

Cellulose Flame-retardant Film using Lettuce Residue as Raw Material

João Câmara¹, Sofia S. F. Santos², Filip Delden³, David Aparício⁴,
Isabel Martins⁵




¹Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (up201805368@fe.up.pt) ORCID [0000-0002-9296-4573](https://orcid.org/0000-0002-9296-4573); ²Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (up201709441@fe.up.pt) ORCID [0000-0002-4743-8988](https://orcid.org/0000-0002-4743-8988); ³Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (up202101980@fe.up.pt) ORCID [0000-0002-4988-0876](https://orcid.org/0000-0002-4988-0876); ⁴Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (up202101831@fe.up.pt) ORCID [0000-0003-3312-8337](https://orcid.org/0000-0003-3312-8337); ⁵LSRE-LCM-Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; ALICE-Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal (isa@fe.up.pt) ORCID [0000-0003-0897-8807](https://orcid.org/0000-0003-0897-8807)

Abstract

This study had the objective of developing a product having as raw material the residual parts of lettuce, which are its roots and residual leaves. To this effect, a thought experiment was performed in order to create a flame-retardant cellulose film using a green-sourced, vegan, and biodegradable raw material. This product was designed with the goal of protecting furniture, however, the product could also be effectively applied in paintings and other cellulose-based materials. A production line was proposed, and through economic analysis, it was determined that the manufacture of this product is profitable, with a production price of 2.15€ per unit (m²) and a retail price of 6€ per unit (m²). This flame-retardant film is unique compared to the others on the market, which are mainly plastic-based, since it is developed from a biodegradable material, making it a sustainable option for a zero-carbon economy. This film has a fire delay of approximately 4.5 minutes when exposed to fire.

Author Keywords. Lettuce. Cellulose Nano-fibres. Flame-retardant. Cellulose Film. Montmorillonite.

Type: Research Article

 Open Access  Peer Reviewed  CC BY

1. Introduction

Necessity creates business and functionality extends it. The value provided by the developed product comes from its flame-retardant properties, while its functionality is enhanced by the invisibility of the film.

While the flame-retardant film was never actually created, the final product, should it ever be manufactured, would be able to protect wood, artwork, and valuables. Its fire protection properties protect the piece from heat damage without affecting its appearance as it is a transparent film (Carosio et al. 2016; Dhali et al. 2021; Barhoum et al. 2019). The developed product is not the first flame-retardant film on the market; however, it has unique features, its biodegradability and sustainable raw material.

2. Raw Material

2.1. Characterisation

The raw material used to develop this idea is lettuce waste, namely the roots and residual leaves. As this material is a residue usually left in the soil and not being repurposed as a raw material for any kind of production, it's generally cheap to obtain. The only cost it would project into the business would be the labour to pull the roots out of the soil and transport them to the production centre.

Some advantages of this raw material are that it's a green, vegan, biodegradable alternative material that is of a non-polluting origin, unlike its plastic-based counterparts (Zhang et al. 2019; López et al. 2014). From the lettuce extract, it was decided to use them to extract cellulose fibres.

Besides cellulose, lettuce's main compounds of interest are sugars, organic acids, phenolic compounds, folates and carotenoids. According to López et al. (2014), in various kinds of lettuce, from a wide range of components, the ones that stand out the most are *Vitamin C*, *Nitrates*, *Caffeic Acid*, *Chlorophyll α* , *Quinic Acid* and *β -Carotene*.

Regarding the cellulose content in the lettuce, its concentration is not very well defined since there are different methods to extract it. The cellulose extraction technique used for this work, which was initially adapted in a laboratory scale from Zhang et al. (2019), conferred a yield of around 20% of the circa 5% of the dry lettuce matter since circa 95% of lettuce is water (LSRE - LCM 2021).

Throughout the initial analysis of lettuce residue as raw material, some components seem to exist in sufficient quantities to make it possible to develop a product. However, cellulose was chosen not only because of its significant concentration but also because of its versatility in integrating several different products.

2.2. Origin and current uses of lettuce residue

Worldwide, taking into account statistics on lettuce production data from 2017, China is the largest lettuce producer globally, followed by the United States, India and then Spain. In gross yield, China produced 151,608,818 tons of lettuce in 2017, the USA 3,836,820 tons, India 1,090,770 tons, and Spain 976,112 tons. Considering data from Shatilov, Razin, and Ivanova (2019), it is also mentioned that Spain is where the largest export of lettuce occurs (circa 76,1902.5 tons), followed by the United States (circa 50,8124.1 tons). In Portugal, until 2020, 61,976 tons of lettuce were produced in 2,452 hectares (INE 2021).

It was also noticed that in Portugal, the residual part of the lettuce is kept in the soil to act as a natural fertiliser. As far as the authors know, the average weight of fully-grown lettuce is 700 g, and the average weight of the roots and wasted leaves is 160g, so in conclusion, 22.9% of the lettuce is wasted. This means that, in Portugal, per year, there are 14,192.5 tons of residue (using the data from 2020) (INE 2021).

Some markets and fairs sell lettuce. After cutting the portion destined for consumption, the roots are planted in the soil after being straightened out or, alternatively, a hydroponic technique can be employed that allows the regrowth of lettuce on the same base in water.

Since only this last practice is applied in Portugal, the product presented in this study would allow the reuse of this unused residue.

3. Cellulose and Cellulose Nano Fibres extraction process

As this flame-retardant cellulose film requires extraction of cellulose from the lettuce roots and residual leaves, it was necessary to choose a reliable and high-yield methodology. Thus, for this project, the cellulose nanofibre (CNF) was obtained by a 3-day extraction procedure adapted from Zhang et al. (2019) and the Laboratory of Separation and Reaction Engineering–Laboratory of Catalysis and Materials (LSRE - LCM 2021).

The process described below is a laboratory-scale CNF production method. This method will later be converted into an industrial-scale process. The scaling up of the process was necessary due to the high volumes of raw matter needed to make the resulting product from the extraction of the lettuce residue economically attractive.

This process begins with drying the lettuce residues to a powder. It was observed that circa 95% of the total initial weight was water. An alkaline treatment was first applied thrice to the remaining dry material (5% of the initial mass). It consisted of supplying 0.5mol/L of sodium hydroxide ($NaOH$) 1:50 to the powder and mechanically stirring it for 2.5 hours at 80°C.

The lettuce sample was filtered and washed with 1L of distilled water per wash between each alkali treatment until obtained a neutral pH . The objective of this process is to remove organic compounds such as pectin. A higher concentration of cellulose on the surface is obtained, improving the adhesion of fibres, and increasing the number of bonds between the polymer and its surface. The diameter of the fibres becomes smaller, which strengthens the fibres. This resulting product presents higher thermal stability due to increased temperature during the degradation process (Zhang et al. 2019).

Then, the insoluble pellets were bleached thrice with $NaClO$ 2.3wt% at 80°C for 3 hours. Between each bleaching treatment, the sample was also filtered and washed with 1L of distilled water per wash (3 washes were made in total) until neutral pH . An interesting factor observed was the disappearance of the green colour between treatments and washes, as the alkali treatment and the bleaching were destroying the chlorophyll pigment.

After the alkali and bleaching treatments, the insoluble pellets were lyophilised, and cellulose was obtained. However, the objective of this study is to get Cellulose Nano-Fibres, having been carried out acid hydrolysis with 50 wt% sulfuric acid H_2SO_4 , for 1.5 hours at 50°C, washed with deionised water ten times and then centrifuged at 9000 rpm. The liquid suspension obtained from the centrifugation was dialysed against distilled water using regenerated cellulose tubes until it reached a neutral pH . Then the sample was again lyophilised, and CNFs were obtained. The yield was circa 20% from the 5% of dry matter from this whole process, as mentioned above.

4. Chemical Product Design (CPD)

4.1. Needs & Ideas

Having the lettuce residue as raw material, it was decided to study its cellulose content due to its abundance within the lettuce and the mechanical and chemical properties of the cellulose itself. This compound is a robust natural fibre and can be used in many different products to increase its tensile strength (Zhang et al. 2019). The research was conducted on sports and climbing equipment and ship sails. Some products could be altered and substituted with cellulose fibres; however, it was noticed a potential safety issue in using the natural fibres for climbing gear that need to withstand extremely high tensile forces over several cycles. Furthermore, it was decided to exclude all fabrics since cellulose is hydrophobic and won't act as a moisture remover in sports clothes.

Finally, manufacturing the cellulose flame-retardant film allows for the future company to maintain a lower investment in marketing since trying to acquire a market share in the more competitive clothing or sport equipment markets would require a far larger commercial campaign than establishing a niche product on the market.

According to APSEI (Associação Portuguesa de Segurança), thousands of household fires occur every year in Portugal. These fires represent a hazard to its occupants and a significant risk to the property's valuable assets. Therefore, there is a necessity for an affordable flame-retardant that can provide substantial protection while also being aesthetically appealing since the object will be permanently exposed.

4.2. Selection – flame-retardant cellulose film

The selected idea has, from the research, a lot of potential to gain a substantial market share because it comes with the unique feature of being wholly renewable and easy to use. The product will protect everyday objects from damage by fire and can be used on most organic surfaces. Since the film is a thin sheet composed of one part cellulose and one part binding agent, it uses drastically less cellulose than many of the other products that were looked up. Therefore, it will be possible to produce and sell more to increase the profit margin.

By analysing other flame-retardant films on the market, it's possible to conclude that they are plastic-based and, therefore, non-biodegradable (Shanghai Huzheng Nano Technology Co., Ltd. UL94 VTM-0). Due to concerns about plastic's impact on earth's ecosystems and human health, there has been a public push to minimise the use of this material in several products. This concern, compounded with the desire to better manage the use of natural resources, means that this plant-based film made from agricultural waste can stand out in the market by appealing to the consumer's environmental awareness.

5. Flame-retardant Film Conception

To create the flame-retardant film, it will be essential to divide the project into two parts, namely the extraction of cellulose nanofibres and the film's design.

For the flame-retardant cellulose film production, a solution of CNF and a solution of *montmorillonite bentonite* (*MTM*) are prepared. The cellulose solution will be prepared by dissolving 1wt% of the extracted cellulose nanofibres in deionised water under high shear mixing. A 1wt% hydrocolloidal *MTM* solution was prepared by dispersing 10g of *MTM* in 1L of deionised water under vigorous stirring. The cellulose solution will be slowly added to the *MTM* dispersion until a 1:1 wt ratio and then stirred for 24h. The mixture is then poured into a Teflon mould and dried in an oven at 55°C until it reaches a thickness of 50-60µm (Carosio et al. 2016).

To industrialise this method, the solutions will be prepared in baffled stainless-steel tanks with continuous stirring. The cellulose solution will then be transferred to the *MTM* solution and mixed until homogeneous. To create the flame-retardant film, the mixture will be extruded onto a conveyor belt which passes through an oven until thickness specifications are met.

6. Manufacture

6.1. Product manufacture

The manufacture of this product will be carried out in three parts. The first stage consists of the pre-treatment of the raw material. The second consists of the solvent treatment to extract the cellulose nanofibres. The third is the conception of the film, together with clay and water.

Figure 1 shows the process flowchart.

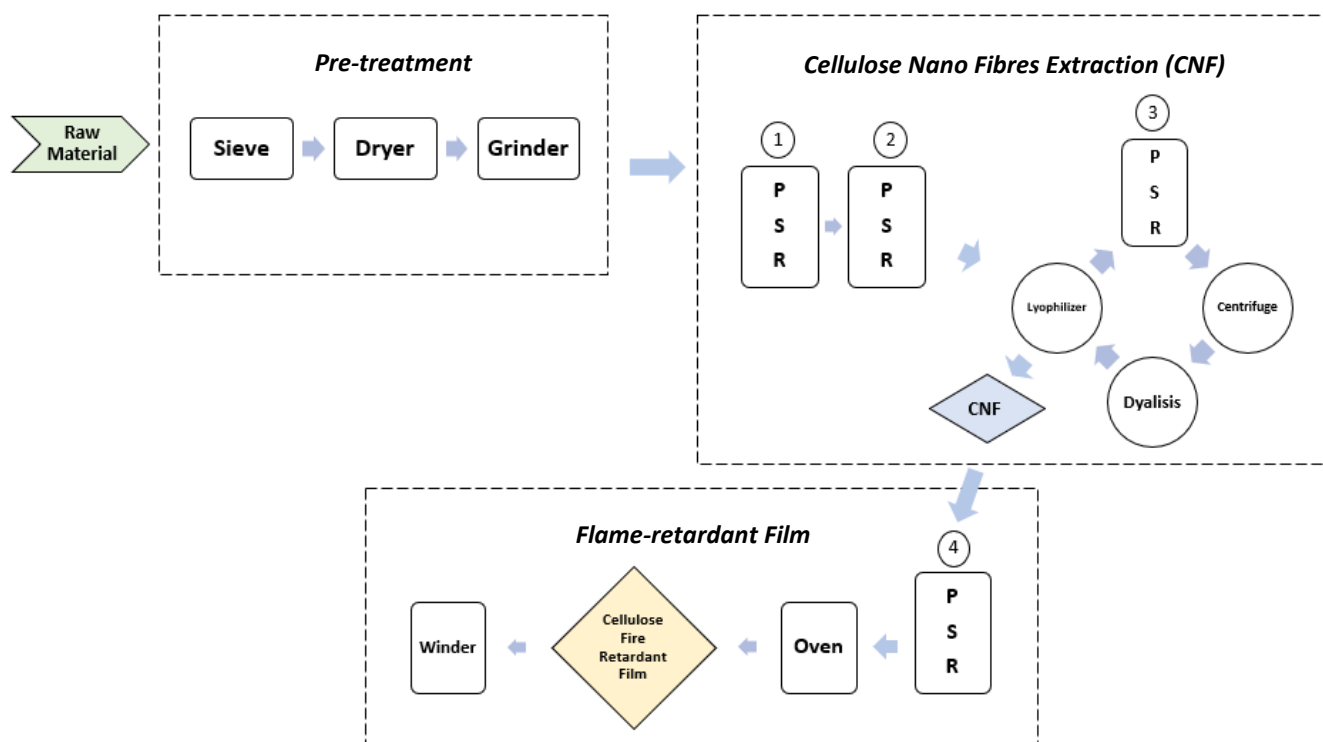


Figure 1: Cellulose Flame-retardant Film production line diagram

As observed in Figure 1, the pre-treatment (the first stage of the process) consists of sieving the lettuce dirt in a rotatory sieve while cleansing it with a hose jet. It is subsequently dried before the milling process, which turns the lettuce residue into a chip. The main idea was to use the saturated air to heat the stirred reactors in the next phase of the process, which is the chemical treatment. It should be noted that the heat capacity of the air is not high, which does not provide much energy in the form of heat to the reactors channeled to heat them, but it was accounted as an energy-saving process. However, this idea was quickly discarded since this water, coming from the air saturation in the dryer, will have another beneficial and better use, washing the lettuce in the first stage of the process.

Related to the chemical treatment of the raw material, in the first stirred reactor, the “alkali” treatment will be carried out on the chips, as explained before. After each treatment, the solvent mixture is drained through the reactor base, and a filtering mesh retains the chips (product of interest in this process step). The same process will happen in the next reactor with the “bleaching” treatment. The lyophilization freeze-dries the pellets, and then they move on to the “acid hydrolysis” treatment, where the reactor will work in the same way, filtering the pellets, but each time, with a much narrower filter mesh, after leaving the reactor, the effluent has to be neutralized, this is done by washing it a total of 10 times with $4,3m^3$ reverse osmosis water. In the original lab scale process, this was done with deionized water instead of reverse osmosis water; however, since the projection of the manufacturing facility already accounts for a distilled water production centre this option was favoured as a more economically viable alternative. This decision was considered to be feasible for industrial-scale adaptation due to the somewhat similar pHs of both samples of water, which is the dominant factor in a neutralization reaction (Kulthanan, Nuchkull, and Varothai 2013; Riché et al. 2006; Rudyk et al. 2022). The solid mixture is then centrifuged to induce particle sedimentation.

The liquid containing the cellulose nanofibres will finally be processed in a dialysis machine. After obtaining the cellulose nanofibres, in a stirred reactor, the film mixture is manufactured with water, montmorillonite clay and cellulose nanofibres to obtain the film, which will leave the treatment station on a *Teflon* coated conveyor belt, which passes through an oven.

The final product will be sold by area. To assess how many square meters of the film are contained within a kilogram, Equation (1) was used. The film nanofibre density (ρ_{film}) was estimated to be $1,575\text{kg/m}^3$ due to it being 50% (w/w) cellulose ($1,500\text{kg/m}^3$) (Hermans and Vermaas 1946) and 50%(w/w) a mixture of slightly wet clay ($1,650\text{kg/m}^3$), the thickness of the film was considered to be the midpoint of the expected range ($55\mu\text{m}$). The m^2/kg ratio was determined to be 11.54. In Equation (1), ε represents the 50-60 μm thickness.

$$A \left(\frac{\text{m}^2}{\text{kg}} \right) = \frac{1}{\rho_{film} \times \varepsilon} \quad (1)$$

6.2. Application procedure

The adhesive used in the application of the flame-retardant film should be selected in accordance with the surface of application. For wood-based products, which are predicted to be the main market for this product, a methylcellulose water-based solution, commonly used as a wood and cellulose content material, "glue," would be a suitable binding agent (Kumar et al. 2012). Since the binding agent is a separate product from the flame-retardant film, it's considered to be out of the scope of this article.

6.3. Environmental Norms for water disposal

Following Portuguese norms, these industrial residual waters need to have the right solvent concentration and pH to be released. Having in mind "Decreto Lei nº 152/97 – Artigo 17 c)" (1997), "Portaria nº 503/92" (1992) and "Decreto Lei nº 236/98" (1998), the waters will be neutralized and drained before going to the sewer.

6.4. Product specifications

This cellulose film has flame-retardant properties that, according to Carosio et al. (2016), delay the ignition time by approximately 4.5 minutes. To achieve its best resistance, the film needs to be made up of one part cellulose nanofibres (CNF) and one-part Montmorillonite Bentonite solution (MMB + water 1:1). In addition to the chemical characteristics, the film must be 50-60 μm , which allows it to be transparent and applied smoothly and continuously on the intended surface.

Table 1 presents additional data that constitutes the flame-retardant properties of this film. The following values were obtained by cone calorimetry.

Sample	TTI [s]	pkHRR $\pm \sigma$ [kW/m ²]	THR $\pm \sigma$ [MJ/m ²]	MARHE $\pm \sigma$ [kW/m ²]	Residue [%]
Wood	89 \pm 5	248 \pm 9	61 \pm 2	138 \pm 10	15 \pm 1
Coated	358 \pm 58	285 \pm 50	41 \pm 5	74 \pm 9	20 \pm 2

Table 1: Cellulose Flame-retardant Film cone calorimetry test results.

Adapted from Carosio et al. (2016)

TTI - time to ignition; pkHRR - peak of heat release rate; THR - total heat release; MARHE - maximum average rate of heat emission. This data for uncoated and coated wood.

Through [Figure 2](#), it is possible to observe how this material will affect the general appearance of the object on which it is applied.

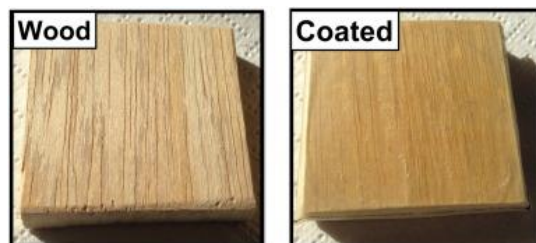


Figure 2: Uncoated and Coated wood with the flame-retardant cellulose film.
Reprinted from [Carosio et al. \(2016\)](#). Copyright 2016 Materials and Design.

The material is transparent, which means that the application of this film does not affect the appearance of the piece of wood.

7. Process Optimisation

7.1. Water and Reagents recuperation

The method that is going to be used in this project to purify the water of chemical agents used during the extraction process, such as sodium hydroxide ($NaOH$), sodium hypochlorite ($NaClO$) and sulfuric acid (H_2SO_4), is going to be reverse osmosis. This method consists of a semipermeable membrane with a pore size of $0.5nm$, with an area of high concentration on one side of the membrane (contaminated water) and an area of low concentration. Only the water with a low concentration of contaminants will pass through. It prevents the passage of chemical agents and other substances that are undesired.

To avoid biofouling (or membrane fouling), a pre-treatment such as a filtration process must be implemented. The water passes through a filter, preventing larger particles such as organic compounds or even solvents used during the process from interfering in reverse osmosis. To accelerate the filtration process, an organic, eco-friendly coadjuvant (land of diatoms) will be used so that the obstruction of the filter is avoided by increasing its porosity. It will also increase the longevity of the membranes used in the reverse osmosis process, improve the water's quality, and decrease the maintenance cost.

At the end of the reverse osmosis process, the water will be tested with ultraviolet light to confirm its purity.

8. Economic Analysis

8.1. Details of production on a large scale

To analyse how much this product is worth on the market and the possible profit margin to be obtained through the use of this raw material (lettuce root and residual leaves), it was decided to scale up to an industrial perspective. This led to the creation of a company headquartered in the district of Leiria, in Alcobaça. The factory would work 20 days a month and 24 hours a day with three 8-hour shifts per day. It is important to note that the market study was conducted between December 2021 and January 2022. The information given below represents only the final results of the economic analysis. A more in-depth evaluation can be found in the given complementary material.

To produce the flame-retardant film as previously mentioned, several pieces of equipment must be procured; the individual pieces of equipment acquired, as well as the costs related to its acquisition, are described below in [Table 2](#).

Machinery	Units	Machine Price (€)	Machine Model
Sieve	1	2,000	Xinxiang Dongzhen Machinery Co.; Ltd.;GT1545
Grinder	1	13,400	Zhangjiagang Camel Machinery Co.; Ltd.; WG-1000
Dryer	1	89,000	Henan Hongji Mine Machinery Co.; Ltd.; $\phi 1.2*10$
Jacketed Reactor	7	35,000	Guangdong Jinzong Machinery Co.; Ltd.;
Liofilizer	1	132,000	Hangzhou Wuzhi Freeze Dryer Co.; Ltd.;FD-200
Centrifuge	1	44,041	Liaoyang Shenzhou Machinery Equipment Co.; Ltd.; LW250 * 1000
Oven	1	31,238	Henan Baixin Machinery Equipment Co.; LtdBX-2*12
Dialysis Machine	1	893	Henan Timoo Import & Export Trading Co.; Ltd.;TYRO-300 I
Winder	1	30,653	Zhejiang Shengchi Machinery Technology Co.; Ltd.; SCP_1300

Table 2: Cellulose Flame-retardant Film production line machinery details: number of units, price, and model

It was also decided to establish a water purification system along the manufacturing process. The equipment required for this endeavour and its costs is shown in [Table 3](#).

Machinery	Units	Machine Price (€)	Machine Model
Reverse Osmosis	1	48,800	IDEAS Y DESARROLLO DEL AGUA S.L.; OI4380
Filter	1	3,551	IDEAS Y DESARROLLO DEL AGUA S.L.; FI 1006-06
UV Lamp	1	305	JARPIS, S.L.; 71427
Membrane	12	12,012	IDEAS Y DESARROLLO DEL AGUA S.L.; RO4037
Water Pump	2	8,432	Depump Technology Shijiazhuang Co.; Ltd.; D6-50x2
Water Tank	30	3,217	Dezhou Huili Water Tank Co.; Ltd.; HL-FRP

Table 3: Water purification machinery details: number of units, price, and model

8.1.1. Reagents

All of the final prices referred were calculated considering the amount of volume of pure reagent needed and its price on the market. The water contribution is going to be discussed later on. For the alkali treatment, a solution of 0.5mol/L NaOH (CAS 1310-73-2) is needed, with a ratio of $1:50_{w/v}$. This means that per day/batch (and considering that this treatment needs to be done thrice), $64,406\text{L}$ are necessary. Therefore, the final annual cost of sodium hydroxide is 124k€ . The same ratio of $1:50_{w/v}$ has been considered for the bleaching treatment, which leads to daily consumption of $64,406\text{L}$ of NaClO (CAS 7681-52-9), reflected in a final annual cost of 194k€ . For acid hydrolysis, the ratio is 10mL/g acid-to-cellulose. Therefore, daily it is necessary to use $858,75\text{L}$ of H_2SO_4 (CAS 7664-93-9) 0.98% , which leads to an annual cost of 35k€ . This cost was lastly consulted on 13-01-2022. Its price is not constant since it is listed on the stock market.

To conceive the nanofilm, 20.6 tons of *Montmorillonite Bentonite* Clay (CAS 1302-78-9) powder are required, with an annual cost of 5.5k€ .

8.1.2. Marketing / Distribution

For marketing, as this product is intended to be purchased by companies (B2B), not direct consumers, we must have a market study and product placement done by someone with a portfolio of clients in the wood industry (carpenters). With this in mind, it was decided that a hardware distributor for furniture would provide the best product placement. As it is going to

be mentioned further, the selling price for the distributor is going to be $6\text{€}/\text{m}^2$. In addition to working with a distributor, the company would participate in fairs and other events to present the flame-retardant film to potential business partners in the industry. To make sure this is properly done, an initial budget of 100k€ will be allocated to implement the company in the market. After that, a yearly budget of 30k€ will be allocated to maintain the acquired market share.

8.1.3. Retail price and profit

In order to start not only a fully operational plant but also an appropriate distribution network, several initial investments in machinery for the plant must be considered, a truck for raw material collection and transportation, a warehouse in which to base the operations, the costs for an initial marketing campaign, a safety net of 50k€ to deal with unforeseen expenses and a start-up cost equal to a month of operational costs to make sure the plant will be fully functional by day one. The total investment cost would equal $1,6\text{€}$, and this would be financed by a loan with an effective interest rate of 12% a year, to be paid in two years (Table 4).

Investment Costs (€)	
Machinery	832,765€
Truck	19,200€
Warehouse	500,000€
Initial Marketing Campaign	100,000€
Start-up cost	85,405€
Safety net	50,000€
Total	1,587,370€

Table 4: Cellulose Flame-retardant Film initial investment costs

To maintain the business fully operational, it's necessary to factor in the costs of reagents, machinery maintenance, truck maintenance, water, electricity, wages, raw matter, quality control, marketing and real estate tax. These costs would amount to $1,024,401\text{€}$ per year (Table 5).

The projected plant, if fully operational, would produce 41.22 metric tonnes or $475,844\text{m}^2$ per year. The product will be sold to distributors at the final price of $6\text{€}/\text{m}^2$. Thus, it can be concluded that the factory would generate an income of $2,855\text{€}/\text{year}$ if all the stock is liquidated. If the stock isn't completely sold, however, the business would need to sell 35.67% of the produced film to break even, or it could sell all of the stock at $2.15\text{€}/\text{m}^2$.

Assuming that the stock is fully liquidated, the company would generate a taxable profit of $1,836,619\text{€}$ every year, except for the first two years in which the initial loan must be fully repaid, and the taxable profit would be $897,710\text{€}$. To the taxable profit, the IRC (Portuguese corporate profit tax) and a Municipal Tax must be deducted, 21% and 1.5% , respectively. The final net profit would be $695,725\text{€}$ in the first two years and $1,423,380\text{€}$ in the years after.

Operational Costs (€)	Yearly
Reagents	358,633€
Machinery Maintenance	50,000€
Truck Expenses	6,220€
Water	17,808€
Electricity ¹	86,784€
Wages	360,800€
Raw Mater	108,141€
Quality Control	5,314€
Marketing	30,000€
IMI	1,500€
Total	1,024,401€

Table 5: Cellulose Flame-retardant Film yearly production costs

Figure 3 represents the cumulative growth of the company every quarter of the year.

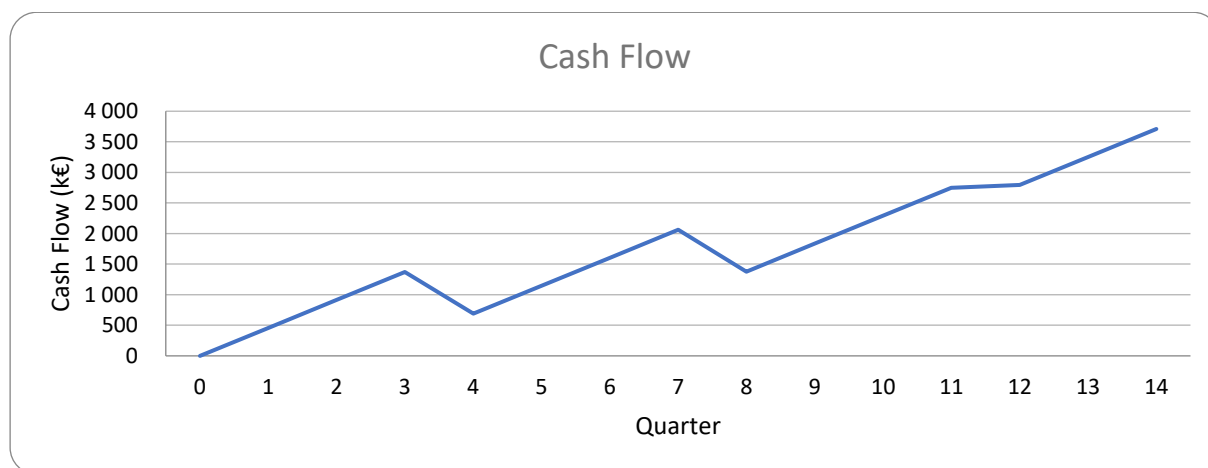


Figure 3: Cash flow projections over time

8.2. Market placement

The authors are aware that there are other flame-retardant films on the market. What distinguishes the current product from its competitors are the biodegradable, non-pollutant, plant-based/vegan properties (Bio raw material). Plus, the conception of this product uses agricultural waste as a raw material, which is a sustainable form of business. The competitive market offers various forms of plastic-based flame-retardant films (Shanghai Huzheng Nano Technology Co., Ltd. UL94 VTM-0) that will be pollutant to the environment and non-biodegradable. They are sold for an estimated value of 2.56€/m² online, which approximately doubles the price when considering the shipping and import fees.

9. Conclusions

Carrying out this project proved that it is possible to use uncommon raw materials to create new products with value on the market and a solid profit margin. Plus, the conception of this product uses agricultural waste as a raw material, which is a sustainable form of business. Besides having a green sourced raw material, this project always looked up to include methods

¹EDP. n.d. "Planos de energia [Empresas]". Accessed December 2021. <https://www.edp.pt/empresas/energia/tarifarios/>.

of resource recovery, such as water and heat exchange (not efficient in this case). This will not only contribute to long-term savings but also diminish waste.

If all the stock is liquidated, the factory will generate an income of 2,855€/year. However, if the stock isn't completely sold, the business would need to sell 35.88 % of the produced film to break even, or it could sell all the stock for 2.15€/m².

Considering a market analysis, it became clear that there are, in fact, other flame-retardant films; however, they are not biodegradable, vegan or green in origin like this product. The product retails at 6€/m² for its distributor. However, there is a good margin to lower the final price if the sales do not meet expectations due to the company's break-even price (2.15€/m²) being lower than the selling price of other similar films on the market that cost 5.12€/m² (including shipping and import fees).

It is then possible to conclude that there is space on the market for this film to be profitable and, more importantly, usable since its purpose is to preserve and give longevity to furniture and valuables.

References

- Barhoum, A., H. Li, M. Chen, L. Cheng, W. Yang, and A. Dufresne. 2019. "Emerging applications of cellulose nanofibers". In *Handbook of Nanofibers*, edited by A. Barhoum, M. Bechelany, and A. S. H. Makhlof, 1131-56. Springer. https://doi.org/10.1007/978-3-319-53655-2_53.
- Carosio, F., F. Cuttica, L. Medina, and L. A. Berglund. 2016. "Clay nanopaper as multifunctional brick and mortar fire protection coating-Wood case study". *Materials and Design* 93: 357-63. <https://doi.org/10.1016/j.matdes.2015.12.140>.
- "Decreto-Lei n.º 152/97 - Tratamento de águas residuais urbanas". 1997. *Diário da República* no. 139/1997, Série I-A. <https://data.dre.pt/eli/dec-lei/152/1997/p/cons/20210827/pt/html>.
- "Decreto-Lei n.º 236/98 - Estabelece normas, critérios e objetivos de qualidade com a finalidade de proteger o meio aquático e melhorar a qualidade das águas em função dos seus principais usos". 1998. *Diário da República* no. 176/1998, Série I-A. <https://data.dre.pt/eli/dec-lei/236/1998/p/cons/20190821/pt/html>.
- Dhali, K., M. Ghasemlou, F. Daver, P. Cass, and B. Adhikari. 2021. "A review of nanocellulose as a new material towards environmental sustainability". *Science of the Total Environment* 775. <https://doi.org/10.1016/j.scitotenv.2021.145871>.
- Hermans, P. H., and D. Vermaas. 1946. "Density of cellulose fibers. I. Introduction and experiments on the penetration of liquids into dry cellulose". *Journal of Polymer Science* 1, no. 3: 149-55. <https://doi.org/10.1002/pol.1946.120010301>.
- INE (Instituto Nacional de Estatística). 2021. *Estatísticas Agrícolas: 2020*. INE. <https://www.ine.pt/xurl/pub/437147278>.
- Kulthanan, K., P. Nuchkull, and S. Varothai. 2013. "The pH of water from various sources: an overview for recommendation for patients with atopic dermatitis". *Asia Pac Allergy* 3, no. 3: 155-60. <https://doi.org/10.5415/apallergy.2013.3.3.155>.
- Kumar, A., Y. S. Negi, N. K. Bhardwaj, and V. Choudhary. 2012. "Synthesis and characterization of methylcellulose/PVA based porous composite". *Carbohydrate Polymers* 88, no. 4: 1364-72. <https://doi.org/10.1016/j.carbpol.2012.02.019>.
- López, A., G. A. Javier, J. Fenoll, P. Hellín, and P. Flores. 2014. "Chemical composition and antioxidant capacity of lettuce: Comparative study of regular-sized (Romaine) and baby-

- sized (Little Gem and Mini Romaine) types". *Journal of Food Composition and Analysis* 33, no. 1: 39-48. <https://doi.org/10.1016/j.jfca.2013.10.001>.
- LSRE-LCM. 2021. "Cellulose Extraction Results". Unpublished report.
- "Portaria n.º 503/92". 1992. *Diário da República* no. 139/1992, Série I-B: 2896-96. <https://data.dre.pt/eli/port/503/1992/06/19/p/dre/pt/html>.
- Riché, E., A. Carrié, N. Andin, and S. Mabic. 2006. "High-purity water and pH". *American Laboratory*, June 1, 2006. <https://www.americanlaboratory.com/913-Technical-Articles/35755-High-Purity-Water-and-pH/>.
- Rudyk, S., P. Spirov, M. Lunde, and A. Jimoh. 2022. "The pH of tap and deionized water at 13, 23, 33, and 43 oC in the range of 0-140 g/L of NaCl salinity". Preprint, submitted April 19, 2022. <https://doi.org/10.21203/rs.3.rs-1567683/v1>.
- Shatilov, M. V., A. F. Razin, and M. I. Ivanova. 2019. "Analysis of the world lettuce market". *IOP Conference Series: Earth and Environmental Science* 395: 012053. <https://doi.org/10.1088/1755-1315/395/1/012053>.
- Zhang, G., F. Wu, T. Ma, B. Zhang, A. Manyande, and H. Du. 2019. "Preparation and characterization of cellulose nanofibers isolated from lettuce peel". *Cellulose Chemistry and Technology* 53, no. 7-8: 677-84. <https://doi.org/10.35812/CelluloseChemTechnol.2019.53.66>.

Acknowledgments

This work was developed under the scope of the course unit of Product Engineering of the Master in Chemical Engineering at the Faculty of Engineering of the University of Porto, during the 1st semester of the 2021/2022 academic year. Professor Cláudia Gomes, Doctor Ricardo Santos, and Doctor Yaidelin Manrique, supervisors of this work, are members of the Associate Laboratory LSRE-LCM funded by national funds through LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC).

Supporting Information

10. Detailed Economic Analysis

10.1. Raw material

Knowing that in 2020, 61,976 tons of lettuce were produced in Portugal, in an area of 2,452 hectares and sold at an average price of 0.525€/kg, it was outlined that this business would cover a radius of 50 km (from producers) and that 2,061 tons per year (171.75t/month, 8,588kg/day) of lettuce residue would be collected, purchased at 10% of the selling price, around 0.05€/kg. As the residual part of the lettuce is kept in the soil to act as a natural fertiliser, the 10% offer in the cost is symbolic of that (INE 2021). Yearly, 2,061 tons of lettuce roots and residual leaves would cost 108,141€. Daily, 8,588kg of lettuce will be dried, taking into account that 95% of the lettuce residue is water that will be evaporated, which leaves circa 429kg of dry raw material to work per day.

10.2. Warehouse

A vast and tall space would be necessary for the machinery and the product, reagents and water storage for the production process. With this in mind, a warehouse in Alcobaça was considered for 500k€, covering 3,950m², representing 1.27€/m². This purchase was located in the investment costs and the cumulative price of the machinery and truck.

10.3. Machinery

To extract the cellulose nano-fibres (CNFs), it was decided to implement an automated production line; the individual machines of this production line were then selected and are visible in Table S1. Each of the machines listed in Table S1 was “purchased” separately to ease the price simulation process. The retail price of the machines was added as an initial-machinery cost, and the electricity spent on each machine was accounted for separately as an operational electricity cost; the total machinery price was then doubled to account for the respective shipping fees and import taxes; however, each piece of machinery mentioned bellow was enunciated with its original retail price. The reference for each machine, as well as its manufacturer, is also listed in Table S1.

10.4. Electricity

The electricity prices were collected from an energy tariffs simulator of a Portuguese electrical provider named EDP. The simulated prices were 0.169€/kw·h, with a standing charge of 0.65€/day; the simulation was performed by using a single electricity rate and a maximum contracted power of 20.7kV².

10.5. Wages

To achieve the intended production goals and have a high-profit margin, it is necessary to implement 3 work shifts per day since the factory will be working 24 hours a day. There are going to be six factory workers, 2 per each 8 hours shift (1,100€ per capita, doubling that value in benefits – social security, food, health and Christmas and vacation bonuses), and three supervisor engineers, 1 per each 8 hours shift (2,200€ per capita, doubling that value in benefits – social security, food, health and Christmas and vacation bonuses). In addition, to collecting the lettuce residue from the lettuce producers, a truck driver is going to work 8 hours a day (1,800€ per capita, doubling that value in benefits – social security, food, health

² EDP. n.d. "Planos de energia [Empresas]". Accessed December 2021. <https://www.edp.pt/empresas/energia/tarifarios/>.

and Christmas and vacation bonuses). Assembling all of these costs yearly, the worker's expenses come to 360k€.

Machinery	Units	Machine Price (€)	Potency (kw)	Energy Used (kw·h/day)	Price/year (€)	Equipment Reference
Sieve	1	2000	7	7	284	Xinxiang Dongzhen Machinery Co., Ltd.,GT1545
Grinder	1	13400	22	22	892	Zhangjiagang Camel Machinery Co., Ltd;WG-1000
Dryer	1	89000	8	38	1521	Henan Hongji Mine Machinery Co., Ltd.,φ1.2*10
Jacketed Reactor	7	35000	28	560	22714	Guangdong Jinzong Machinery Co., Ltd.,
Liofilizer	1	132000	32	582	23618	Hangzhou Wuzhi Freeze Dryer Co., Ltd., FD-200
Centrifuge	1	44041	8	15	608	Liaoyang Shenzhou Machinery Equipment Co., Ltd., LW250 * 1000
Oven	1	31238	65	129	5248	Henan Baixin Machinery Equipment Co., LtdBX-2*12
Dialysis Machine	1	893	3	5	203	Henan Timoo Import & Export Trading Co., Ltd., TYRO-300 I
Winder	1	30653	12	24	973	Zhejiang Shengchi Machinery Technology Co., Ltd., SCP_1300
Total Costs	-	756448	172	1358	56218	-

Table S1: Equipment References for the conception of the Cellulose Flame Retardant Film and its respective costs

10.6. Transportation costs

Since the lettuce residue is left in the field, it is impossible to rely on previously established supply lines. Thus, the company must ensure the collection and transport of lettuce. For that purpose, a truck must be acquired and maintained. The selected model was the Toyota Dyna M35.25 due to its reliability, cargo capacity and availability on the used vehicle market. The estimated annual running cost of the vehicle, for a traveled distance of 15,000km, is split

between tires, simple diesel, insurance and general maintenance (oil, mechanic, inspection and tax). Four 195/70 R15C tires should cost around 280€, while insurance costs would be 400 € and general maintenance 600€. Finally, assuming a price of 1.50€/L, the fuel cost would be 4,940k€³.

10.7. Quality control

For this matter, a specialised laboratory, “*Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial*” (INEGI), is going to analyse samples of this product by conducting a weekly cone calorimetry mechanical test in order to guarantee the quality of the manufactured product. These quality control experiments may guarantee this product's continuous improvement and help detect malfunctions in the production process. This requires 442.86€ monthly, which reflects 5,314k€ yearly.

10.8. Water

Water is crucial to manufacturing cellulose nanofibers, mainly in the extraction process from the lettuce. Approximately 129m³ are required daily to wash the lettuce; preparing the NaOH, and NaClO solutions require nearly 129m³ of water daily split evenly among both.

Regarding the manufacturing process itself, the sulfuric acid used in the acid hydrolysis phase needs to be diluted by 1.7m³ per day. The neutralization reaction that occurs prior to liophilization is done exclusively with reverse osmosis water, and this water is readily available; however, this process will further increase the overall need for water by 4.3m³ per day. Preparing the clay from its initial powder also requires water at a rate of 1.7m³ per day.

The total volume of water required for the whole process is 261m³, with the cost of water in the municipality of Alcobaça being 0.85€/m³ plus a monthly fee of 17.63€. These costs would add to a total of 221.76€/day or 53,434k€/year⁴.

Taking into account the above considerations, open tanks were acquired to store rainwater. This water will be used to clean the lettuce in the first step of the process by hose jet in the rotational dirt sieve and the recuperated water from the dryer. In order to calculate how much rainwater could be collected per month/year in Alcobaça, data was researched in *Weather Spark* and *IPMA* (Instituto Português do Mar e da Atmosfera).

Month	<i>h</i> (m)	<i>V</i> (m ³)
1	0.07	5.21
2	0.06	4.04
3	0.04	2.76
4	0.05	3.34
5	0.04	2.72
6	0.01	0.98
7	0.00	0.26
8	0.01	0.40
9	0.03	1.86
10	0.07	4.88
11	0.09	5.97
12	0.08	5.86
Total	0.55	38.29

Table S2: Rainwater per month in Alcobaça
h(m) – (rainfall) water height that falls by m², *V* (m³) – volume of rain water.

³ Toyota. 2013. Toyota Dyna.

⁴ Câmara Municipal de Alcobaça. 2021. Tarifário Águas 2021.

10.9. Water recuperation

Since the environmental and economic cost of using such a large amount of water would be significant, it was decided to implement water-saving measures. The first measure was to condense the water in the moist air that exited the tubular dryer, a measure that saves, on average, $8.16m^3$ or $6.94€$ every day.

The second measure was to implement a reverse osmosis plant for water treatment that could retrieve up to 75% of water processed.

The retail cost for the main reverse osmosis equipment, which can filter $264 m^3/day$, is $48.8k€$ (IDEAS Y DESARROLLO DEL AGUA S.L., OI4380); this equipment uses 12 membranes that cost $12k€$ (IDEAS Y DESARROLLO DEL AGUA S.L., RO4037). The retail cost for the pre-treatment filter is $3.5k€$ and can filter $360m^3/day$ (IDEAS Y DESARROLLO DEL AGUA S.L., FI 1006-06).

For the pump selection, it was decided to contact a company that provides personalised industrial pumping solutions. After researching a $50bar$ pump that would meet the given specifications, it was decided to use two D6-50x2 pumps (Depump Technology Shijiazhuang Co., Ltd.D6-50x2) operating in parallel to be obtained at the cost of $8.4k€$.

At the end of the process, an ultraviolet- light would be used for quality control, costing $305€$ (JARPIS, S.L., 71427), and 30 tanks would be used to store the water for a price of $3.2k€$. (Dezhou Huili Water Tank Co., Ltd., HL-FRP).

The total investment cost of the reverse osmosis plant is $76k€$. The annual cost of electricity is $30.5k€$ (working 22 hours a day and 240 days a year), but since the plant saves 75% of the daily water consumption ($260m^3$), the plant's financial impact is a net gain of $9.3k€$. When also considering the water obtained from the dryer, $1,958m^3/year$, the company can save up to $48,930m^3$ of water every year.