800°C	Onset temperature 219°C	Overall mass left is 53%	Hemicellulose decomposition at 263°C
Purified lignin	Onset temperature 179°C	Overall mass left is 45%	(No hemicellulose decomposition)
Oxidized Lignin+ Hemicellulose 50-800°C	Onset temperature 227°C	Overall mass left is 60%	Hemicellulose decomposition at 260°C

The thermal studies (TGA) indicated that this "mix" leaves around 53% residue after heating to 800°C, whereas the "purified" lignin from the same material leaves only 45% (in agreement with other observations on lignin in general). In addition, when the 'mix' is oxidised (ie that being the mix/blend of lignin and hemicellulosic material), the residue after heating to 800°C increases again to 60%. This suggests that the better flame-retardant behaviour (at least based on "charring" or "char promotion" potential) is exhibited by the "mix" product (i.e. the flame retardant composition obtained from the straw pulping) and its oxidized version, rather than a purified lignin.

Example 7: Smoke suppression

As a further step, it was observed that, even though flames were demonstrably suppressed by the flame retardant composition of the present invention as applied to wood and wood fibres, some continued smoking was still observed after flame had disappeared. To address this, Calcium Carbonate and Iron Oxide were added to the flame retardant composition at levels between 1-3%, which resulted in an effective reduction, almost elimination, of this smoke.

Example 8: Upscaled wood treatment fire tests

MiniSBI-tests were performed at DBI - Dansk Brand- og sikringsteknisk Institut (Danish Fire and Security Institute). Mini-SBI is a geometrically scaled down version of the SBI-test (EN13823) which is the predominant fire test for classification of building materials within Europe. SBI test = Single Burning Item test. Geometrically, the samples for the Mini-SBI are scaled by a factor of 6.25 from the original SBI, and symmetrical on both sides. Sample sizes are 200mm (wide) X 600mm (high) with a maximum thickness of 50 mm. Two boards are required in order to assemble a corner / 90 degree angle / L-shape configuration.

The apparatus measures the Heat Release Rate (HRR) using "oxygen consumption calorimetry", which is the same method used in the SBI-method. Based on these measurements, the S-THR (a Scaled value for Total Heat Release) can be determined, as well as the S-FIGRA (a Scaled value for FIre Gowth RAte).

Samples: The following samples were tested using the mini-SBI apparatus:

- Scots pine wood treated with a flame retardant liquid composition prepared according to Example 1, sample (a) (test 414 and test 415)
- Untreated scots pine wood (negative control, test 417)

The treated samples were impregnated. Process parameters treatments: 0.1 bar for 60 min followed by 13 bar for 120 min; dry pre-vacuum.

Heat Release Rate (HRR): Heat Release Rate is the amount of energy released by a burning object as a function of time, given in kW. This energy rate is measured with use of oxygen consumption calorimetry through the gas measuring equipment in the apparatus. The performance of the sample is determined from how much and how fast the energy is released. Therefore, a good performance would be a sample releasing a low amount of energy over an extended period, effectively delaying combustion.

As seen in Figure 3A, the samples treated with the flame retardant composition of the present invention showed good performance by releasing low amounts of energy, compared to the non-treated sample.

Total Heat Release (THR): Total Heat Release is the accumulated energy which the sample release during the test, given in MJ.

As seen in Figure 3B, the samples treated with the flame retardant liquid of the present invention showed good performance by releasing lower amounts of total energy, compared to the non-treated samples.

Fire Growth Rate (FIGRA): FIGRA is an expression for how fast the HRR develops during a test. This can also be described as the acceleration of the fire given in W/s.

As seen in Figure 3C, the samples treated with the flame retardant composition of the present invention show better performance than the untreated sample as indicated by their lower FIGRA values after 900 s. The lower values indicate slower heat release and slower fire spread. In addition, all the scot pine samples presented an initial high peak followed by a reduction in FIGRA values, however the untreated sample sustained higher heat release for longer, suggesting that it is more hazardous overall than the samples with the compositions of the present invention.

Example 9: Upscaled wood treatment fire tests– additional testing

The Mini-SBI test disclosed in Example 8 was again applied.

Samples: The following samples were tested:

- Scots pine wood treated with a flame retardant liquid composition prepared according to Example 1, sample (b), and further comprising 2% calcium carbonate and 0.5% iron oxide (PFE1, PFE2, and PFE3)
- MDF Firax: commercially available flame retardant MDF board
- Untreated scots pine wood (negative control, test 416)

A set of samples were impregnated. Process parameters were 0.1 bar for 60 min followed by 13 bar for 120 min; dry pre-vacuum.

The quantity of lignin-hemicellulose composition absorbed by the wood was measured. Both before and after treatment, the wood was conditioned to a moisture content of 12% and the uptake was calculated by determining the weight difference. Due to wood variability, different levels of uptake were achieved. The set of samples was divided into three groups according to the uptake level. Sample PFE1 was randomly selected from the group that achieved 377±56 kg/m^3 uptake; sample PFE2 was randomly selected from the group that achieved 111±13 kg/m^3 uptake; while sample PFE3 was randomly selected from the group that achieved 36±4 kg/m^3 uptake.

In the previous Example 8, the data Figures 3A, B, and C reflect the values directly obtained from the SBI-mini test. As mentioned, the apparatus used is a geometrically scaled down version of the European standard SBI-test.

In the present Example 9, the values presented in Figures 4A, B, C, and D are 'scaled' values, meaning that the values obtained from the mini-SBI test have been scaled to be comparable to standard SBI-test values.

Scaled Average Heat Release Rate HRRav(t): A lower and stable HRRav(t) indicates a material that releases heat at a slower and more consistent rate, which can contribute to delaying fire spread and reducing fire intensity. Conversely, a higher and increasing HRRav(t) suggests a material that releases heat rapidly over time, which can lead to faster fire growth and greater fire hazards. Therefore, materials with lower and stable HRRav(t) values are considered more effective in delaying fire spread and enhancing fire safety.

As seen in Figure 4A, all treated samples performed better than the non-treated sample. Especially sample PFE1 and sample FIRAX had lower and stable HRRav(t) values, compared to the untreated sample, and are therefore considered more effective in delaying fire spread and enhancing fire safety.

Scaled Total Heat: As seen in Figure 4B, the untreated sample showed a rapid increase in heat compared to treated samples, indicating a potentially distinct behavior. Here it is again observed that that the sample PFE1 sample performed very similar to FIRAX. It was further observed that samples PFE2 and PFE3 performed more like FIREX than to the untreated sample.

For example, Table 3 reports the Time to Heat Release (THR600) and its scaled values. Lower THR600 values indicate slower ignition times. The percentage-of-untreated column indicates how much faster or slower the ignition times are for each test or material relative to the untreated sample.

Table 3

	THR600 scaled [MJ]	**% of untreated (THR600 of scaled sample/THR of untreated)**

Test 416 (Untreated)	15.34	100%
PFE1	4.88	32%
PFE2	6.75	44%
PFE3	5.59	36%
FIRAX	3.63	24%

As seen in the table, all treated samples performed better than the untreated sample.

Scaled Fire Growth Rate (S-FIGRA): In Figure 4C, each line represents how the intensity of a fire grows and then decreases over a period. At first, all samples show a peak which then goes down. This initial peak can indicate when a fire beginning to grow rapidly. FIRAX and sample PFE1 performed best. At the beginning of the tests, there was highest peak in heat release rate for the untreated sample, and a little bit less for PFE2 and PFE3, this may represent the initial combustion phase of the wood. For all treated samples, the fire was suppressed over time, despite the initial peak.

Smoke production: In Figure 4D, it is seen that all treated samples effectively reduced smoke, unlike the untreated sample.

Example 10: Application on other cellulose-based products and resistance over time

10.1 Performance in other cellulose-based products

Standing products made from cellulose components, such as fiber boards and plywood, typically require the addition of fire retardants for safety.

Two types of samples were tested: A medium-density fibreboards (MDF) and three-layer plywood specimens both made from pine. These commercially available specimens measured 10 cm x 10 cm x 0.3 cm and had smooth, even surfaces to facilitate the uniform application of fire-retardant compositions by brushing.

It was tested whether the flame retardant composition of the present invention, prepared according to Example 1 sample (b) could be successfully applied by brushing and so have the potential to protect standing cellulose products.

Reference composition: To serve as a reference, a known intumescent coating formulation was used. Intumescents chemicals are known to cause swelling, and are typically used in passive fire protection, i.e. causing swelling behind the protective char layer, thereby providing much better insulation. This reference formulation was composed of ammonium polyphosphate (Exolit 422), Melamine (Sigma) and Pentaerythritol (Sigma). These components were mixed in a 3:1:1 ratio, as

recommended in patents and scientific literature. A polymeric aqueous dispersion (Mowilith LDM 2301) was used as the film-forming agent for the fire-retardant coatings.

Preparation of coatings: The specimens were conditioned at room temperature (20-25°C). The MDF and plywood samples were prepared by painting one face of each specimen with a common brush. Multiple layers were applied until the specimens could no longer absorb more composition, as indicated by the composition running off. Typically, this saturation point was reached after 3 layers for plywood and 6 layers for MDF.

After treatment wet specimens were dried in a convection oven at 25°C for a week. Subsequently, both treated and untreated specimens were conditioned at room temperature (20-25°C) for three days before testing.

Furnace and butane burner test: The coatings formed by both the intumescent reference compositions and the flame retardant composition of the present invention were annealed in a furnace at 600°C and with a butane burner. A carbon layer was observed for both compositions. The presence of carbon layers, which delays the spread of fire, confirms that the reference composition was a fair comparison for the flame retardant composition of the present invention. The test however happened too fast to make comparative measurements. Thus, a small-gas-flame test was selected as test method instead.

Gas-Flame Test Setup: A small-gas-flame test setup was used to evaluate how the coatings react to a direct flame. Here combustion occurs slowly and in the vertical direction. Ignition was applied using an industrial lighter (selected randomly from a group of 10 lighters), positioned against the surface at the bottom edge of each sample. Based on the ignition patterns observed in untreated samples (the time at which the untreated started to combust), specific ignition times were calculated for the test: MDF samples were ignited for 90 seconds. Plywood samples were ignited for 45 seconds.

The main observations were that the flame retardant composition of the present invention exhibited self-extinguishing properties and did not sustain a flame after the lighter was turned off. Photo documentation of the test is found in Figure 5. The back of the treated samples was stained much less than that of the untreated samples, as indicated by a lighter color. The same was observed in the intumescent coating samples. As mentioned, the control sample ignited in the applied time.

Treated samples have carbon layers that appear as droplets on top of the cellulose materials. Untreated samples also form a carbon layer (as the material is itself carbonaceous in nature), but it appears as small depressions, see Figure 6.

Flame spread in the horizontal direction was measured on both the front and back of the samples. An average of three measurements was taken for each side (see Table 4).

Table 4. Width of the flame spread in the horizontal direction. Each data is the average of nine measurements (three measurements for three specimen) and the corresponding standard deviation (S.D).

		Coated face		**Uncoated face**	
Material	**Composition**	**Width (cm)**	**S.D**	**Width (cm)**	**S.D**
MDF	Untreated	2.21	(0.18)	1.07	(0.49)
	Sample	1.72	(0.10)	0.82	(0.36)
	Reference	1.87	(0.33)	1.29	(0.34)
Plywood	Untreated	2.58	(0.13)	2.04	(0.37)
	Sample	2.16	(0.26)	1.88	(0.17)
	Reference	1.53	(0.25)	1.27	(0.17)

Despite the inherent variability of cellulose products, the data consistently show that flame retardant composition of the present invention tends to significantly reduce the spread of fire. In the case of the MDF samples, the effect was even better than the reference coatings, which could be due to the easy absorption of the flame retardant composition of the present invention compared with the more hydrophobic intumescent coating. In the case of plywood sample, the effect was less visible as these samples did not absorb the composition as profusely as the MDF sample.

10.2 Accelerated weathering test

Fire protection treatments can significantly enhance the fire performance of cellulose products; however, exposure to moisture or weathering can substantially reduce this protection. Flowing water, changes in moisture content, and UV radiation can also reduce the amount of fire retardant in the products. Therefore, it is essential to verify the functionality and long-term durability of fire-protected products.

To this aim, an additional set of the samples were prepared as described in Example 10.1, conditioned for two week at 50% relative humidity at 23°C, and put in an accelerated weathering chamber at the Danish Technological Institute. 336 hours or 28 repetitions of the cycle shown in Table 5 were performed:

Table 5

Step	Program step Weathering cycle 1	Duration (h:min)	Summarized duration (h:min)
1	Sub-cycle step 2 -8, repeated 9 times		6:45

2	Spray	0:01	
3	Dark	0:04	
4	Spray	0:01	
5	Dark	0:04	
6	Spray	0:01	
7	Dark	0:04	
8	UV	0:30	
9	UV	1:15	5:15
10	Dark	0:15	
11	UV	1:45	
12	Dark	0:15	
13	UV	1:30	
14	Dark	0:15	
15	Final step -go to step 1		

After the exposure, the samples were dried slowly at 25°C in a convection oven, and conditioned for one week at 50% relative humidity at 23°C. Then the small-gas-flame test was applied.

The plywood samples did not resist the intensity of the accelerated weathering test as the layers were separated. While the fire-retardant effect could not be tested, this indicated that the exposure was rough. The layer with the fire retardant composition has different color than the other layers, suggesting, some of the solution did remain in the solution.

For MDF samples, surprisingly, the samples with the fire-retardant composition of the present invention outperformed the untreated and the reference intumescent coating mainly because the samples did not degrade. The composition resisted the change in conditions better because absorption was not limited to the outer layer, as it was the case for the intumescent coating. Thus, the samples comprising the fire-retardant composition of the present invention appear intact -even in better shape than the untreated-, while the samples comprising the intumescent coating were rough, uneven, and gritty. The physic reactions of the intumescent coating to the changing conditions of the test perhaps contribute that two out of three samples were broken.

In addition, the fire retardancy effect remained as seen in the small-gas-flame test, see Table 6.

Table 6. Width of the flame spread in the horizontal direction. Each data is the average of three measurements for number of specimens and the corresponding standard deviation (S.D).

		Coated face		Uncoated face	
Material	**Composition**	**Width (cm)**	**S.D**	**Width (cm)**	**S.D**
MDF	Untreated (3 specimens)	1.81	(0.30)	0.44	(0.59)
	Sample (3 specimens)	1.08	(0.24)	0.00	(0.0)
	Reference (1 specimens)	1.06	N/A	0.00	N/A

Example 11: Composition prepared from purified alkaline lignin, xylose, arabinose and glucose

The hydrolysis of hemicelluloses using NaOH can result in the release of various monosaccharides, including xylose, arabinose, and glucose. Thus, these monosaccharides were used as analogs for hemicelluloses in the following example.

Sample 1: Purified alkaline lignin, xylose, arabinose and glucose were bought from Sigma. The three monosaccharides were mixed in a 7:2:1 ratio to mimic their original proportion in the hemicelluloses of cereal straw. Sample 1A comprised 60% lignin and 40% hemicelluloses (weight basis). Sample 1B comprised 40% lignin and 60% hemicelluloses (weight basis). Demineralized water was added to reach a 15% dry matter content in each solution. The pH was adjusted to 10.5 using 27% NaOH solution. The compositions were stirred for 2 hours at a temperature of 95°C.

Sample 2: An additional set of samples was prepared, adding 2% calcium carbonate and 0.5% iron oxide to the Sample 1 compositions.

Sample 3: An additional set of samples was prepared, adding 2% calcium carbonate and 5% expandable graphite (ProGraphit Shop, Germany) to the Sample 1 compositions.

The different compositions were used to treat wood samples (beechwood sticks - "tongue-depressors") of dimension 115mm x 20mm x 1.5mm thick, via dip-immersing half of the length in the relevant solution and allowing to soak for 20 min followed by wiping off excess liquid with tissue paper, and drying the treated sticks in an convection oven at 70°C for 45 minutes. The samples were conditioned for 48 hours at ambient temperature together with untreated counterparts.

The treated sticks were then tested via application of the direct flame of a candle lighter, to the lower face of the stick. The time needed for the tongue depressor to catch fire was recorded.

Results: The main observations were that all compositions exhibited self-extinguishing properties, and did not sustain the flame, unlike untreated samples which were completely consumed if the flame was not quenched (see Figure 7). Notably, the compositions spiked with expandable graphite demonstrated superior performance by extinguishing the flame more quickly and forming a foamier carbon layer. This indicates that the composition effectively acts as a binder for expandable graphite, a known fire retardant additive. Additionally, the composition also functioned as binders for other fire-retardant additives such as calcium carbonate and iron oxide.

In addition of the self-extinguished behavior, the data in Table 7 indicate that the treated wood took longer to catch the flame, when the composition comprised minerals such as calcium carbonate, iron oxide, and expandable graphite.

Table 7. Time is seconds for a beechwood sticks "tongue-depressors" to catch fire after application of a direct flame. Each data represents the average of three samples and in parentheses is the standard deviation.

Composition	1. Without additives	2. Added additives: 2% $CaCO_3$ 0.5% Fe_3O_4	3. Added additives: 2% $CaCO_3$ 5% expandable graphite
	Time (seconds)		
Sample A	15 (2.5)	18 (0.5)	22 (1.4)
Sample B	19 (0.0)	18 (0.9)	29 (2.9)

CLAIMS

1. A method of preparing a flame retardant composition comprising hemicellulose components and lignin components from plant material, said method comprising the steps of:

(i) providing plant material,

wherein the plant material is selected from cereal straw and grasses;

(ii) mechanically dry-treating said plant material to reduce its size;

(iii) suspending the plant material in an aqueous solution;

(iv) adjusting the pH to alkaline conditions and increasing the temperature of the suspension, and agitating the suspension, to dissolve and/or disperse hemicellulose components and lignin components in the aqueous solution, wherein said hemicellulose and lignin components originates from the plant material; and

(v) separating the material obtained in step (iv) into a solid fibrous fraction and a liquid flame retardant fraction being a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components;

(vi) optionally concentrating the liquid flame retardant composition to increase the % dry matter content.

2. The method according to claim 1, wherein the temperature in step (iv) is increased to >80 °C and the pH is between 9-12.

3. The method according to claim 1 or 2, wherein the average particle size of the plant material in step (iii) is less than 1 cm.

4. The method according to any one of claims 1-3, wherein the suspended plant material in step (iii) is enzymatically treated using one or more hemicellulase enzymes, such as xylanases and/or ferulic esterase.

5. The method according to any one of claims 1-4, wherein the ratio of hemicellulose components and lignin components in the flame retardant composition is between 40:60 – 60:40, based on dry matter content.

6. The method according to any one of claims 1-5, wherein the flame retardant composition comprises at least of 60, 70, 80, or 90% hemicellulose components and lignin components, based on total dry matter content.

7. The method according to any one of claims 1-6, wherein the plant material suspended in the aqueous solution in step (iii) is dewaxed cereal straw, such as dewaxed cereal straw obtained by a method comprising the steps of:

(a) enzymatically treating the cereal straw suspended in an aqueous solution in step (iii) with protease and/or pectinase enzymes,

(b) optionally subjecting the mixture obtained in step (a) to wet mechanical treatment, and

(c) removing wax from the solution prior to adjusting pH and increasing the temperature in step (v).

8. The method according to any one of claims 1-7, further comprising

step (vii) adding a flame retardant additive to the liquid flame retardant composition from step (v) or (vi).

9. The method according to claim 8, wherein the flame retardant additive is selected from calcium carbonate, iron oxide, and expandable graphite.

10. A flame retardant composition obtainable by the method according to any one of claims 1-9.

11. The flame retardant composition according to claim 10, wherein the composition comprises dissolved and/or dispersed hemicellulose components and lignin components in a ratio of between 40:60 – 60:40, based on dry matter content.

12. The flame retardant composition according to claim 10 or 11, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

13. The flame retardant composition according to any one of claims 10-12, comprising a flame retardant additive.

14. The flame retardant composition according to claim 13, wherein the flame retardant additive is selected from iron oxide, calcium carbonate, and expandable graphite

15. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components as a flame retardant.

16. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, obtainable by the method according to any one of claims 1-9, as a flame retardant.

17. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components for enhancing fire resistance of an item, such as an item selected from solid wood elements, wood composite materials, paper, cardboard, MDF, insulation materials based on wood fibres and/or other natural fibres (such as cotton, flax, hemp, sisal, jute), and textiles.

18. Use of an aqueous composition comprising dissolved and/or dispersed hemicellulose components and lignin components, obtainable by the method according to any one of claims 1-9, for enhancing fire resistance of an item, such as an item selected from solid wood elements, wood composite materials, paper, cardboard, MDF, insulation materials based on wood fibres and other natural fibres (such as cotton, flax, hemp, sisal, jute), and textiles.

19. Use according to any one of claims 15-18, wherein the ratio of hemicellulose components and lignin components in the aqueous composition is between 40:60 – 60:40, based on dry matter content (w/w).

20. Use according to any one of claims 15-19, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

21. Use according to any one of claims 15-20, wherein the hemicellulose components and lignin components constitute at least 60, 70, 80, or 90% of the total dry matter content of the aqueous composition.

22. Use according to any one of claims 17-21, wherein the aqueous composition is applied to the surface of the item.

23. Use according to any one of claims 17-22, wherein the aqueous composition is applied to the item by brushing and/or spraying the composition on the surface of the item, soaking the item in the composition, and/or impregnating the composition into the item, such as by vacuum pressure impregnation.

24. A cellulose- or lignocellulose-based item or material, comprising a flame retardant composition comprising dissolved and/or dispersed hemicellulose components and lignin components obtainable by the method according to any one of claims 1-9.

25. The cellulose- or lignocellulose-based item or material according to claim 24, selected from solid wood elements, wood composite materials, paper, cardboard, MDF, insulation materials based on wood fibres and/or other natural fibres (such as cotton, flax, hemp, sisal, jute), and textiles.

26. A method of enhancing fire resistance of an item, said method comprising applying a flame retardant composition comprising dissolved and/or dispersed hemicellulose

components and lignin components, obtainable by the method according to any one of claims 1-9, onto the item.

27. Method according to claim 26, wherein the ratio of hemicellulose components and lignin components in the aqueous composition is between 40:60 – 60:40, based on dry matter content.

28. Method according to claim 26 or 27, wherein the hemicellulose components comprise monomers, oligomers and/or polymers of arabinoxylan, and wherein the lignin components comprise mono-methoxylated (guaiacyl (G)), dimethoxylated (syringyl (S)), and non-methoxylated (p-hydroxyphenyl (H)) phenylpropanoid.

FIGURE 1

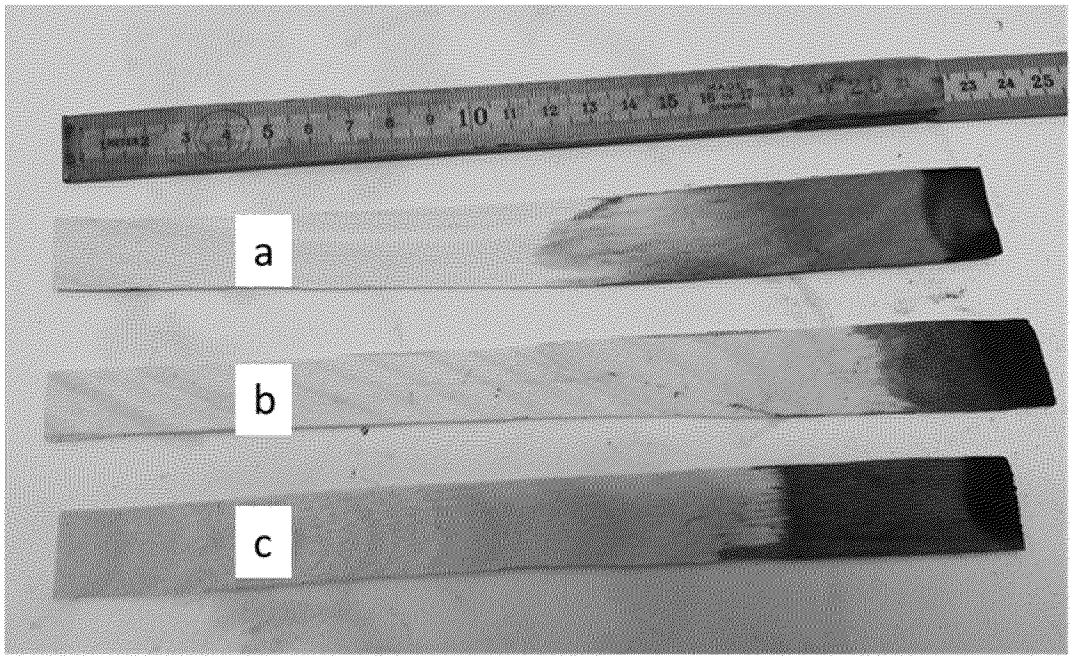


FIGURE 2

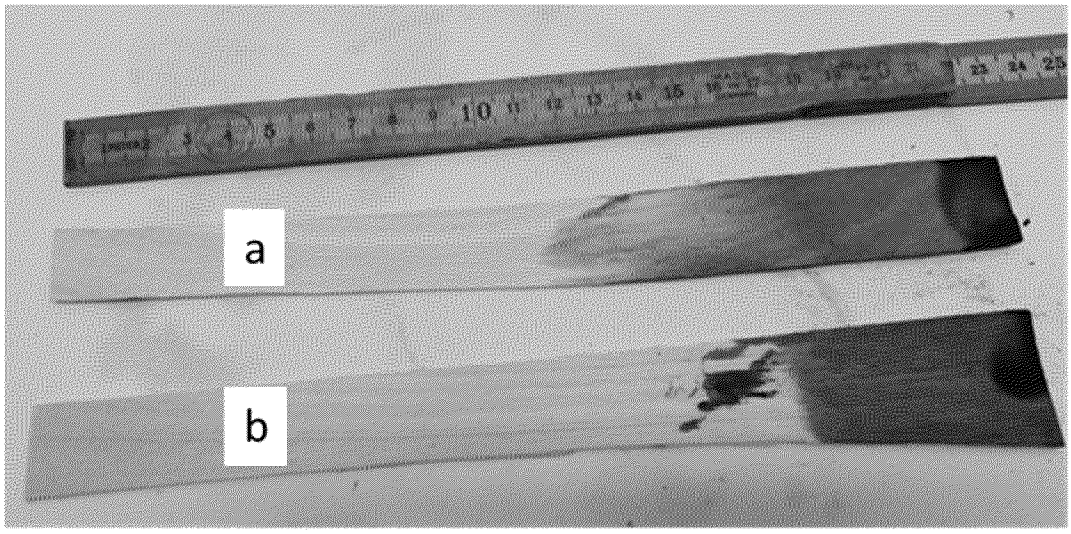


FIGURE 3A

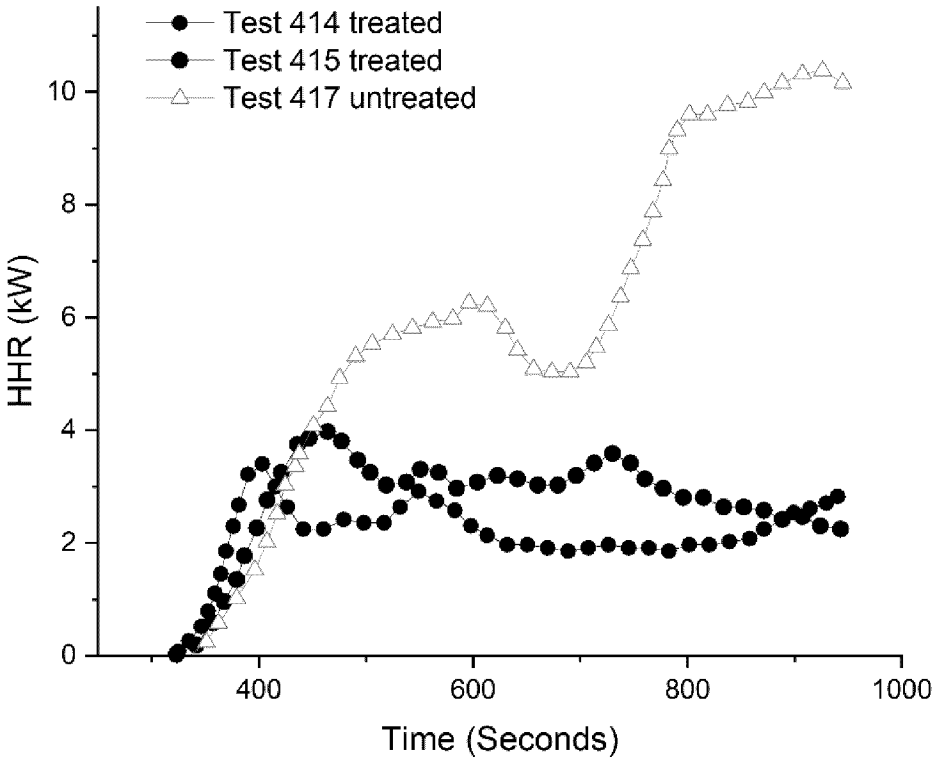


FIGURE 3B

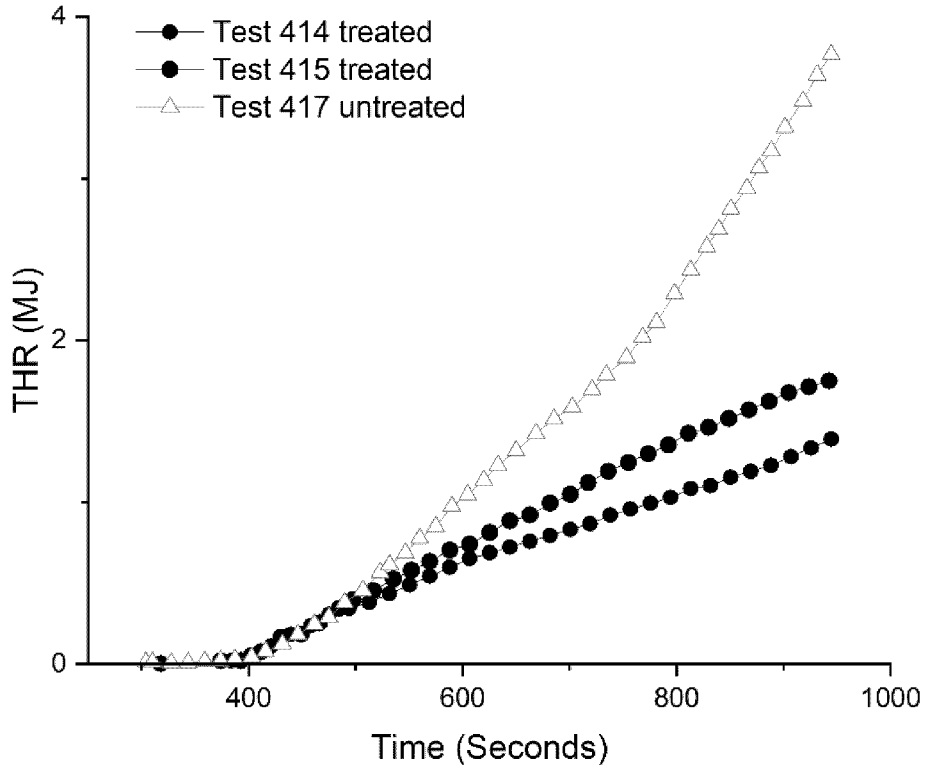


FIGURE 3C

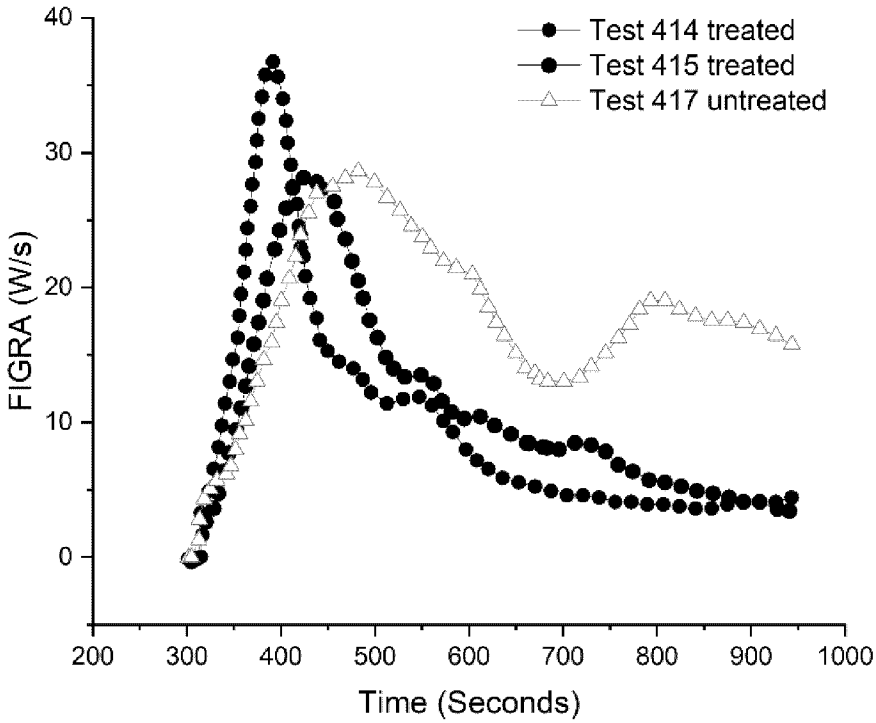


FIGURE 4A

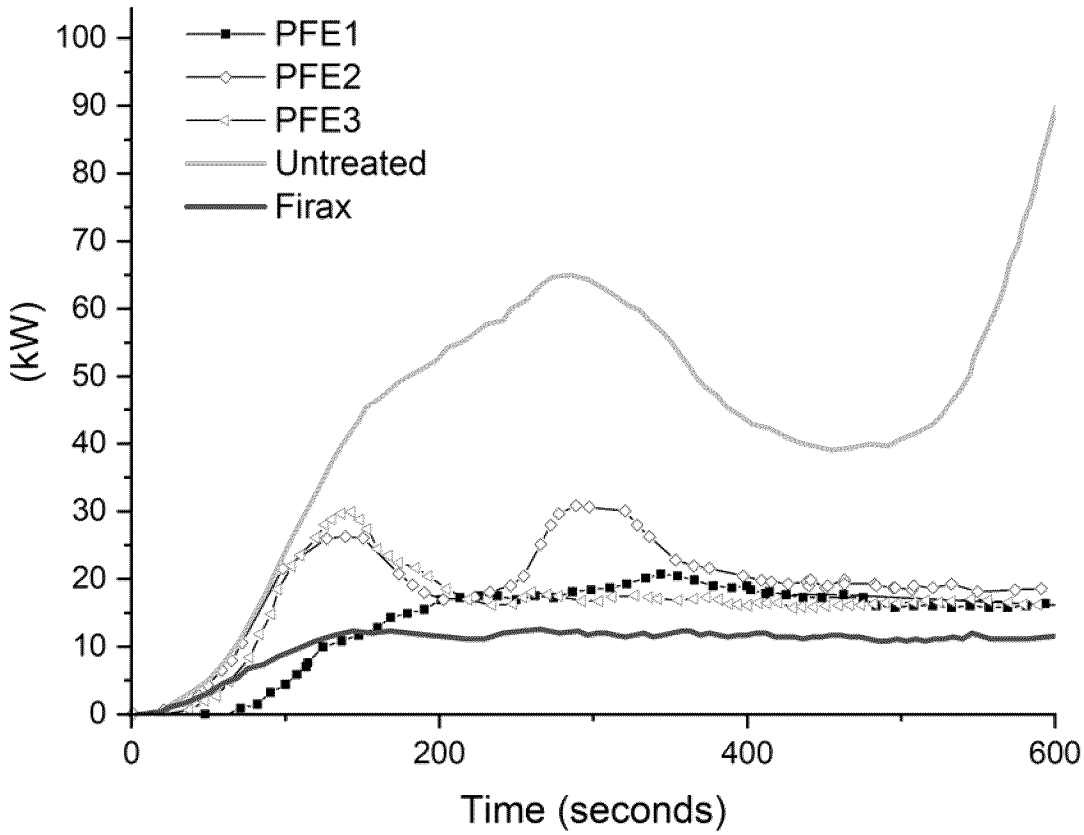


FIGURE 4B

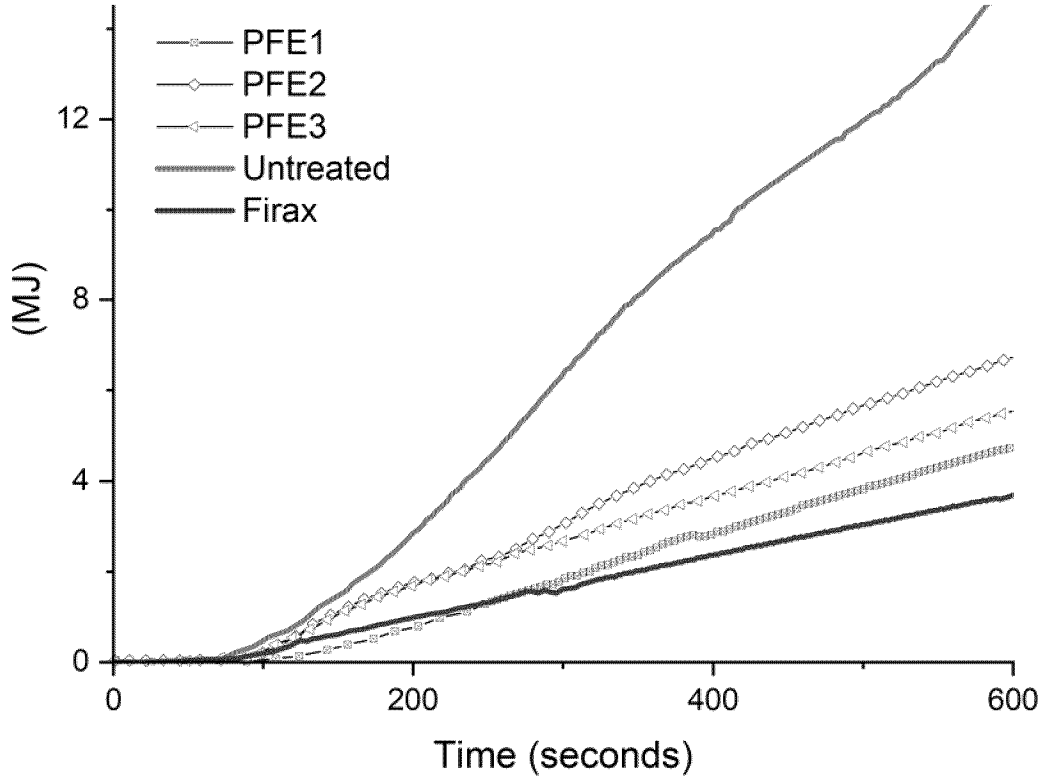


FIGURE 4C

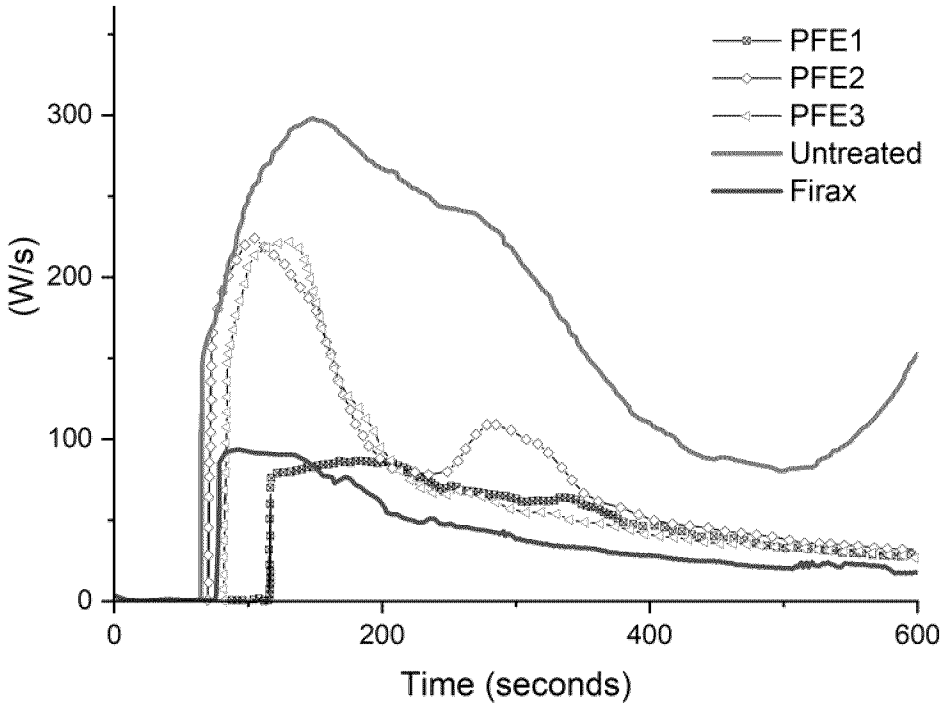


FIGURE 4D

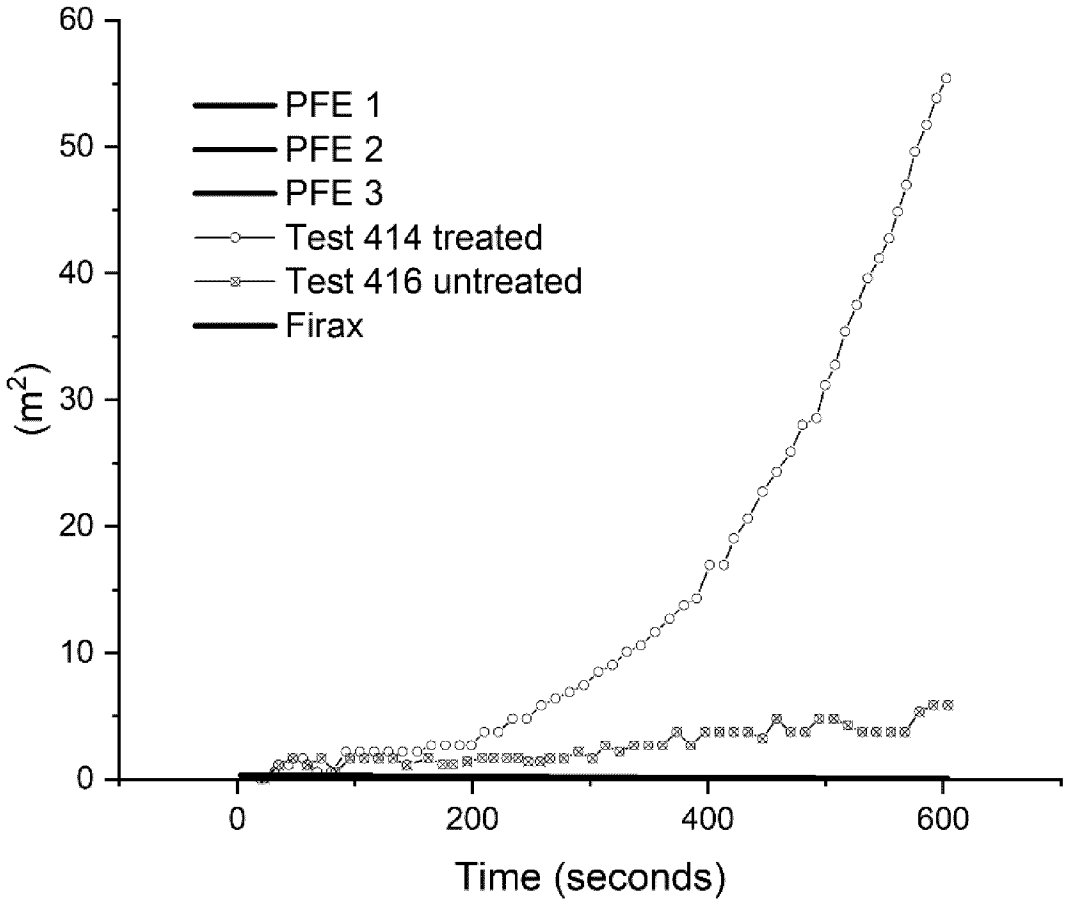
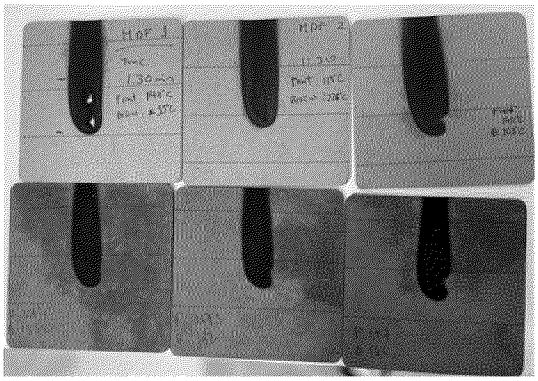


FIGURE 5

A



B

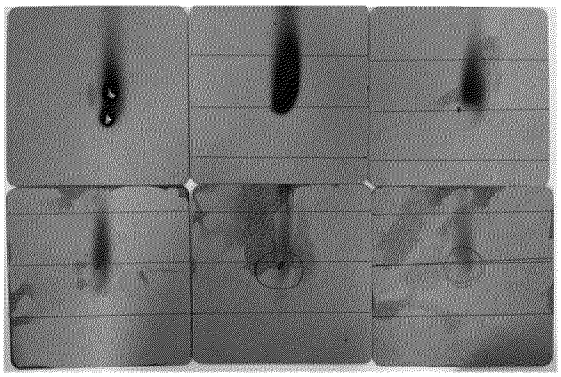
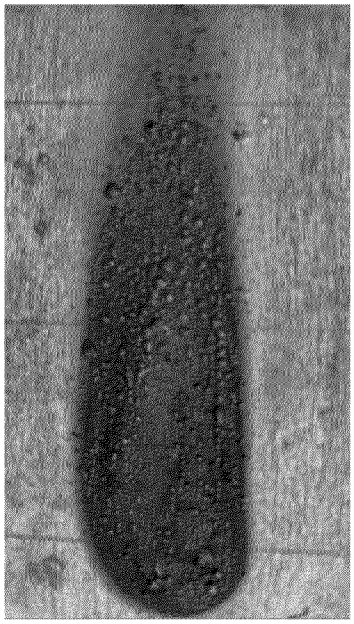


FIGURE 6

A



B

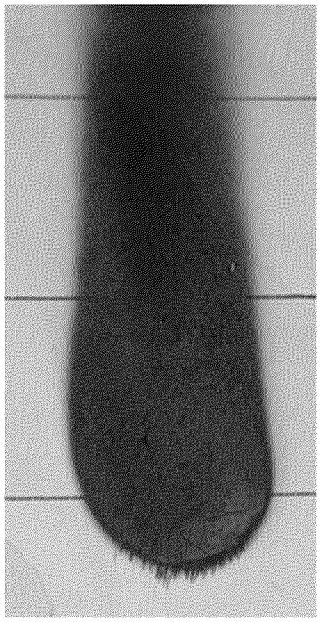
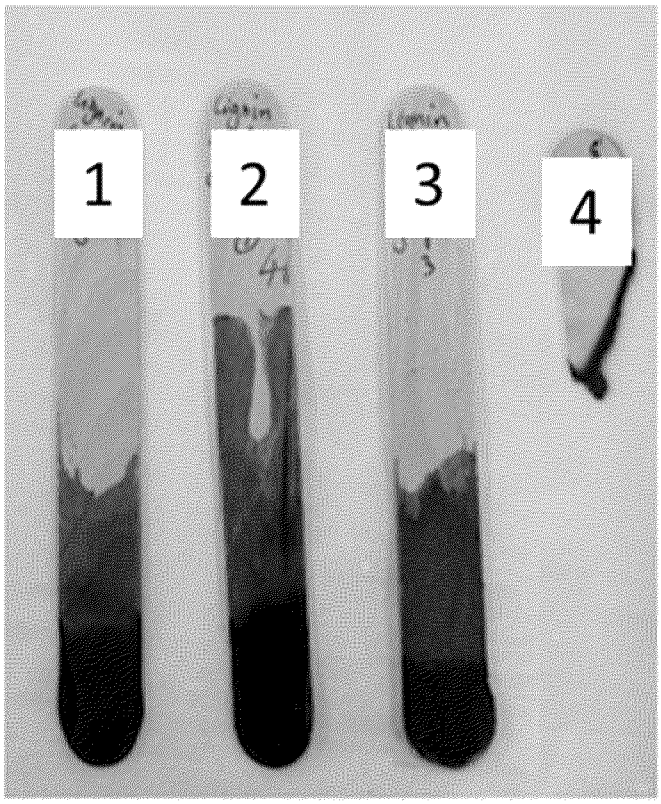


FIGURE 7



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/065768

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K21/14 C07G1/00 C08H7/00 C08H8/00 C08L5/14
C08L97/00 C08L97/02 C09D5/18 C09D105/14 C09D197/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K G02F C09J C07B C07G C08H C08L C09G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2022/081833 A1 (VINTHER PER [DK] ET AL) 17 March 2022 (2022-03-17) paragraph [0216] ----- WO 2018/086672 A1 (TEKNOLOGISK INST [DK]) 17 May 2018 (2018-05-17) examples 1-4 ----- CN 112 852 447 A (UNIV JILIN JIANZHU) 28 May 2021 (2021-05-28) example 1 ----- EP 3 540 027 A1 (UNIV DRESDEN TECH [DE]) 18 September 2019 (2019-09-18) claim 1; example 8 ----- -/--	1-7, 10-13 8,9, 14-28 1-7, 10-13 8,9, 14-28 1-18 1-18

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 September 2024	11/09/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pötzsch, Robert

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/065768

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/292615 A1 (BRIZIUS GLEN LEON [US]) 7 November 2013 (2013-11-07) claims 1,15 -----	1-18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/065768

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2022081833 A1	17-03-2022	AU 2020211300 A1	16-09-2021
		CA 3137354 A1	30-07-2020
		CN 113950550 A	18-01-2022
		EP 3914767 A1	01-12-2021
		JP 7520873 B2	23-07-2024
		JP 2022520891 A	01-04-2022
		US 2022081833 A1	17-03-2022
		WO 2020152178 A1	30-07-2020
WO 2018086672 A1	17-05-2018	DK 3538592 T3	03-04-2023
		EP 3538592 A1	18-09-2019
		WO 2018086672 A1	17-05-2018
CN 112852447 A	28-05-2021	NONE	
EP 3540027 A1	18-09-2019	DE 102018105716 A1	19-09-2019
		DK 3540027 T3	22-06-2020
		EP 3540027 A1	18-09-2019
		PL 3540027 T3	28-12-2020
US 2013292615 A1	07-11-2013	US 2013292615 A1	07-11-2013
		US 2014235132 A1	21-08-2014
		US 2014378671 A1	25-12-2014
		WO 2013165425 A1	07-11-2013