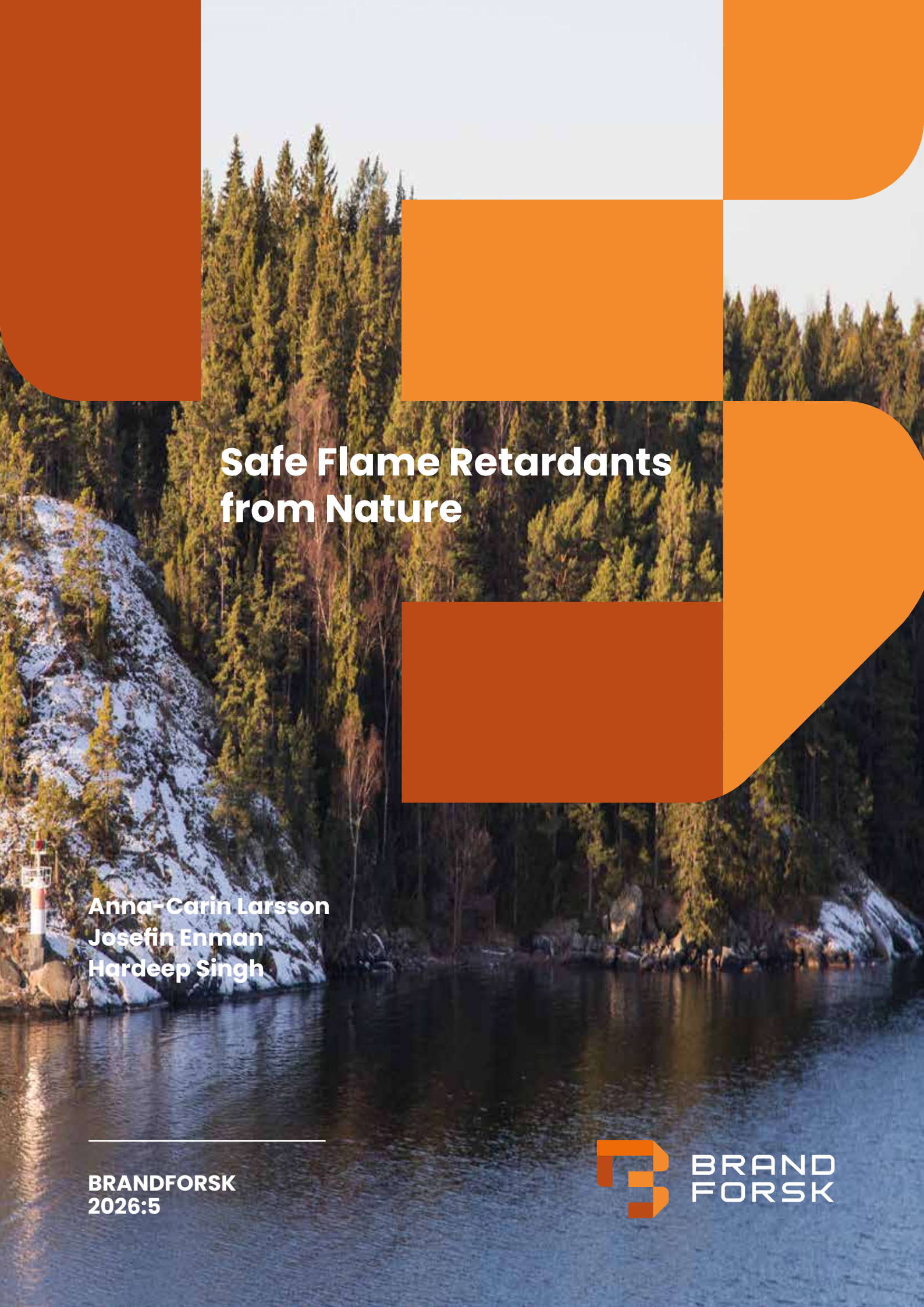

Safe Flame Retardants from Nature

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2026:5

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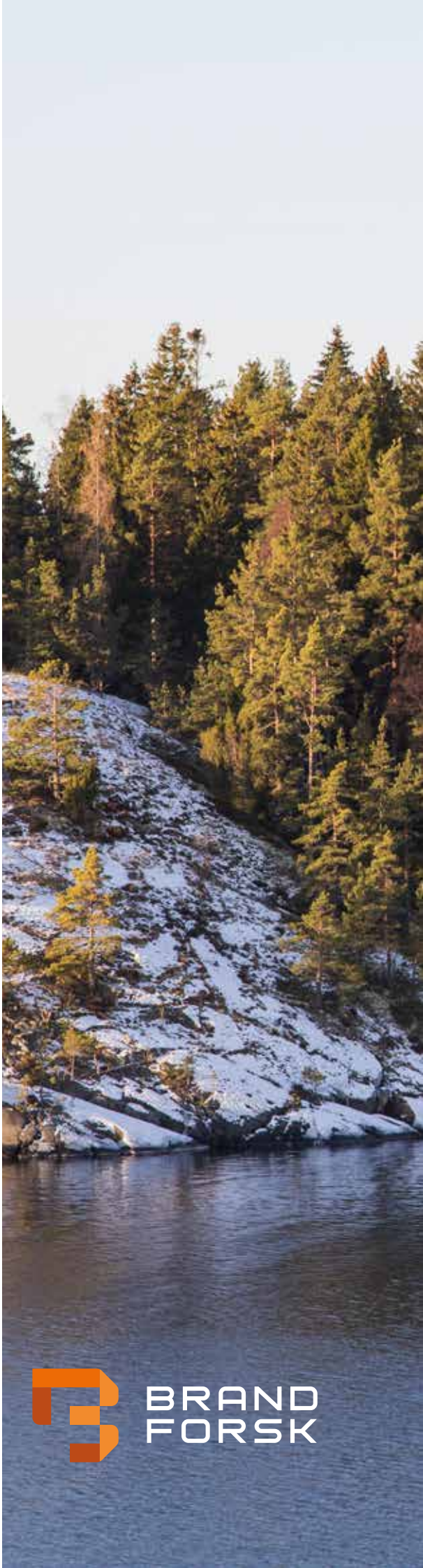

This report constitutes a final working manuscript for the headlined project. The official project report, to which reference should be made, can be found on the Luleå TUniversity of Technology´s website.

”Safe Flame Retardants from Nature”

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Preface

This report summarizes Brandforsk project 325-004. We want to express our gratitude for the financial support from Brandforsk.

The reference group has provided valuable input to the project plan and raised many interesting questions and suggestions: Mattias Delin from Brandforsk, Björn Källander from WoodHolz, and Anna Sandinge from RISE.

We are grateful to Rhoda Afriyie Mensah for helping with cone calorimetry measurements.

Abstract

The aim of this project was to develop flame retardants that are safe for both the environment and human health. In the project, harmless molecules that can be found in nature and in various waste streams were selected and investigated to develop flame-retardant candidates for cellulose-based textiles. Among the compounds investigated, creatinine showed particularly promising flame-retardant properties. Combining creatinine with phosphorylation further improved the fire performance of cotton, viscose, and linen, with the strongest effect observed for viscose. The treatments considerably reduced heat release and promoted char formation, although their durability after water exposure still needs to be improved.

Sammanfattning

Syftet med detta projekt var att ta fram flamskyddsmedel som är säkra både för miljön och människors hälsa. I projektet valdes ofarliga molekyler som kan hittas i naturen och i olika avfallsströmmar ut och undersöktes, för att ta fram flamskyddsmedelskandidater för cellulosabaserade textilier. Bland de undersökta föreningarna uppvisade kreatinin särskilt lovande flamskyddsegenskaper. Kombinationen av kreatinin och fosforylering förbättrade ytterligare brandegenskaperna hos bomull, viskos och linne, där den starkaste effekten observerades för viskos. Behandlingarna minskade värmeavgivningen avsevärt och främjade bildandet av ett skyddande kolskikt, även om hållbarheten efter vattenexponering fortfarande behöver förbättras.

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1 Introduction

1.1 Aim

The aim of this project was to develop flame retardants that are safe for both the environment and human health. In the project, harmless molecules that can be found in nature and in various waste streams were selected and investigated to develop flame-retardant candidates for cellulose-based textiles.

1.2 Background

Flame retardants are of great importance to society in reducing the risk of fire in homes and public spaces, and in protecting personnel exposed to high temperatures in their work. The use of fire-resistant or flame-retardant furniture and interior fittings can significantly improve fire safety in homes and public buildings [1–4] by delaying the onset of a fire or reducing the rate of spread. In some countries, such as the UK and the USA, all upholstered furniture must meet certain fire safety requirements by law, which often means that it must be treated with flame retardants [1,4]. The use of flame retardants can also be a cost-effective way of increasing fire safety if they can be easily applied to existing interior fittings such as curtains, sofas, blankets, wallpaper, etc.

Although flame retardants are an important component of a fire-safe society, unfortunately, many of them are hazardous to health, and the spread of persistent and toxic flame retardants is a major environmental problem. In particular, various brominated flame retardants, which are bioaccumulative, persistent, and toxic, are particularly problematic [5–7]. Some flame retardants can also emit unhealthy fumes into the indoor air or cause harm to children if ingested [7]. In addition, the production of many flame retardants involves chemical processes with high energy consumption and the use of hazardous chemicals and flammable solvents, which can cause health problems for industrial workers and emissions to the environment [7]. While the most dangerous flame retardants are no longer allowed to be used, the demands for a fire-safe environment from authorities and other stakeholders are increasing, so there is a great need to find new flame retardants that do not harm health and the environment.

As part of a fire-safe society, the availability of safe and environmentally friendly flame retardants is linked to all dimensions of sustainability. Preventing fires and the methods used to do so have a major impact on ecological, economic, and social sustainability. To meet higher fire safety and environmental standards, environmentally friendly and safe flame retardants are becoming even more relevant and in demand. By using flame retardants, many fires can be prevented, which leads to reduced emissions of toxic gases and less water used to extinguish fires in the environment. If traditionally used flame retardants are replaced with sustainable alternatives, the environmental impact can be further reduced, as both the production and the products themselves limit the use of hazardous solvents and the amount of toxic waste generated and spread. Since harmless ingredients are used in the flame retardants, waste from discarded flame retardant products can also be landfilled without having negative consequences for the environment. In a circular bioeconomy, it is also of interest to be able to recycle the waste and use it in new flame-retardant products.

In addition to the fact that a fire-safe society leads to fewer calls, reduced healthcare costs, and material losses, there are also other potential economic benefits. Since many natural flame retardant candidates can potentially occur in residual streams and waste of various kinds, there is an opportunity to use these in the long term as raw materials to produce future flame retardants. It can also contribute to achieving economic sustainability for a circular bioeconomy if these low-value materials are converted into high-value products with low environmental impact and with an accompanying increased income for the industry. If the product is also easy to apply to existing interior design, homes, and public environments can become more fire-safe at a lower cost compared to impregnating building materials or purchasing new interior design details.

Nevertheless, fire safety is also a social sustainability issue, as reducing the risk of fire means that many of the injuries, deaths, traumas, and material losses caused by fires can be avoided. Fire safety is even more important for children, patients, or people with disabilities who have more difficulty extinguishing or escaping a fire. Replacing hazardous flame retardants with harmless ones also reduces toxins in the home and public environments and increases the safety of professionals who encounter flame retardants.

The pursuit of both a fire-safe and sustainable society is a challenge, but also an opportunity to develop new flame retardants that are safe for health and the environment. Many of the global goals from the 2030 Agenda will be addressed in the proposed project, but special emphasis will be placed on minimizing emissions of hazardous chemicals and materials (6.3).

2 Theoretical background

2.1. Flame-retardant mechanisms

When combustible materials such as textiles, plastics, and wood are heated, they break down into small fuel fragments in a process called pyrolysis. The pyrolysis fragments are very reactive and can ignite if mixed in the right proportions with oxygen from the air. The heat released during the reaction radiates back to the combustible material, and more pyrolysis fragments are formed, and a fire develops, see Figure 1. The chemical composition of the combustible material determines which pyrolysis fragments are formed and thus also how flammable the material is [4,8,9].

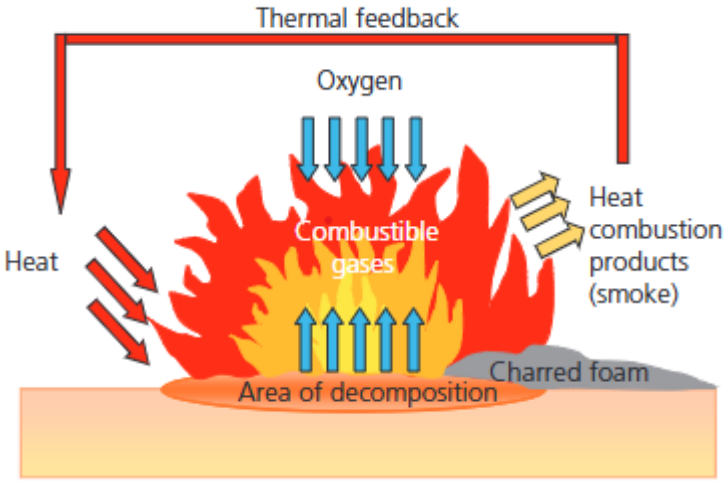

***Figure 1**. Schematic diagram of thermal degradation of materials [4].*

For a fire to start, fuel, oxygen, and heat are needed, and the fire process then proceeds via chain reactions. To prevent or extinguish a fire, at least one of these four components needs to be removed. Flame retardants achieve this through four main mechanisms of action, roughly one for each component, see Figure 2. These mechanisms can be explained based on the chemical properties of the molecules that make up the flame retardant. When the flame retardant is heated, it breaks down into smaller components, which removes heat from the fire source. Molecules containing phosphorus (P) form phosphoric acid, which chars the combustible material so that it cannot ignite, removing the fuel. Molecules containing carbon rings (C) in their structure form a graphite-like layer on the surface of the material to be protected. The layer can conduct heat away and prevent pyrolysis gases (fuel) from escaping into the air. Molecules containing nitrogen (N) remove oxygen by forming gases during decomposition, which displace oxygen from the fire zone and dilute the air-fuel mixture so that it does not ignite. The non-combustible molecular fragments formed when the flame retardant decomposes will also stop the chain reaction by reacting with the gaseous components that sustain the fire [4,8,9]. Metal ions can also stop the chain reaction [10]. Relevant flame-retardant properties to investigate are therefore decomposition temperature, flammability, heat generation, and self-extinguishing ability.

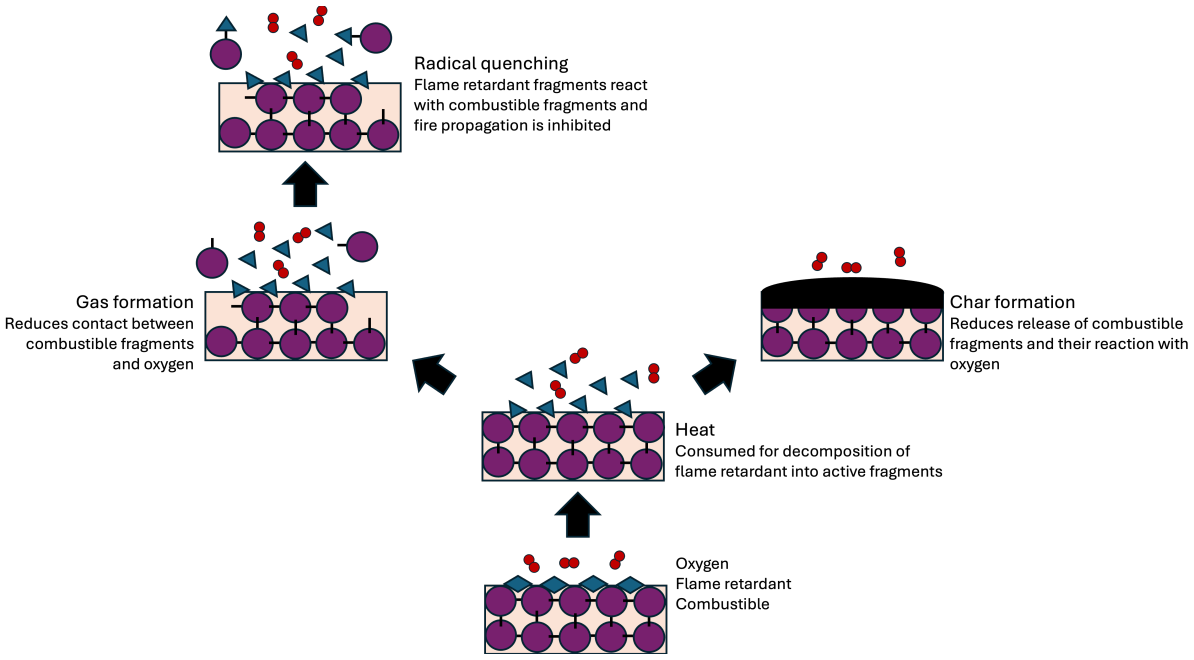

Figure 2. *Flame retardant mechanisms.*

2.2 Environmentally friendly flame retardants

The chemical properties are related to the chemical structure of the molecules, which makes it possible to predict which molecules can be used as flame retardants, and through which mechanism they mainly act. Many bio-based molecules have structures and properties indicating that they can function as environmentally friendly flame retardants. They occur naturally in plants and animals and can be extracted from waste or produced by microorganisms. In recent years, several research efforts have therefore been made to investigate various such molecules with the hope of finding a replacement for today's dangerous flame retardants. Examples of waste where suitable molecules can be found are industrial waste containing phosphates, silicates and metal ions, for example from process water and mines; forest waste can contain lignin, organic acids and nitrogen-rich molecules, for example from pine cones, roots and garden plants; household waste can contain lipids and nitrogen-rich molecules, which can be found in, among other things, coffee grounds, shellfish residues and wastewater.

Some examples of biobased molecules that have been studied are phytic acid, proteins, and DNA [4,6,11]. Phytic acid contains a carbon ring and phosphate groups; proteins contain nitrogen, and DNA contains both nitrogen and phosphate groups. By combining molecules containing P, C, and N, a flame retardant can be produced that removes two, three, or all four of the components needed to sustain a fire [12–15]. In our latest study [16], we combined phytic acid with metal ions and adenine, a component of DNA. Although demonstration tests at RISE Fire Research in Trondheim, Norway, showed that the flame retardant worked, it did not work well enough to meet the requirements of more challenging environments, and was not resistant to water.

There are many other bio-based molecules that can be extracted from various wastes and that have greater potential to form a more durable flame retardant. Based on the knowledge and experience we have from previous Fire Research projects [16–18], we are now even better positioned to effectively select possible molecules with the right properties to both prevent ignition and be durable on the fabric.

2.3 Project idea

In this project, we investigated a number of suitable molecules based on structure and the possibility of extracting them from different wastes. Based on known knowledge about which chemical structures give rise to different flame-retardant mechanisms, suitable molecules were identified. The existing chemical stock at the Chemical Engineering division was inventoried, and a list of possible candidates to investigate was created. Among the molecules tested were phosphoric acid, creatinine, L-glutamine, hippuric acid, and sodium succinate, see Figure 3.

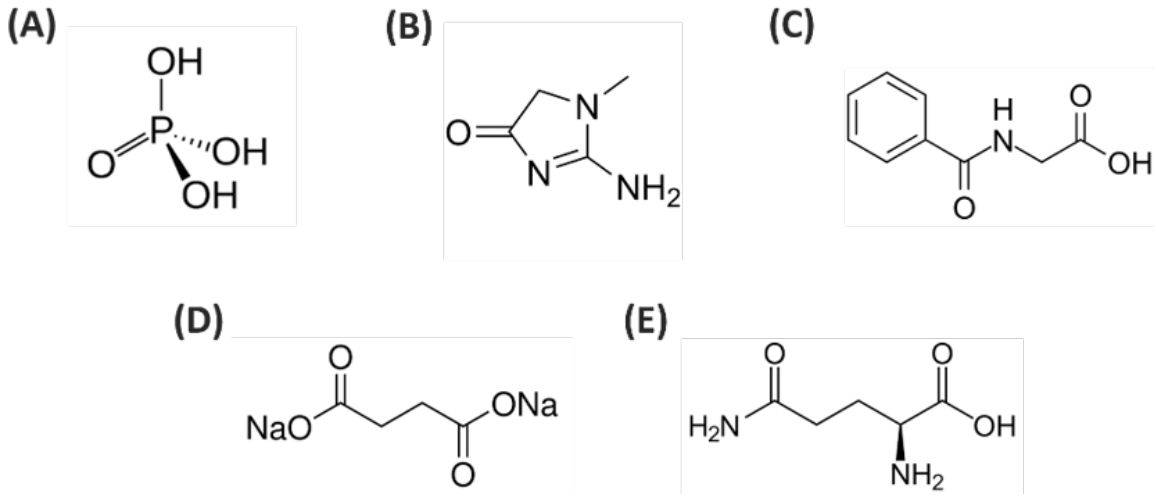

Figure 3. *(A) Orthophosphoric acid; (B) creatinine; (C) hippuric acid; (D) sodium succinate; (E) L-glutamine*

Phosphoric acid (orthophosphoric acid) (Figure 3A) is an inorganic acid with many industrial uses in everything from fertilizers to food and pharmaceuticals. Phosphate systems derived from phosphoric acid are very common in nature, and since phosphate rocks and apatite minerals are important natural sources of phosphorus, phosphoric acid/phosphate compounds can also be found, for example, in mining waste streams.

Phosphoric acid is also renowned for its flame-retardant properties; when heated, it promotes dehydration of organic materials and char formation. The protective carbonizing layer that forms leads to poorer heat and oxygen transport and fewer combustible gases being released. Heating phosphoric acid can also produce phosphate-containing compounds that can help create glass layers that act as protective barriers for underlying materials against heat and oxygen [19].

Phosphoric acid has three OH groups and oxygen atoms with lone electron pairs, which allow it to form extensive hydrogen-bonding networks with other compounds. Phosphoric acid can interact with cellulose through hydrogen bonding and, under suitable conditions, react with the hydroxyl groups of cellulose to form cellulose phosphate esters containing P–O–C bonds. Phosphorylated cellulose materials have thus been constructed, resulting in highly phosphorylated cellulose fibers with preserved structure and improved flame-retardant properties [20].

Creatinine (Figure 3B) is a naturally occurring nitrogenous organic acid produced in the body from the breakdown of creatine phosphate. Hence, it is a waste product of muscle energy metabolism and is primarily found in blood plasma, urine, and muscle tissue. Consequently, it is commonly used as a biomarker of kidney function. Creatine can be found in dietary protein, where it is converted to creatinine after cooking [21], and the latter could therefore potentially be extracted from food waste.

Creatinine is a small, water-soluble molecule containing both nitrogen and oxygen. These atoms allow creatinine to form hydrogen bonds with other molecules, including the hydroxyl groups in cellulose. Creatinine is also of interest as a potential flame retardant. When exposed to high temperatures, it may promote the formation of a protective char layer and release nitrogen-containing gases during thermal decomposition. These gases can help dilute flammable gases in the fire zone and thereby reduce combustion.

Hippuric acid (Figure 3C) is a naturally occurring metabolite commonly found in urine and widely used as a biomarker in toxicology and metabolism studies. Its structure contains both oxygen and nitrogen, which allow it to form hydrogen bonds with other molecules, including the hydroxyl groups in cellulose. Hippuric acid also has structural features that may be beneficial for flame retardancy. When exposed to high temperatures, its aromatic structure may promote the formation of a protective char layer, while its nitrogen-containing group may contribute to the release of non-flammable gases. Together, these effects could help reduce combustion.

Sodium succinate (Figure 3D) is a water-soluble salt of succinic acid that naturally occurs as part of the metabolism of animals and plants. It is widely used as a flavor enhancer and buffering agent and is commonly produced from fermentation-derived succinic acid. Its oxygen-containing groups can interact with the hydroxyl groups in cellulose. Sodium ions (Na^+) are also known to influence how cellulose decomposes when heated. Studies have shown that sodium-containing biomass can form more char than biomass from which the minerals have been removed, as sodium can promote char formation during heating [22]. Sodium succinate could therefore potentially improve the flame resistance of cellulose materials by promoting the formation of a protective char layer.

L-glutamine (Figure 3E) is a naturally occurring amino acid widely distributed in plant, animal, and microbial proteins, with high concentrations in foods such as meat, dairy products, and some vegetables. This amino acid could therefore potentially be obtained from food waste or produced by microbial fermentation.

L-glutamine contains both nitrogen and oxygen, which allow it to form hydrogen bonds with other molecules, including the hydroxyl groups in cellulose. L-glutamine is also of interest as a potential flame retardant. When exposed to high temperatures, it may release non-flammable

nitrogen-containing products and promote the formation of a protective char layer. These effects could help reduce combustion.

In the present study, all selected molecules were investigated by flame tests on the cellulose-based textiles cotton, viscose, and linen. To improve the flame-retardant properties, the fabrics were also phosphorylated with phosphoric acid in some cases before further treatment with any of the other selected compounds.

Metal ions were also investigated as a possible way to reduce the water solubility of the flame retardant and improve its durability. Copper(II) ions were used for this purpose, with the aim of strengthening the interactions between the different components and reducing leaching from the fabric.

The solubility and charge of the molecules at different pH values are important for their interactions with each other and with the fabric. These properties were therefore considered when selecting and combining the different compounds.

Finally, the most promising treatments were studied using TGA, MCC, and cone calorimetry to characterize their flame-retardant properties based on parameters such as decomposition temperature, mass loss, char formation, and heat release.

3 Experimental methods

3.1 Sample preparation

Tests were conducted on 100% cotton (300 g/m²), 100% linen (269 g/m²), and 100% viscose (108 g/m²). The fabrics were washed before use. 10×3 cm^2 pieces of each fabric were used, except for the cone calorimeter tests, where 10×10 cm^2 pieces were used.

A selection of compounds that can be found naturally was tested for their ability as flame retardants (FR). Aqueous solutions were prepared for each of the compounds, and pH was adjusted by adding hydrochloric acid or sodium hydroxide to get slightly acidic, neutral, and slightly alkaline pH. One of the pH values was the natural one without adjustment. The concentration of each solution varied based on the solubility of the compounds. The pieces of fabric were dipped for five minutes in the solutions and dried overnight. Table 1 shows data for the solutions used.

Table 1. *Data for sample preparation.*

Sample	Concentration (mol/L)	pH
Humic acid	0.015*	4; 7; 10
Sodium succinate	0.22	3; 6; 9
Mannitol	0.50	3; 5; 10
Hippuric acid	0.020	4; 7; 9
Creatinine	0.71	4; 8; 10
L-glutamine	2.3	5; 7; 9
Cysteine	0.10	4; 7; 10
Glycine	0.10	4; 7; 10
H_3PO_4	1.0	1
KH_2PO_4/K_2HPO_4 buffer	0.10	6
$CuNO_3{\cdot}6H_2O$	0.10	6

* Not completely dissolved.

As it is known that the combination of nitrogen and phosphorus enhances the FR ability, hippuric acid and creatinine, which contain nitrogen and showed the best results in the screening tests, were mixed with phosphoric acid, and fabrics were dipped in the solutions at pH 4 and a 1:1 molar ratio to be comparable with the tests on the individual solutions.

Different ways to make the FR coating less water-soluble were investigated by using copper(II) nitrate. Copper(II) nitrate was chosen because of its blue color and not too strong interaction with phosphate to displace the nitrogen source from the system. In this case, creatinine was used as the nitrogen source, as it showed the overall best performance in the screening tests.

As a first attempt, the fabric was placed in a 0.1 M solution of creatinine and phosphate buffer at pH 6, and after five minutes, copper(II) nitrate with a molar ratio of 1:1:1 was added dropwise

to the solution under stirring for two hours, and a slurry was formed. The precipitate did not bind very strongly to the fabric and did not improve the FR ability compared to only creatinine and phosphate. When the slurry was pressed into the fabric, the result was better.

In the most successful attempt, the fabrics were put in a 1 M aqueous solution of phosphoric acid for one hour at 80°C and then dried overnight. Thereafter, the fabrics were dipped in a solution of creatinine and copper(II) nitrate in a 1:1 molar ratio and again dried overnight.

The blue color confirmed the presence of copper(II) ions on the fabric, a pH change confirmed the presence of phosphoric acid, and UV-Vis measurements were used to confirm the presence of creatinine.

To evaluate the durability of the FR coating, the dried samples were dipped in pure water for ten seconds, and after drying, tests of the FR ability were performed on the samples and compared to the results before the dipping. The mixture that showed the best results in MCC was selected for cone calorimetry studies.

3.2 Screening tests

The FR-treated samples were mounted on a rack inside a fume hood and ignited with a gas lighter by touching the bottom of each sample. If the sample ignited, the flame was removed, and the samples were allowed to burn. If the samples did not ignite within ten seconds or if they self-extinguished, they were selected for further investigation.

3.3. Microscale Combustion Calorimeter (MCC)

The Microscale Combustion Calorimeter (MCC, Fire Testing Technology (FTT), East Grinstead, UK) was used to measure the burning properties of the samples. Prior to testing, all samples were conditioned under ambient laboratory conditions. Approximately 5-10 mg of each sample was accurately weighed and placed in the ceramic sample holder. The measurements were carried out under a nitrogen atmosphere during thermal decomposition, followed by the complete combustion of the evolved volatile gases in an oxygen-rich environment, in accordance with the standard MCC procedure [23]. The samples were heated from 150 to 750 °C at a constant heating rate of 1 °C s^{-1} (60 °C min^{-1}). The heat release rate (HRR), peak heat release rate (pHRR), total heat release (THR), and heat release capacity (HRC) were obtained directly from the instrument software. Two measurements were made for each sample, and if the values showed large deviations from each other, a third measurement was conducted.

3.4 Thermal Gravimetric Analysis (TGA)

The thermal stability of the untreated and treated samples was investigated using a thermogravimetric analyzer (TGA, PerkinElmer, USA). Approximately 5-10 mg of each sample was placed in an alumina crucible and heated from 30 to 600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere with a gas flow rate of 50 mL min^{-1}. The weight-loss curves were recorded as a function of temperature. The onset degradation temperature,

maximum degradation temperature, and residual char yield at 600 °C were determined from the obtained thermograms.

3.5 Cone Calorimetry

The fire performance of the samples was also evaluated using a cone calorimeter (NETZSCH TAURUS Instruments GmbH) in accordance with ISO 5660-1 [24] . The specimens were prepared with dimensions of 100×100 mm^2 and mounted horizontally in a specimen holder. The samples were exposed to an external heat flux of 35 kW m^{-2} and 50 kW m^{-2}. During the test, parameters such as time to ignition (TTI), heat release rate (HRR), peak heat release rate (pHRR) and total smoke production (TSP) were recorded.

4 Results and Discussion

4.1 Screening tests

The results of the screening tests were very varied. Some of the compounds had too low solubility in water to be useful; others did not bind very well to the fabric, resulting in a dust layer and poor FR ability. Other compounds burned well, thus had poor FR ability. In most cases, low pH gave better results than high pH. In general, low pH is expected to be better because it enhances the charring of the fabric, but in the case of sodium succinate, the high pH gave the best result. Examples from the screening tests are shown in Figures 4 and 5.

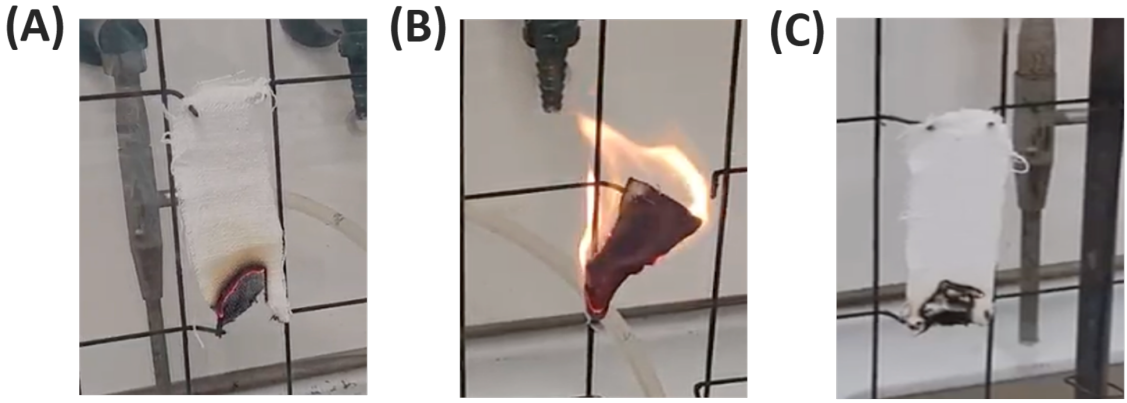

Figure 4. *Fabrics treated with potential FR compounds. (A) Hippuric acid on linen, pH 7, two minutes after exposure to flame; (B) Mannitol on cotton, pH 3, one minute after exposure to flame; (C) Sodium succinate on viscose, at pH 9, two minutes after exposure to flame.*

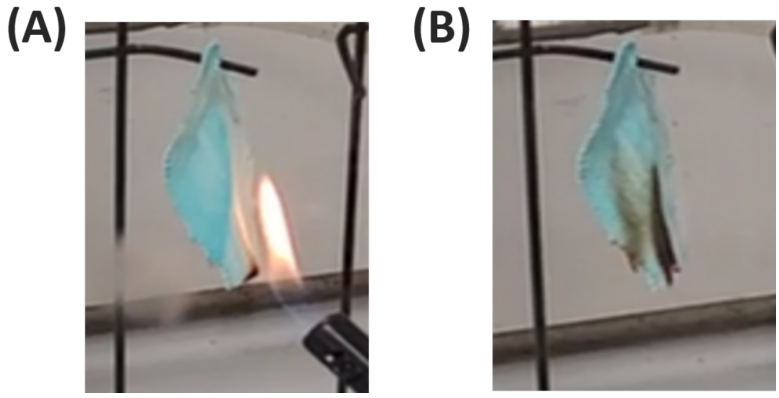

Figure 5. *Cotton treated with a slurry of creatinine, phosphoric acid, and copper(II) ions. (A) at ignition; (B) after approximately 15 s.*

The samples that passed the test were self-extinguishing or had a very slow progression of the flame front. Interestingly, hippuric acid performed very well considering the small amount absorbed on the fabrics. Table 2 shows the amount of FR that was absorbed on the different fabrics. The results were consistent for all duplicates of samples.

Table 2. *Amount (%) of FR absorbed by the different fabrics.*

Flame retardant	Cotton	Viscose	Linen
Creatinine	20	22	20
Phosphate	17	23	15
Creatinine-Phosphate	25	34	25
Creatinine-Cu-Phosphate	28	30	26
Hippuric acid	5	6	5
Hippuric-Phosphate	7	6	15
Succinate	18	22	15

4.2 Microscale Combustion Calorimeter (MCC)

Microscale combustion calorimetry (MCC) was performed on the best-performing samples after the screening test. Consequently, cotton, linen, and viscose fabrics treated with creatinine, hippuric acid, L-glutamine, and sodium succinate were investigated with MCC. Cotton, linen, and viscose fabrics phosphorylated with phosphoric acid and further treated with creatinine, or hippuric acid, and, in the case of cotton and viscose, additionally with Cu(II) ions, were also analyzed.

Table 3 summarizes the average values from the MCC measurements, while representative heat-release rate curves are shown in Figures 6–13. The results show that the tested compounds and their combinations improved the flame-retardant performance of the different fabrics. Among the individual treatments, creatinine and phosphoric acid resulted in the largest reductions in pHRR, THR, and HRC, particularly for viscose and linen.

Table 3. *MCC results for untreated and treated cotton, viscose, and linen. With a few exceptions, deviations from the mean value are between 1 and 15%.*

Sample	pHRR (W/g)	THR (kJ/g)	HRC (J/gK)	pTemp (°C)	Char (%)
Cotton	312	13.2	318	377	5
Cot-Hip	110	6.2	112	313	25
Cot-Glu	139	7.2	142	356	18
Cot-Succ	100	4.5	100	331	29
Cot-Cre	67	5.4	68	372	25
Cot-Fos	75	2.2	74	322	39
Cot-Hip-Fos	124	5.0	124	310	24
Cot-Cre-Fos	40	1.5	40	294	44
Cot-Cre-Fos-Cu	69	2.8	69	292	30
Cot-Cre-Fos-Cu-S*	66	2.9	74	304	32
Cot-Cre-Fos-Cu-D*	130	6.9	131	338	29
Viscose	243	12.0	248	355	10
Vis-Hip	109	6.5	111	322	17
Vis-Glu	81	4.9	82	323	25
Vis-Succ	66	3.7	65	301	32
Vis-Cre	27	3.0	27	279	31
Vis-Fos	26	1.2	27	293	43
Vis-Hip-Fos	108	5.0	107	276	25
Vis-Cre-Fos	18	1.0	18	255	36
Vis-Cre-Fos-Cu	60	3.0	61	312	35
Vis-Cre-Fos-Cu-D*	215	4.6	224	293	16
Linen	213	9.8	216	375	9
Lin-Hip	161	7.8	164	344	10
Lin-Glu	127	6.1	129	350	23
Lin-Succ	99	4.0	99	329	29
Lin-Cre	26	3.4	24	345	27
Lin-Fos	39	1.5	39	309	43
Lin-Hip-Fos	123	4.9	123	308	10
Lin-Cre-Fos	31	1.3	31	276	40

*S = Slurry pressed into the fabric; D = Dipped in water for ten seconds

A comparison between cotton treated with the five potential flame retardants creatinine (Cot-Cre), hippuric acid (Cot-Hip), L-glutamine (Cot-Glu), sodium succinate (Cot-Succ), and phosphoric acid (Cot-Fos) is shown in the heat release curves in Figure 6.

Here, it can be observed that all five compounds cause an improvement in the fire resistance of cotton. The samples start to degrade and release heat at lower temperatures than the untreated cotton.

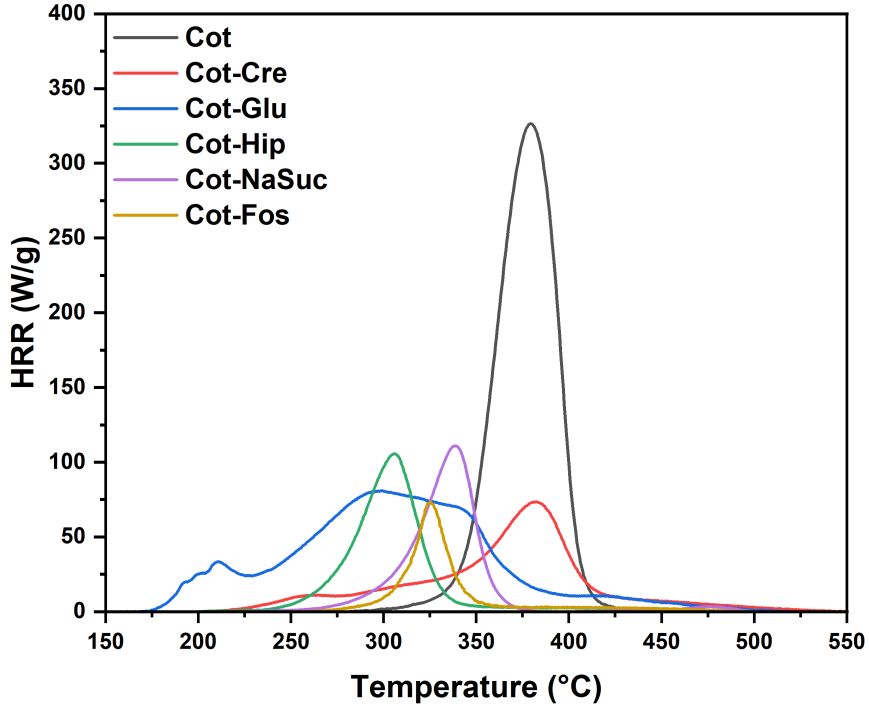

Figure 6. *MCC heat release rate (HRR) curves of untreated cotton and cotton treated with five potential flame retardants: creatinine (Cot-Cre), hippuric acid (Cot-Hip), L-glutamine (Cot-Glu), sodium succinate (Cot-Succ), and phosphoric acid (Cot-Fos).*

Similar trends were observed for the linen and viscose fabrics, with slightly better overall performance compared with cotton. The corresponding results for viscose and linen are presented in Figures 7 and 8, respectively.

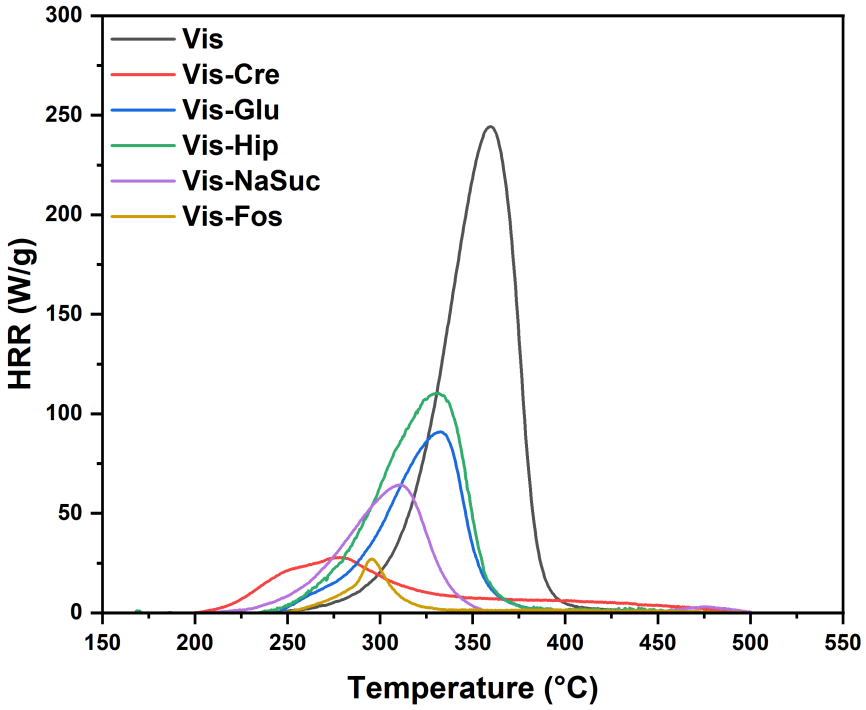

Figure 7. *Heat release rate (HRR) curves of untreated viscose and viscose treated with five potential flame retardants: creatinine (Vis-Cre), hippuric acid (Vis-Hip), L-glutamine (Vis-Glu), sodium succinate (Vis-Succ), and phosphoric acid (Vis-Fos).*

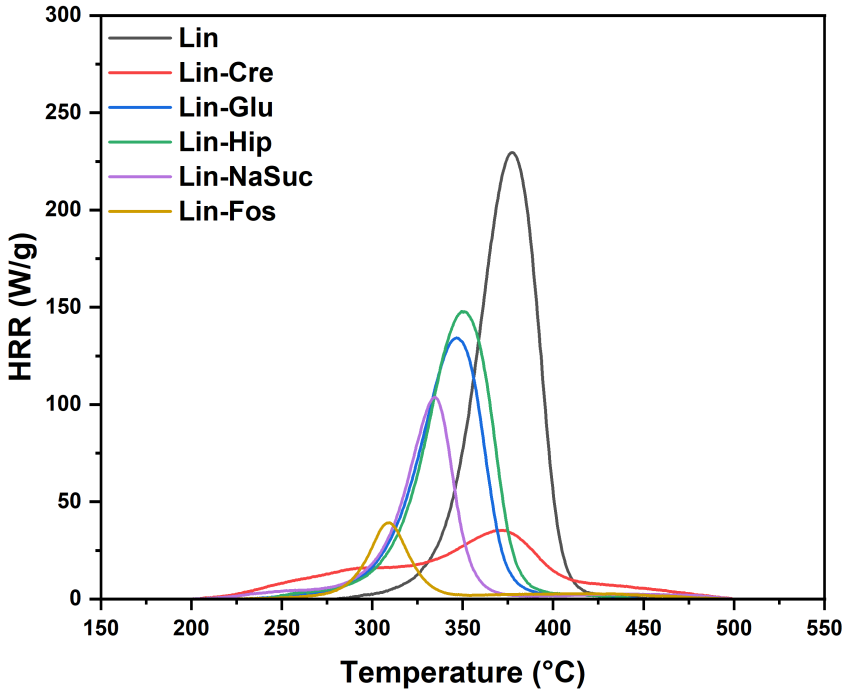

Figure 8. *Heat release rate (HRR) curves of untreated linen and linen treated with five potential flame retardants: creatinine (Lin-Cre), hippuric acid (Lin-Hip), L-glutamine (Lin-Glu), sodium succinate (Lin-Succ), and phosphoric acid (Lin-Fos).*

To take advantage of the well-known nitrogen-phosphorus (N-P) synergism [8-9], nitrogen-containing creatinine, which exhibited the lowest MCC values, was mixed with phosphoric acid to improve FR efficiency. Phosphorylation with phosphoric acid introduces phosphorus-containing groups into the material, which can promote char formation when the material is heated. During thermal decomposition, phosphate groups in the treated fabric decompose into phosphoric or polyphosphoric acid, which catalyze dehydration and promote char formation.

In this way, the material dehydrates and forms a carbon-rich char layer, which acts like a protective barrier against heat transfer and oxygen access to the underlying fibers. Creatinine, in turn, is a nitrogen-rich compound that can contribute to flame retardancy by generating non-flammable gases during thermal degradation, thereby diluting the oxygen concentration around the burning zone and slowing the combustion process. The combination of phosphorylation and creatinine treatment had the most pronounced effect in terms of fire resistance for viscose compared with cotton and linen, as shown in Figure 9.

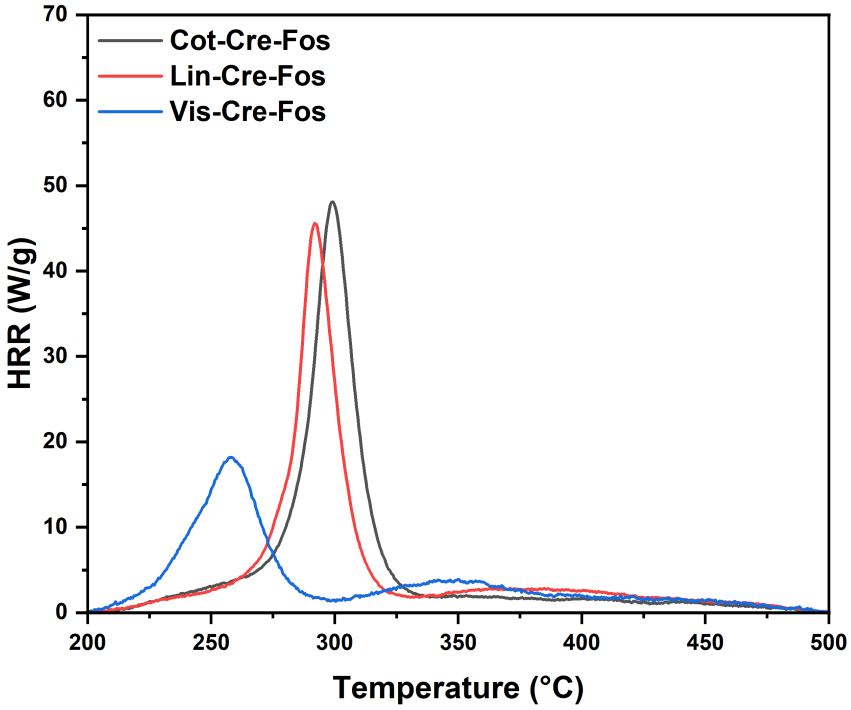

Figure 9. *MCC heat release curves for cotton (Cot), linen (Lin), and viscose (Vis) treated with a mixture of creatinine (Cre) and phosphoric acid (Fos).*

For comparison, the heat release rate curves for untreated cotton and cotton subjected to various treatments with phosphoric acid, creatinine, and Cu are shown in Figure 10.

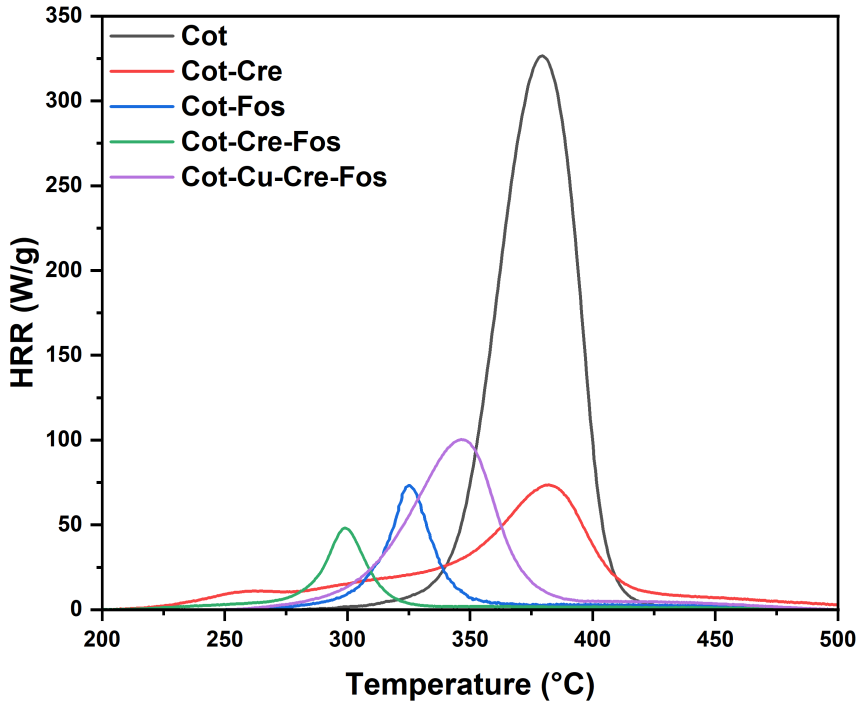

Figure 10. *MCC heat release curves for untreated cotton (Cot), cotton treated with creatinine (Cre), phosphoric acid (Fos), a mixture of creatinine and phosphoric acid (Cre-Fos), and a mixture of creatinine, phosphoric acid and copper(II) ions (Cu-Cre-Fos).*

Cotton treated with creatinine or phosphoric acid individually (Cot-Cre, Cot-Fos) reduced the flammability parameters significantly compared to untreated cotton (Cot), indicating an improvement in fire resistance; the HRC and pHRR dropped almost 80%, and the amount of char left increased considerably. By combining phosphorylation with creatinine treatment (Cot-Cre-Fos), a further improvement could be observed as a reduction in the HRC and pHRR of close to 90% and more than 40% residual char. THR is also significantly reduced in all three of the treated samples compared to untreated cotton. However, the addition of copper(II) ions did not result in a further improvement in the flame-retardant performance. Although Cot-Cre-Fos-Cu still showed considerably lower pHRR and HRC than untreated cotton, both pHRR and THR were higher than for Cot-Cre-Fos. This may be related to differences in the treatment conditions and interactions of Cu^{2+} with the phosphate groups, which could influence the amount or availability of phosphorus in the fabric.

Viscose and linen samples show the same trend of peak HRR and THR as cotton, see Figures 11 and 12. Treatment with creatinine or phosphoric acid individually (Vis-Cre, Vis-Fos, Lin-Cre, Lin-Fos) reduced HRC and pHRR by 80% or more and left 25-40% char. The combination of creatinine and phosphoric acid (Vis-Cre-Fos, Lin-Cre-Fos) provides further fire-resistance improvement, with THR decreasing to approximately 1 kJ/g. As with cotton, introducing Cu into the treatment of viscose resulted in a slightly lower reduction in HRC and pHRR.

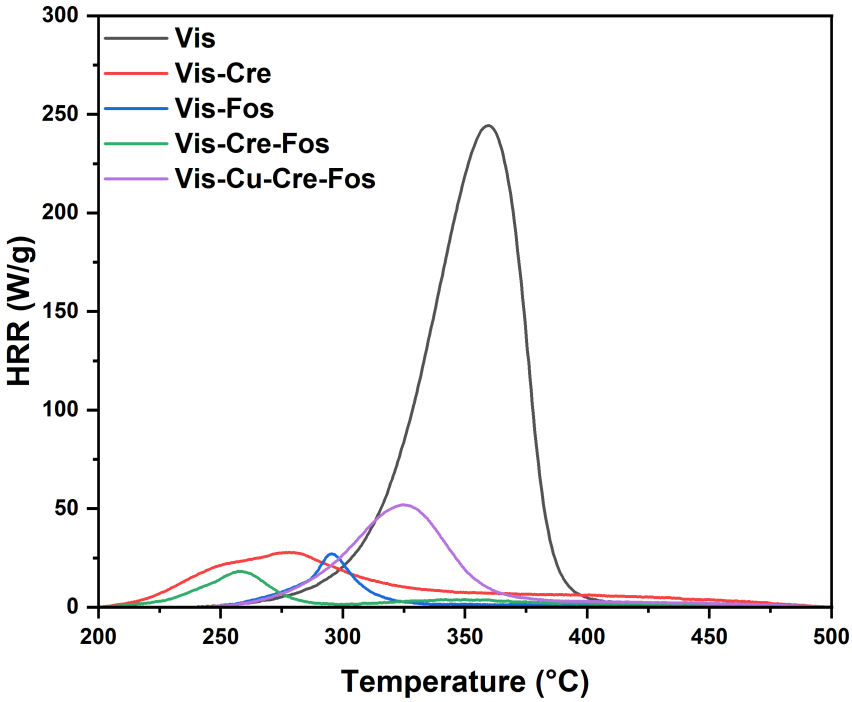

Figure 11. *MCC heat release curves for untreated viscose (Vis), viscose treated with creatinine (Cre), phosphoric acid (Fos), a mixture of creatinine and phosphoric acid (Cre-Fos), and a mixture of creatinine, phosphoric acid, and copper(II) ions (Cu-Cre-Fos).*

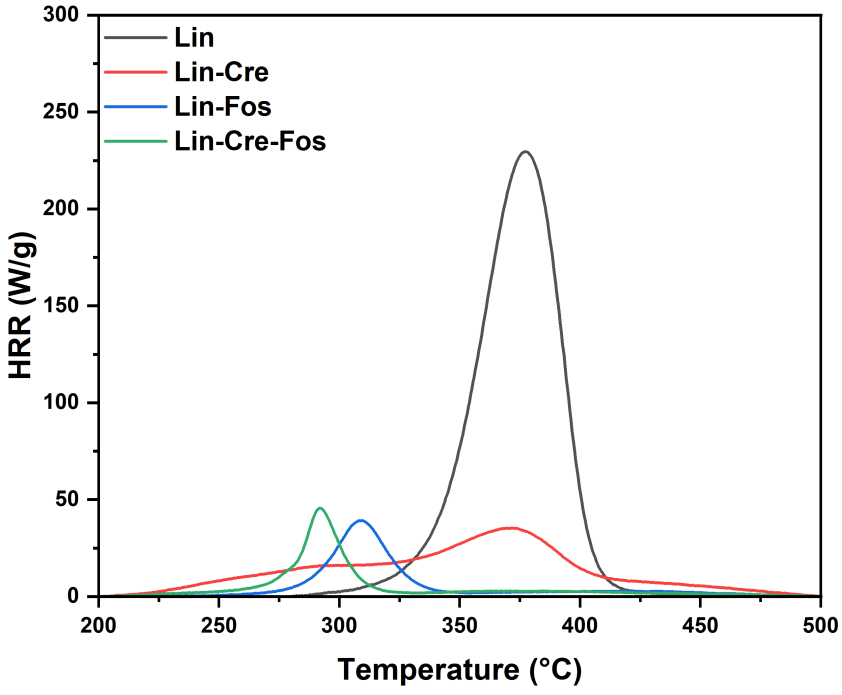

Figure 12. *MCC heat release curves for untreated linen (Lin), linen treated with creatinine (Cre), phosphoric acid (Fos), and a mixture of creatinine and phosphoric acid (Cre-Fos).*

To investigate the fabric's resistance to water, a leaching test was performed on cotton and viscose treated with phosphoric acid, creatinine, and Cu (Figure 13). After dipping the treated cotton in water, pHRR and THR increased compared to before dipping, but remained low compared to untreated cotton. For viscose, pHRR reached the same level as untreated viscose, whereas THR only reached 50% of the value for untreated viscose. This indicates that cotton retained more FR than viscose after the dipping in water.

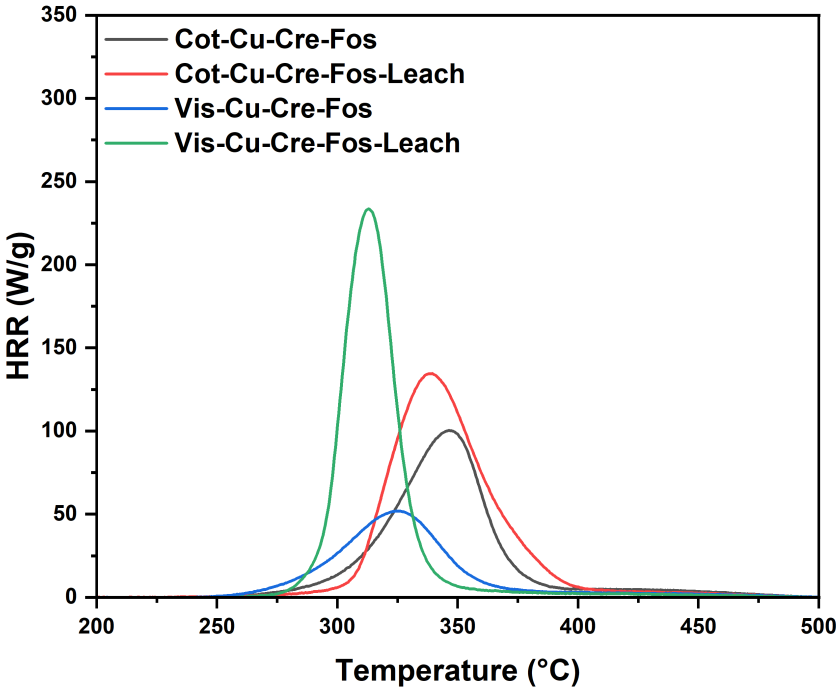

Figure 13. *MCC heat release curves for cotton (Cot) and viscose (Vis) treated with a mixture of creatinine and phosphoric acid (Cre-Fos) before and after dipping in water (Leach).*

4.3 Thermal Gravimetric Analysis (TGA)

Figure 14 shows the degradation of cotton treated with creatinine and/or phosphoric acid in inert atmosphere compared to untreated cotton.

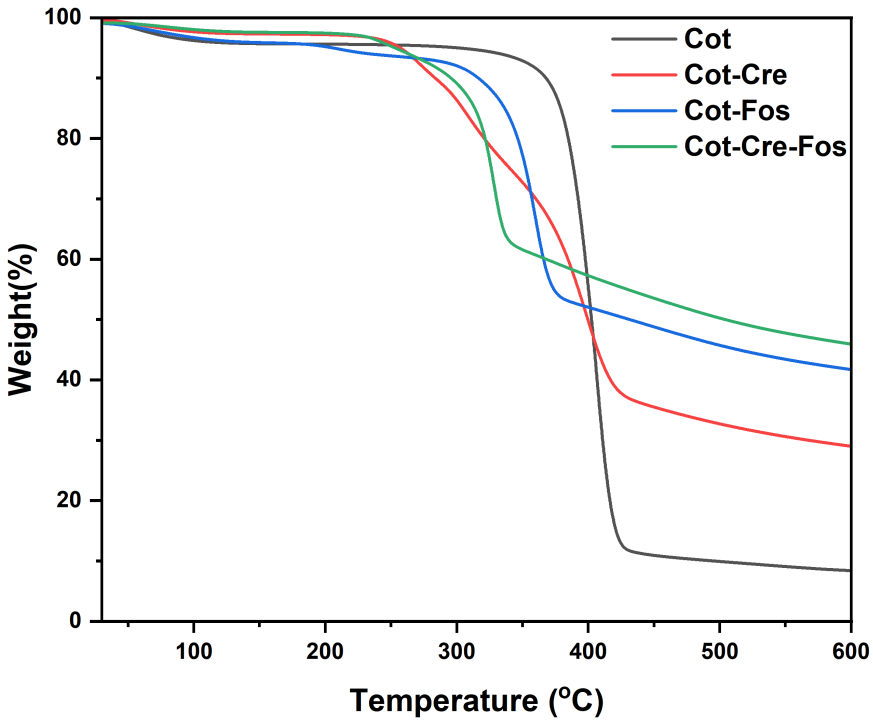

Figure 14. *TGA thermograms of untreated cotton (Cot) and cotton treated with creatinine (Cre), phosphoric acid (Fos), and a mixture of creatinine and phosphoric acid (Cre-Fos).*

Samples containing creatinine start to degrade at approximately 250°C, which is lower than the degradation temperature of untreated cotton. As can be seen in MCC, the degradation occurs over a wide temperature range. Samples containing phosphoric acid begin to degrade slightly at approximately 200°C, but most of the degradation occurs above 300°C. The initial small degradation is consistent with water release during polymerization of the phosphate groups, which causes early charring of the cotton surface and prevents further degradation by forming a protective coating.

Samples containing both creatinine and phosphoric acid show enhanced behavior, meaning that both dilution of pyrolysis gases and charring of the cotton occur before the cotton reaches a temperature at which it can ignite. The charring effect is more efficient than gas formation at reducing sample degradation, leaving approximately 50% of the mass at 600°C for samples containing phosphoric acid, compared to 30% for samples containing only creatinine. As can be seen in Figures 15 and 16, the same pattern repeats also on viscose and linen.

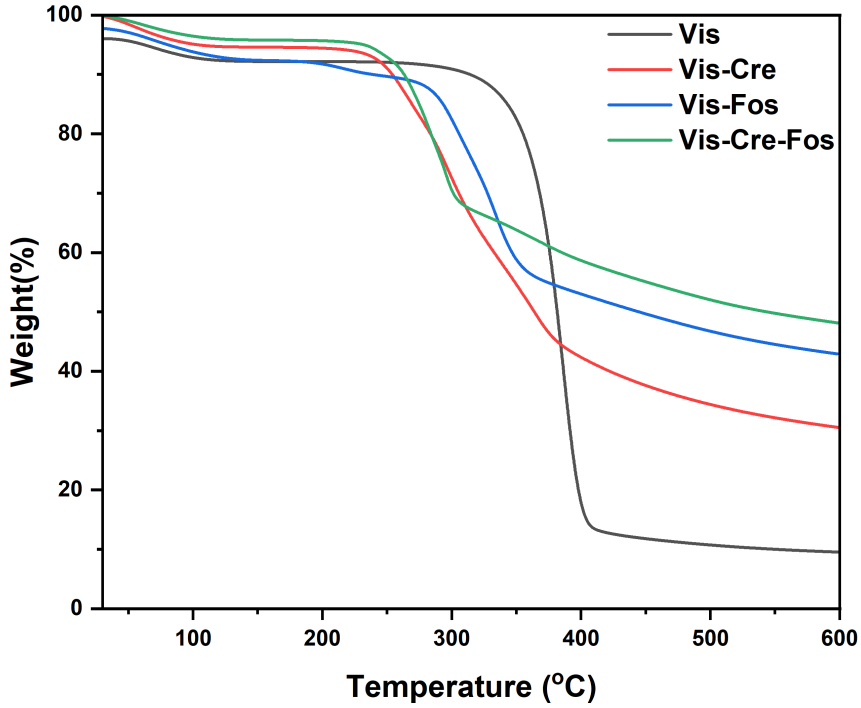

Figure 15. *TGA thermograms of untreated viscose (Vis) and viscose treated with creatinine (Cre), phosphoric acid (Fos), and a mixture of creatinine and phosphoric acid (Cre-Fos).*

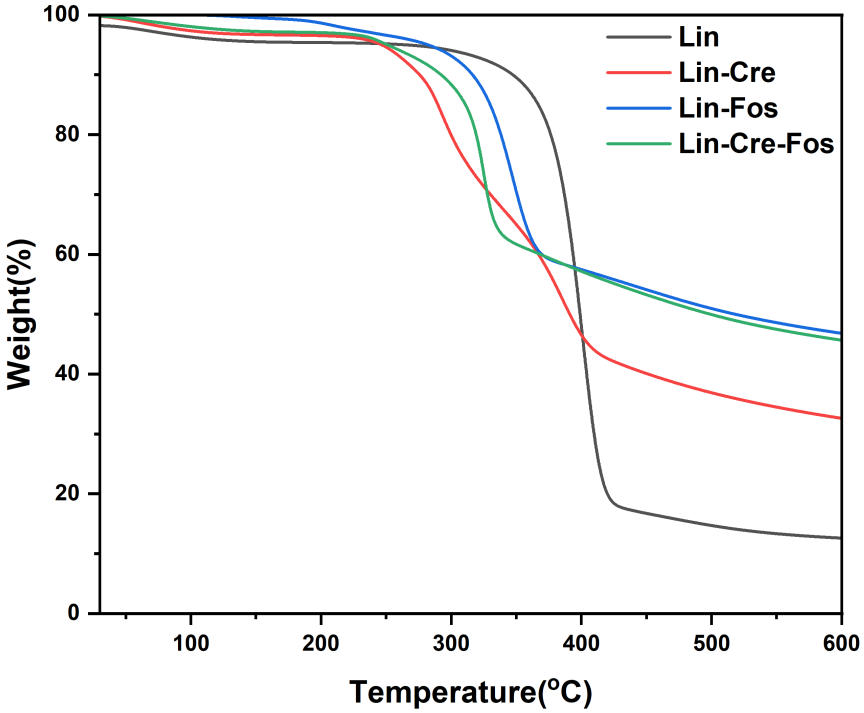

Figure 16. *TGA thermograms of untreated linen (Lin) and linen treated with creatinine (Cre), phosphoric acid (Fos), and a mixture of creatinine and phosphoric acid (Cre-Fos).*

Samples containing copper(II) ions, creatinine, and phosphoric acid exhibit behavior similar to that of samples without copper ions, although they degrade to a greater extent. After dipping in water, the behavior becomes more similar to untreated cotton, although more mass is retained at 600°C, as shown in Figure 17.

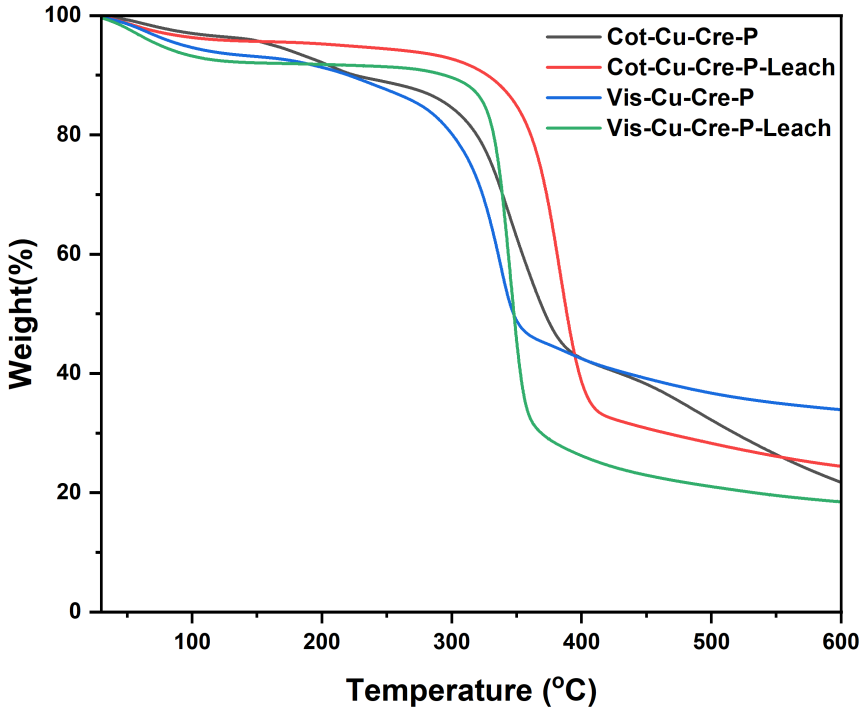

Figure 17. *TGA curves of samples containing copper(II) ions as well as creatinine and phosphoric acid, before and after water dipping.*

4.4 Cone Calorimetry

Cone calorimetry was performed on fabrics treated with the best-performing mixture, consisting of creatinine and phosphoric acid mixed in a 1:1 ratio at pH 4. Table 4 shows the amount of FR adsorbed onto the fabric. The amounts are consistent with those for the smaller-sized fabrics in Table 2 (section 4.1).

Table 4. *Amount of creatinine phosphate adsorbed on different fabrics.*

Sample	Mass absorbed (%)
Cotton	25
Viscose	34
Linen	27

Figure 18 shows the heat release rate curves for the samples at a heat flux of 35 kW/m^2.
Figure 19 shows a close up of the treated samples and Table 5 summarizes important data.

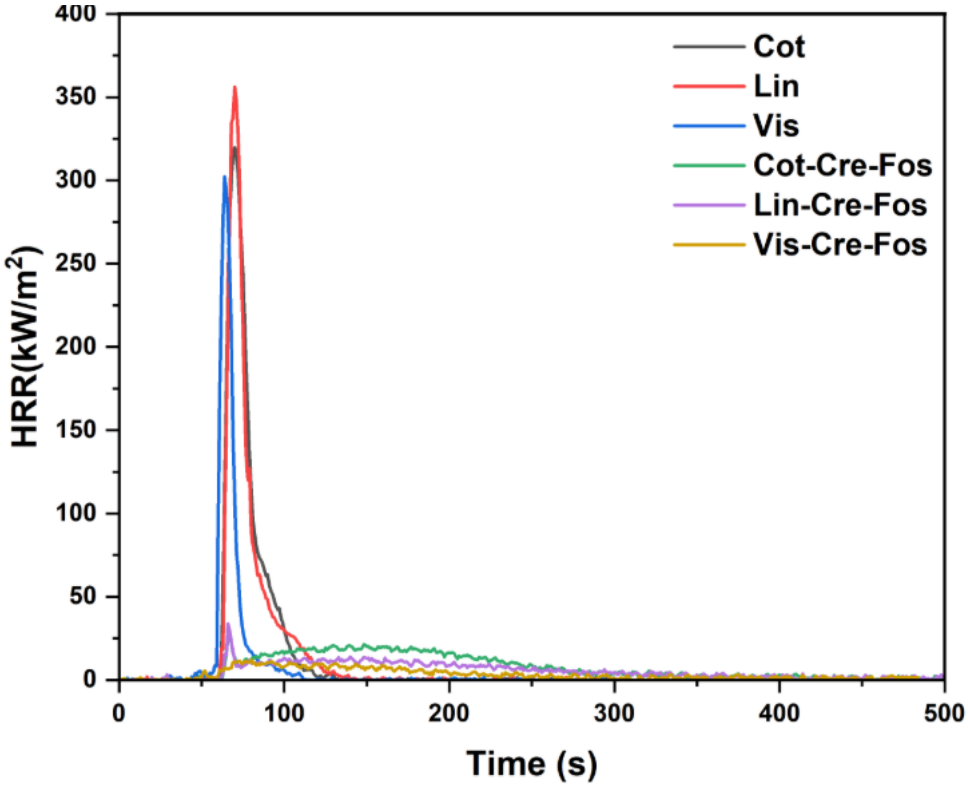

Figure 18. *Heat release rate curves for fabrics treated with creatinine and phosphate compared to untreated fabrics. Heat flux 35 kW/m².*

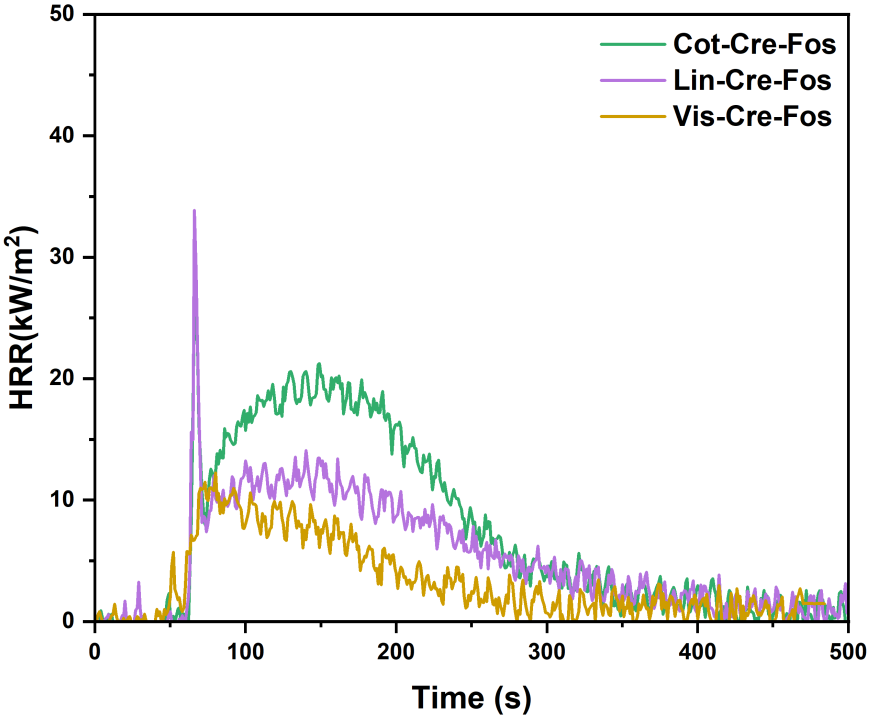

Figure 19. *Heat release rate curves for fabrics treated with creatinine and phosphate. Heat flux 35 kW/m².*

Table 5. *Cone calorimeter results for fabrics treated with creatinine and phosphate at 35 kW/m², compared with untreated fabrics.*

Sample	THR (MJ/m²)	pHRR (kW/m²)	TSP (m²)	Remaining mass (%)
Cotton	5.5	315	3.0	0
Cotton-Crea-PO_4	3.7	21.6	61	21
Linen	5.4	326	10.0	0
Linen-Crea-PO_4	3.5	15.9	68	25
Viscose	3.0	206	2.0	0
Viscose-Crea-PO_4	1.8	10.9	38	36

Both THR and pHRR are significantly reduced in the treated samples compared with the untreated samples. The trend is similar to the MCC data, where viscose is slightly better protected than linen and cotton. Possibly, this can be explained by the higher amount of FR adsorbed on viscose. None of the treated samples ignited, but the fabric charred and produced substantial smoke; see Figure 20 for the sample residues after the experiment.

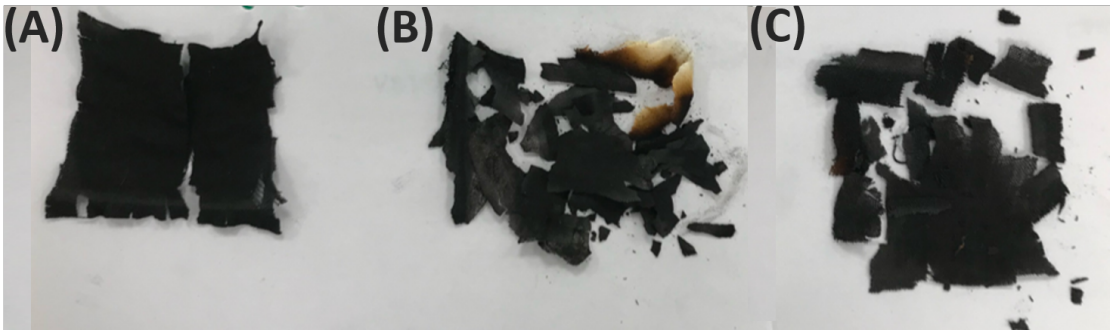

Figure 20*. Sample residues after cone calorimetry experiments at 35 kW/m². (A) Cotton; (B) Viscose; (C) Linen.*

The cone calorimeter experiments were repeated at a heat flux of 50 kW/m² with similar results. The samples did not ignite but charred and produced smoke (see Table 6 and Figure 21), and the remaining sample mass was lower.

Table 6. *Cone calorimeter results for fabrics treated with creatinine and phosphate at 50 kW/m², compared with untreated fabrics.*

Sample	THR (MJ/m²)	pHRR (kW/m²)	TSP (m²)	Remaining mass (%)
Cotton	5.4	368.5	5	0
Cotton-Crea-PO_4	4.2	24.2	58	17
Linen	5.9	283.7	7	0
Linen-Crea-PO_4	3.3	20.7	97	15
Viscose	2.1	101.5	0	0
Viscose-Crea-PO_4	2.6	18.8	65	23

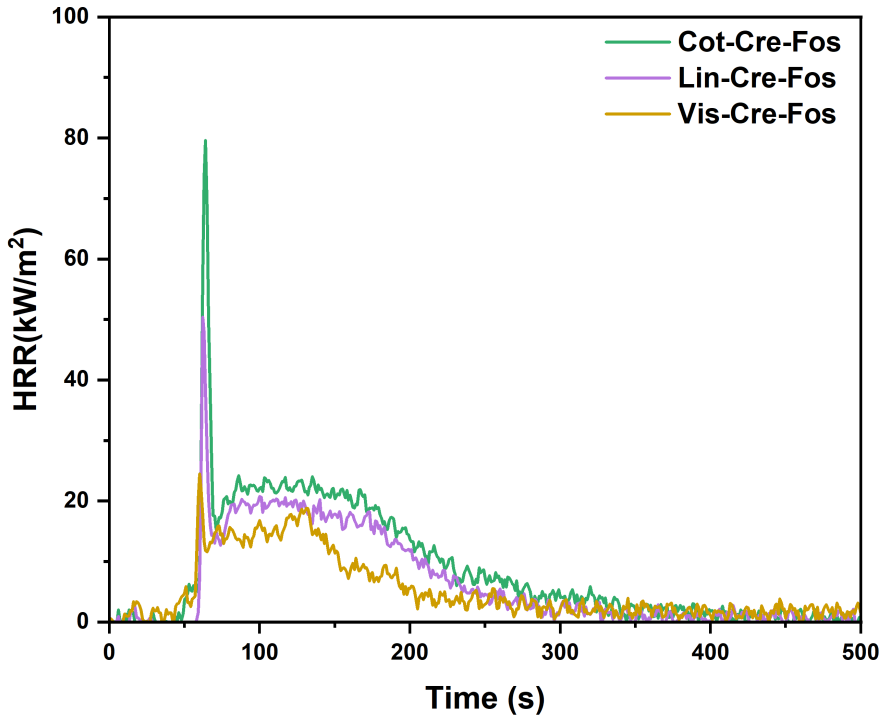

Figure 21. *Heat release rate curves for fabrics treated with creatinine and phosphate. Heat flux 50 kW/m².*

5 Conclusions

In this project, several naturally occurring compounds were investigated as potential flame retardants for cellulose-based fabrics. The initial screening showed that the flame-retardant performance strongly depended on the type of compound, its concentration, pH, and its ability to remain on the fabric. Among the compounds investigated, creatinine showed the most promising overall performance, while sodium succinate also considerably improved the flame resistance of the fabrics.

The MCC results showed a considerable reduction in heat release after treatment of cotton, viscose, and linen. Among the investigated compounds, creatinine was particularly effective and considerably reduced pHRR, THR, and HRC for all three fabrics. Combining creatinine with phosphorylation resulted in a further improvement in flame-retardant performance. The strongest effect was observed for viscose, where the pHRR decreased from 231 W/g for untreated viscose to 18 W/g after the combined treatment. Cotton and linen also showed considerable improvements. Overall, viscose showed the strongest response to the treatments, followed by linen and cotton.

The TGA results showed that the treatments changed the thermal degradation behaviour of the fabrics. The treated samples generally started to degrade at lower temperatures but retained more mass at higher temperatures. This indicates that the treatments promote char formation during thermal degradation, which reduces the amount of material available for further combustion.

The cone calorimetry experiments further confirmed the improvement in fire behaviour on larger samples and under higher heat exposure. The treated fabrics showed lower heat release compared with the untreated fabrics and retained more material after the experiments. The residues after the tests also showed considerable char formation, in agreement with the behaviour observed in MCC and TGA.

The addition of copper(II) ions did not result in a further improvement in flame-retardant performance. In addition, after dipping the treated samples in water, their behavior became more similar to that of the untreated fabrics. This shows that although the developed treatments can considerably improve the fire behavior of cellulose-based fabrics, their water resistance still needs improvement.

Overall, the results show that creatinine is a promising naturally occurring compound for improving the flame resistance of cellulose-based textiles, particularly when combined with phosphorylation. The results also show that treatment effectiveness depends on the type of cellulose-based fabric, with viscose showing the best overall response in the present study.
Overall, viscose showed the best response to the treatments, followed by linen and cotton. The results demonstrate that combinations of naturally occurring nitrogen- and phosphorus-containing compounds can provide a promising route towards safer flame-retardant treatments for cellulose-based textiles. However, the durability of the treatments, particularly towards water, still needs further improvement before practical application.

6 Recommendations

Based on the results obtained in this project, further development should mainly focus on the creatinine-phosphorylation treatment, as this combination showed the best overall flame-retardant performance. Viscose showed a particularly strong response to the treatment, although considerable improvements were also obtained for cotton and linen.

One of the main challenges is the resistance of the treatment to water. The results after dipping in water showed a clear loss in flame-retardant performance. Therefore, improving the binding of the flame-retardant compounds to the cellulose fibers should be given priority. The addition of copper(II) ions was investigated as one possible way to improve this, but it did not provide the expected improvement under the conditions used in this project. Other approaches to improve the durability of the treatment should therefore be considered.

The treatment conditions should also be further optimized. The concentration and ratio of the compounds, treatment temperature, pH, and treatment time can be varied to determine whether similar or better flame-retardant performance can be achieved with a lower amount of chemicals. This would also be beneficial from an environmental and practical point of view.

7 Future work

Future work should focus on improving the water durability of the creatinine-phosphorylation treatment, which showed the best overall flame-retardant performance in this study. Since the addition of copper(II) ions did not improve the performance after water exposure, other approaches to strengthen the interaction between creatinine, phosphate groups, and cellulose should be investigated. The treatment conditions and chemical ratios should also be optimized to maintain the low heat release while improving durability. Finally, the most promising durable formulation should be evaluated by cone calorimetry and larger-scale fire tests.

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This project was funded 2025 by the organisations below

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