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Resinut: a Bio Phenol Formaldehyde Resin using Chestnut Shells

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Abstract

The concerns for environmental impact due to the agricultural industry are increasing. One example is the waste associated with the removal of the chestnut shells for this fruit's preservation and selling. On the other hand, the search for biological alternatives to chemical products is increasing, as environmental-friendly options are a must for brands. This work proposes the development of a bio phenol formaldehyde resin, substituting 40 % of the phenol for bio-oil obtained via pyrolysis of the chestnut shells. The product, Resinut, has the potential to have the same properties as a traditional PF resin.

1. Introduction

In the face of escalating climate change concerns, there is an urgent need to reassess and revolutionize the way goods are produced, and services are provided (Ellen MacArthur Foundation 2019). The industrial processes and products that have fueled global economic growth for decades are now recognized as major contributors to the escalating carbon emissions responsible for climate change (Eurostat 2023). Reducing these emissions requires a change in the market's approach, necessitating the redesign of products and processes across industries (Ellen MacArthur Foundation 2019).

In this context, this paper explores various applications for the compounds extracted from the agricultural wastes of the chestnut industry. For example, the production of a bio leather from the leaves, the application of microencapsulated phenolic compounds with antioxidant properties in the food industry as well as a packaging film with lignin extract. The main focus of this work was the development of a nutshell bio-based phenolic formaldehyde (PF) resin, which contributes to a significant reduction in the reliance on fossil fuels. As one stands at the intersection of environmental consciousness and technological innovation, it is crucial to understand the pressing need for sustainable materials in the market.

The primary objective of this work is to introduce an alternative bio-PF resin that addresses the environmental concerns associated with conventional processes. The synthesis of phenolic resins typically involves a substantial percentage of phenol, derived predominantly from fossil fuel sources. The main goal focuses on reducing this dependency by presenting a bio-PF resin that maintains performance characteristics and reduces the overall phenol requirement by substituting a considerable percentage of phenol for bio-oil form extracted from chestnut shells.

2. State-of-the-Art

Portugal is one of the biggest chestnut producers in Europe. In addition, there is a strong cultural connection to this fruit, with festivals and traditional chestnut markets all over the country during fall, which corresponds to the harvest season. In 2018, this sector’s economic value in the market was over 95 million euros (Cabo et al. 2019).

According to the 2019 report by the Food and Agriculture Organization (FAO), worldwide chestnut tree cultivation, in 2018, occupied about 613 thousand hectares (FAO 2019). There was a production of roughly 2.4 million chestnuts, of which 83 % were produced in China (Pinto et al. 2021). Europe produced 155 thousand tonnes of chestnuts, 34 of which were produced in Portugal, mainly in the north of the country (FAO 2019). The production in Portugal saw its highest in 2019, with 44 thousand tonnes of chestnuts; after that, it decreased to 37 thousand in 2021 (INE 2022).

One of this sector’s main challenges are the pests and diseases that affect the chestnut trees and cause the reduction of their exploration productivity. Some examples are the chestnut ink disease and the chestnut blight (Robin and Marchand 2022). Another problem that this sector has been facing is the labor shortages caused by the flux of people from the countryside to the coast looking for better job opportunities, causing the producers to hire immigrants to assure the production (Ferreira and Pinto 2023). Most of the producers are over 55 years old. A lot of them only have an elementary level of education, which represents a limitation to investment and innovation in the sector due to the lack of knowledge of new techniques (EFFP 2016). Climate change is also a big threat to chestnut production since it has been making extreme climate events, like drought and floods, more frequent every day and has influenced the development of the plant species at phenological, physiological, biodiversity and genetic levels (Freitas et al. 2021).

The main goal of this sector now is to increase chestnut production in order to increase its consumption by the public. To invest in units of second transformation, in other words, to use chestnuts to make other products instead of freezing them as they are after peeling them (EFFP 2016). To invest in research to improve the disease resistance of the trees. And to do all of this while improving the sustainability of the process.

In Portugal, about 40 % of the chestnuts produced are sold or exported as fresh fruit, while the remaining 60 % are processed in the country or exported to be processed in a different one. The main products that result from the processing of the fruit are frozen chestnuts, which almost represent the total of processed chestnuts, and, in smaller quantities, chestnut flour and liquors. Portugal's main chestnut processing companies are Sortegel, Alcino Nunes & Irmão, AgroAguiar e Monsurgel (EFFP 2012).

Given the importance of this sector to the economy there is an interest in finding new high value products and innovative economic resources from the chestnut production (Aires, Carvalho, and Saavedra 2016). In order to come up with a new product that would have a positive impact in the world and in the sector all of the tree components were considered when choosing the raw material, from the branches to the actual fruit. Chestnuts are already being used for the production of chestnut flour and starch, liquors and nut drinks, jams, fillings and other food products (Li et al. 2022). The authors' intention was to focus more on the residues of the industry in order to improve the sustainability of the sector through a circular economy approach and to solve part of the waste disposal problems. The main residues of chestnut processing are chestnut shells, burrs, wood from pruning and leaves. All of these, even if in different percentages, represent sources of natural bioactive compounds that can be used as an added value in several areas, such as the food, pharmaceutical and cosmetic industries (Squillaci et al. 2018). The main compounds of the extracts from these wastes are phenolic acids, flavonoids and hydrolysable and condensed tannins. The leaves extracts, with higher percentage of phenolic acids, are known for their antimicrobial activity and protection against oxidative stress (D. B. Rodrigues et al. 2023). The wood from pruning is not suitable for domestic use, however, it has a great number of polyphenol compounds (M. Â. Rodrigues et al. 2021). Some examples of applications for each of these residues are skin care products with chestnut leaves extract, for the prevention and treatment of oxidative stress-mediated disease and photoaging (Almeida et al. 2008), and animal feeding with chestnut wood for boiler chicks that improves their growth performance and intestinal inflammatory response (Schiavone et al. 2008).

The production of frozen chestnuts, especially their peeling process, results in high amounts of shell residue, since the shells represent about 20 % of the total fruit weight (Conidi et al. 2022). These shells can be discarded, used as a natural fertilizer or as combustion fuels. In this work, the chestnut shells (CSS) were chosen as the raw material for creating a new product, so that their antioxidant potential won't be wasted. This choice was made based on their composition rich in bioactive compounds such as gallic acid, polysaccharides and polyphenols. One of these polyphenols is lignin, which gives ultraviolet light protection and has antioxidant and antimicrobial properties (Galiñanes, Freire, and González-Álvarez 2015). It acts as an important structural material that supports the tissues of vascular plants, giving them compressive strength and rigidity, which are interesting properties for their incorporation in adhesives and coatings (Khan, Lee, and Kim 2019). Such properties represent a valuable resource for possible applications under study, for example anti-aging face creams (Silva et al. 2022) and fortified yogurts with less synthetic preservatives (Ferreira and Santos 2023). This paper explores the use of bio-oil extracted from chestnut shells for the production of a bio-PF resin in order to benefit from the phenolic compounds with antioxidant attributes present in the shells. The application of these compounds in several materials would enhance product stability, quality and lifespan (D. B. Rodrigues et al. 2023). The sustainability of the resin would also increase in comparison with the PF resins currently in the market by substituting the bio-oil for a part of the phenol needed in the production of the phenolic formaldehyde resin.

3. Chemical Product Design (CPD)

The methodology involved in designing and developing a new product consisted of establishing the market needs and identifying the market demands, environmental considerations, or specific application requirements. The next step is to have a brainstorming session, by thinking about product ideas that may resolve said needs, taking into account the properties of the raw materials available. Then, it proceeds with selecting and scoring the best ideas following a list of important parameters, being the final product the best-scored idea. The final product must satisfy the needs considered to be useful, desirable, and essential. Lastly, the manufacturing process must be designed and carried out in a process simulation program. The steps described were followed and are presented in the following sections.

3.1. Needs and Ideas

Nowadays, the chestnut sector has achieved more and more value because it emerges as an answer to the needs of the market. This sector, for example, is able to respond to needs as an alternative to traditional sources of carbohydrates and as a compositional option in the new natural fertilizers. In addition, the chestnut sector can be an option for reducing the production of animal hides, thus contributing to the increase of vegetable hides. Chestnuts can also contribute to the production of jams with a greater feeling of satiety and the manufacture of antidepressants and natural options to preserve products against oxidation.

However, it is necessary to pay attention that for the chestnut sector to respond to the needs of the market, the needs of the sector itself arise, such as the reduction of waste from chestnut production, the reduction of the environmental impact of its industry and alternatives that economically value waste produced by the sector. The good news is that these needs of the chestnut sector can be met through the usage of natural products or the production of biomaterials.

Keeping in mind the properties that can be obtained from the chestnut shell and the products or services that the market may need, a brainstorming session of which needs of the market and the chestnut sector could be “solved” through the use of the chestnut shell occurred. The bio-oil extracted from the pyrolysis of this biomass can be used as a partial substitute of phenol in phenol-formaldehyde resins to apply on polymers or wood. From this process, two other products can be produced: biofuel and activated carbon. Through a variety of extraction methods, phenolic compounds could be obtained and microencapsulated to give antioxidant properties to food, for example, in the cheese industry (Gonçalves et al. 2020). The next idea consisted of producing a substrate for agricultural use. The combination of a bio-polyurethane resin with the sawdust from the chestnut tree can create a composite panel. Lignin could be used as a component of packaging film, providing UV protection and antioxidant properties. The adhesive characteristic of tannins may be useful for the creation of glue for polymeric and wood materials. The combination of the chestnut tree leaves, an epoxy resin and cotton may lead to a bio leather. Finally, chestnut shell biomass could lead to an improved extraction resource of ellagic acid, which is needed in the pharmaceutical industry.

3.2. Selection

So as to select the best idea, a selection matrix was developed with rationalized parameters and respective scores; the three top ideas and their scores are in Table 1. Table S.1, in the Supplementary Information, presents the full matrix. Different weights were attributed to the parameters considered for the calculation of the scores according to the relative importance that seemed more adequate given the current state of the market. Each parameter will therefore be followed by the respective percentage of weight on the scores. The first parameter to be analyzed was scientific maturity (10 %), which was evaluated based on the number of articles that came up on Scopus when searching for the main process involved in each idea; innovation (10%), from the number of articles obtained by searching the keywords that describe each product. In order to evaluate the engineering (25%), factors such as demand, technology, materials availability, cost, and rules that limit product commercialization need to be considered. Another parameter was the environmental impact (25%) of the product and its production. To finalize, the market (15%) and its competition (15%), or in other words, its availability in the market and competition with other products and brands. The superior weight of the environmental impact and engineering criteria derived from the author's view since the goal was to make a product that reduces the environmental impact of the waste of the chestnut industry that is feasible.

The three top ideas with the highest scores were the bio-PF resin, the ellagic acid extraction and the bio leather.

The bio resin is produced based on pyrolysis and the synthesis of phenol-formaldehyde, processes that are well studied, low cost and have a low environmental impact (Yu et al. 2023). The protection from UV radiation allows it to be distinguished from other bio resins in the market. The PF resin has been used for years; however, with the growing demand for greener products, the necessity for bio resins rises. On the other hand, since there is a high demand, there are already a lot of options in the market.

The extraction of the ellagic would be based on supercritical fluid extraction (SFE), which is a process well studied but more expensive than pyrolysis. This process would be different from those in the market since the ellagic acid is extracted from chestnut shells, needing less raw material for the same quantity of extract. The SFE technique is known for being a green method but could have a higher water and energy consumption. Moreover, there is no high demand for it in the current market (An et al. 2021).

The bio leather consists of wetting the leaves, overlapping, and drying them after applying a layer of resin with cotton. It is a green technique that is well studied and comes as a necessity to substitute traditional and toxic leather production. The main disadvantage is its industrialization. Bio leather is, in fact, a sustainable product, however the scalability of its production is not as practical as bio resin's. Additionally, the market demand for a 'greener' resin is higher than for a bio leather or an improvement of ellagic acid extraction. The list of useful, desirable, and essential needs for the top three ideas is listed below (Table 2).
After debating these three ideas, the bio-PF resin was the best option.

Product/Process	Scientific Maturity (10%)	Innovation (10%)	Engineering (25%)	Environmental impact (25%)	Market (15%)	Competition (15%)	Total
Bio-PF resin	7	8	9	9	8	5	8.0
Bio Leather	9	8	5	10	8	3	7.1
Ellagic Acid extraction	7	6	9	7	4	6	6.8

Table 1: Selection matrix and parameters and respective scores for the top 3 ideas.

Product	Useful	Desirable	Essential	Raw material quantity
Bio-PF resin	Easy application Longer storage time	Versatile	Good adhesion UV protection Rain protection Low toxicity	7.15 kg of chestnut shell / kg of resin
Bio Leather	Resistance to water and stains Good breathability	Good durability	Sustainable production Low toxicity	660 g of leaves / kg of bio leather
Ellagic Acid extraction	Decrease the process environmental impact	Much cheaper than the standard process	High purity	4.64 g of ellagic acid / kg of chestnut shell

Table 2: List of useful, desirable and essential needs for the top three ideas and respective raw material quantity needed for its production.

4. Product

The selected product was chosen by analyzing the scores from Table 1 and identifying the product with the highest score, which was the bio-PF resin produced from chestnut shells. This bio resin can be used as a coating or adhesive agent for wood-like materials (Jia et al. 2020; Pienihäkkinen et al. 2023). It consists of formaldehyde that is mixed with bio-oil produced from the pyrolysis of chestnut shells together with some phenol to transform the formaldehyde into its reticulated form. In order to increase the viscosity of the mixture, water and butanol solvents are added (Pienihäkkinen et al. 2023). The composition of this resin is specified in the Supplementary Information in Table S.2. This way, the resin has good adhesion (Pienihäkkinen et al. 2023a; Mao et al. 2018). In comparison with the common PF resins, this product has a longer storage time due to the polyphenols from the bio-oil that work as antioxidants. The resin gets UV protection properties from the compound lignin and has a lower toxicity since it uses a lower quantity of phenol than it would use if the bio-oil were not incorporated (Xu et al. 2022; Sadeghifar et. al. 2020). Therefore, it represents a valuable substitute for the PF resin currently on the market. The main advantage of Resinut is the fact that it has similar chemical and physical properties but better price competitiveness (Yu et al. 2023), while decreasing the use of the non-renewable resource, petroleum. Besides, the production of bio-oil through fast pyrolysis allows fast biomass decomposition and is easy to scale up with no further environment complications (Jia et al. 2020). The production of secondary products such as biogas and char could be used to feed pyrolysis, leading to a self-sustained process with low energy consumption. This possibility was not further studied in this report, however it is a possibility for future studies.

On the other hand, the product, Resinut, is only theoretical, therefore, it wasn't studied how the different organic components in the bio-oil, such as phenols, ketones, aldehydes, acids and sugars, can affect the resin's structure and properties (Yu et al. 2023).

5. Manufacture

The manufacture of the selected product was based on the study of Pienihäkkinen et al. (2023) and Misailidis & Petrides (2021), which involves the production of bio-oil through fast pyrolysis and its separation, so lignin bio-oil is obtained. In the end, phenol formaldehyde resin is synthesized by substituting 40 % of the phenol for bio-oil. The raw material is provided by Sortegel (2023).

5.1. Biomass treatment

The biomass that arrives from Sortegel is assumed to contain 40 % moisture, according to Misailidis and Petrides (2021), and must be dried. Since the purpose would be to buy all the raw material at once, 1500 ton per year, the chestnut shells would be dried during the first four weeks after its arrival and then stored in a silo until use. When needed, before proceeding to bio-oil production, the biomass must go through a crushing process to reduce the size of the particles.

5.2. Pyrolysis

As mentioned above, the process used to produce the bio-oil is fast pyrolysis. Pyrolysis is the thermal decomposition of biomass into gas, liquid and solid. Fast pyrolysis maximizes the production of liquid or bio-oil. The biomass is heated so rapidly that it reaches the peak temperature before it decomposes (Basu 2010). The pyrolysis reactor would operate at atmospheric pressure and be heated using natural gas, with a reaction temperature of 500 °C. Table 3 shows a summary of the pyrolysis reaction as defined by (Pienihäkkinen et al. 2023).

The full reaction with the specific components is indicated in Table S.3 of Supplementary Information.

Reactant		Products
100 CSS biomass	5.81	HMW lignin
	1.18	Lignin extractives
	17.3	Char
	8.79	CO
	0.925	CO_2
	1.39	H_2
	11.70	Water
	13.36	Cellulose
	25.4	Lactic Acid
	14.15	others

Table 3: Pyrolysis reaction (weight percentage).

The pyrolysis products would go through a cyclone to separate char from the pyrolysis gases. The bio-oil would be separated from the non-condensed vapors through a flash tank at 85 °C.

5.3. Bio-oil separation

Hypothetically, the bio-oil composition that results from the flash tank is not ready for resin synthesis. Therefore, the bio-oil should be mixed with water in a proportion of 1:0.65 (Pienihäkkinen et al. 2023). The water-soluble phase, in the initial stage of the project, wouldn't be used in our process, and it is disposed of. However, its implementation could be further studied to have a higher bio-oil yield. The non-soluble phase, also designated lignin bio-oil, would move on to the next step.

5.4. Resin synthesis

In a reactor at 80 °C, the bio-oil would be mixed with phenol in a mass proportion of 1:1.5 (Pienihäkkinen et al. 2023). Theoretically, the mixture of phenol and bio-oil reacts with formaldehyde and NaOH in a mass proportion of 5:6:1, respectively (Pienihäkkinen et al. 2023) and forms a primary bio resin with high viscosity. Thus, a solvent consisting of water and n-butanol (70:30 wt%) (Pienihäkkinen et al. 2023) would be mixed in. Besides lowering the viscosity, this solvent is predicted to allow a longer storage time. The expected final product would consist of a bio resin of phenol formaldehyde, with 0.038 % of free formaldehyde.

6. Process Simulation

Following the manufacturing plan, the process to produce the bio-PF resin was carried out using the process simulation software *SuperPro Designer* version 13 (Intelligen 2022). The operation would be semi-continuous, which means that the process would restart every workday; however, the process would remain continuous during that day. All the biomass would be dried during the first 4 weeks of activity. On the second and third days, the production of bio-oil and resin would finally start.

6.1. CSS biomass drying

This section would dry all the CSS biomass to handle throughout the year of activity and the process, whose diagram is shown in Figure 1, would work for 7 hours a day for 4 weeks. The incoming stream, with a mass flowrate of 75 ton/day, containing about 40 % moisture (Misailidis and Petrides 2021), was split (FSP-101) into 4 streams and fed to a rotary dryer (RDR-101 and 102). Indeed, the diagram shows only two streams and two dryers; however, for the defined time and flow rate, four units would be needed, so the software automatically defined them. The outlet moisture content was set at 8 %, and the dried biomass had a temperature of about 95 °C. These were fed into a solid's storage (SL-101 and 102), via a screw conveyor (SC-101 and 102). The dryers were set with a specific evaporation rate of 14.85 (kg/h)/m^3, and the power consumption of 75 kW per dryer.

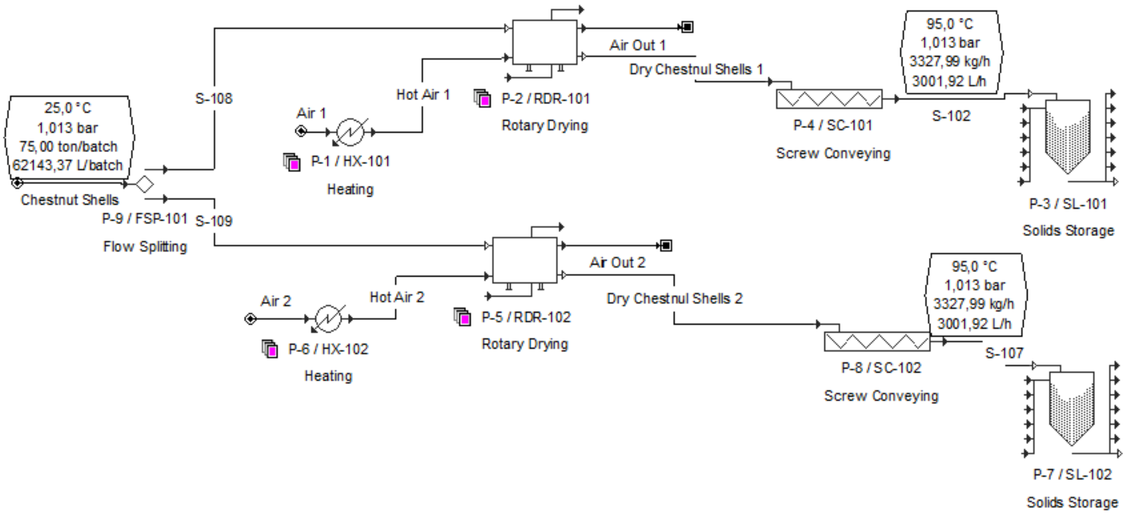


Figure 1: Flow diagram of the simulation in *SuperPro Designer* of Chestnut Shells Biomass Dry.

6.2. Production of lignin bio-oil

Before proceeding to the pyrolysis, 6 ton/day of dried biomass would be split into 2 streams and fed into shredders (SR-101 and 102), as represented in Figure 2. They are set to be mixed again and fed into the pyrolysis reactor, simulated with a generic box (GBX-101), via a screw conveyor (SC-101). The final temperature set for the reaction was 500 °C at atmospheric pressure, and the reactor would be heated using natural gas. The pyrolysis products, which are found in Table S.3 of the Supplementary Information, must go through a gas cyclone (CY-101) to separate the char from the pyrolysis gases. To separate the non-condensable gases from the bio-oil, the gaseous stream at 501.1 °C goes through a condenser, modeled as a heat exchanger (HX-101). The outlet stream at 85 °C would enter a flash tank (V-101), obtaining the biogas and bio-oil streams. As said before, the bio-oil would be mixed with water in a MX-102 and then, to obtain the final lignin bio-oil, separated in an oil separator (OS-101). The water-soluble bio-oil was discarded, and the water non-soluble bio-oil stored in V-102. The composition of the lignin bio-oil stream is found in Table S.4 of Supplementary Information. The power consumption of every equipment is as described in the article by Misailidis & Petrides (2021).

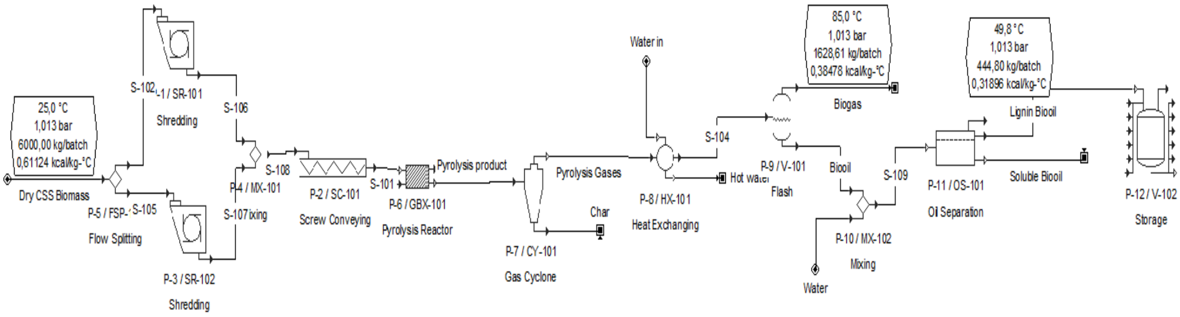


Figure 2: Flow diagram of the simulation in *SuperPro Designer* of Lignin Bio-oil Production.

6.3. Bio-PF resin synthesis

The lignin bio-oil that would be obtained from the last section, 444.8 kg/day, was separated in a splitter (FSP-101) in 2 streams that were fed into a reactor, simulated with batch generic boxes (BGBX-101 and 102), Figure 3. The reactors had a power consumption of 0.05 kW/m^3. According to the proportions mentioned before, the bio-oil stream was mixed with a charge of phenol to create a phenol/bio-oil mixture. After that, the reactor was fed a charge of formaldehyde and NaOH so that the reaction would occur and the primary resin would be generated. Next, a charge of n-butanol and water entered the reactor, promoting the formation of the final bio-PF resin. At the end of the day/batch, after transferring all the resin, the reactors would be washed. The final resin would have a percentage of 0.038 wt% of free formaldehyde, with a conversion percentage of 95.99 %. The final step would be packaging the resin for sale in barrels of 20 kg (FL-101 and FL-102). Table S.2 in the Supplementary Information presents the full composition of the product obtained as a result of the carried out simulation. The expected amount of resin produced per day would be of 840.8 kg.

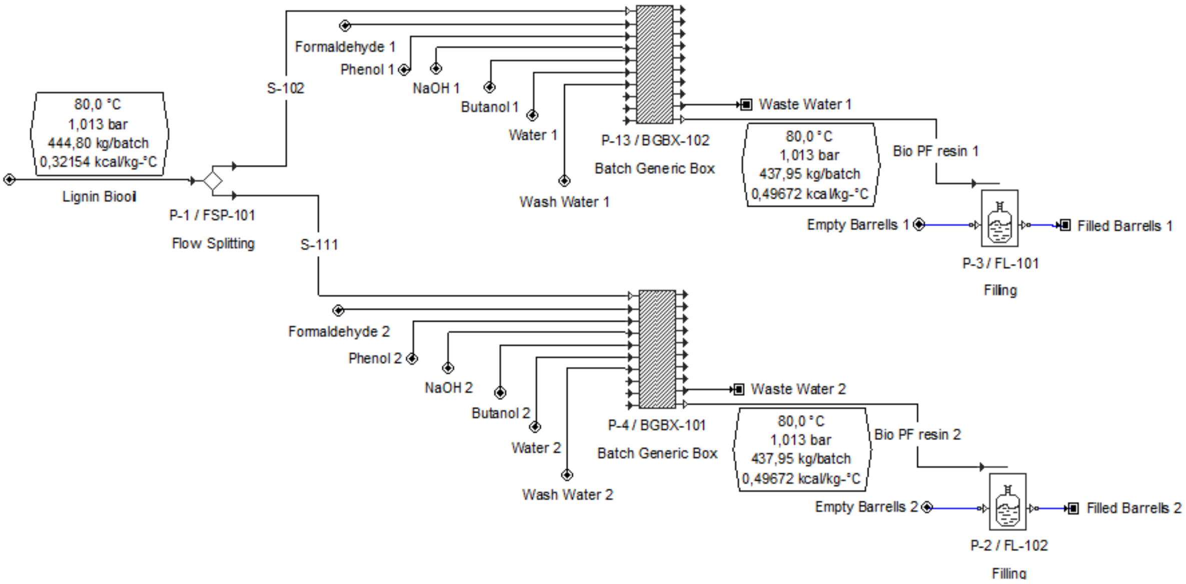
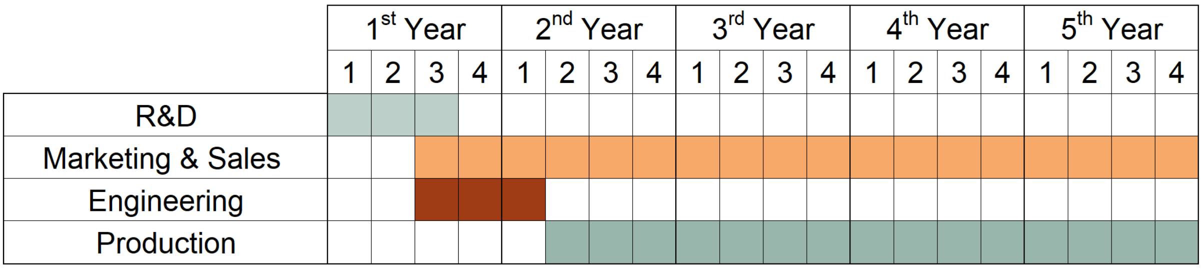


Figure 3: Flow diagram of the simulation in *SuperPro Designer* of Bio-PF Resin Production.

7. Economic analysis

The bio-PF resin production project adopts a "Business to Business" (B2B) approach. The raw material is planned to be bought from Sortegel, as mentioned, and transported to the company manufacturing plant, which is based in Mirandela, Bragança, bought at 275,000 € with an estimation of 200,000 € worth of restoring. The business is expected to function 250 days a year, 8 hours per day. The resin production would last 7 hours per day, with one extra hour for initialization of the factory or washing of the reactors at the end of the day.

The economic assessment of the project considers a 5-year return period. Figure 4 contains the Gantt chart showing the project involvement for the 5 years since the beginning of the company and production (marketing/sales, research/development, engineering, and production).



	1st Year				2nd Year				3rd Year				4th Year				5th Year			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
R&D	🟩	🟩	🟩																	
Marketing & Sales			🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Engineering			🟫	🟫	🟫															
Production						🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

Figure 4: Gantt chart for 5 years since the beginning of the company and production.

7.1. Production Costs

7.1.1. Raw materials

The production of each barrel with 20 kg of resin relies on 142.9 kg of dried chestnut shells to produce bio-oil. Additionally, the manufacturing of this primary resin involves utilizing 17.3 kg of phenol (CAS 108-95-2), 34.6 kg of formaldehyde (CAS 50-00-0) and 5.8 kg of sodium hydroxide (CAS 1310-73-2). The separation process of bio-oil consumes 0.44 m^3 of water. Furthermore, the primary resin is blended with an aqueous solution, containing 8.3 kg of n-butanol (CAS 71-36-3) and 0.02 m^3 of water.

The cost of each of these materials is shown in Table 4. All these factors culminate in a cost of 7.27 € per kilogram of resin, which translates to a cost of 145.36 € per barrel of bio resin.

Materials	Cost (€/kg)	Cost per barrel (€/20 kg)
Barrel	0.11	2.18
Butanol	0.34	6.80
CSS biomass	2.85	57.00
Formaldehyde	2.11	42.20
NaOH	0.17	3.40
Phenol	1.66	33.20
Water	0.03	0.58

Table 4: Cost of materials used in the production of bio-PF resin.

7.1.2. Manufacture process

The simulation software *SuperPro Designer* gives the cost of the equipment, fuel, electricity, and water consumption for the manufacturing process. The total initial cost of equipment needed to produce the bio resin is 4,022,000 € and the cost of utilities, per kilogram of resin and per barrel, are detailed in Table 5.

Utility	Cost (€/kg)	Cost per barrel (€/20 kg)
Electricity	0.07	1.38
Natural Gas	0.07	1.39
Water	0.01	0.14

Table 5: Cost of utilities.

This sums up to a cost of 0.15 € per kilogram of resin, which translates to a cost of 2.90 € per barrel, just from utilities.

The personnel cost must also be included. Table 6 presents each position, salary, and respective number of employees.

Position	Salary (€)	Nº of employees
Management	3000	2
Administrative	920	1
Commercial	1200	2
Operational	820	5
Others	1000	4

Table 6: Number of employees and salary for each position within the company.

7.2. Sales Volume and product cost

The selling price of the resin was set at 9.50 € per kg, ensuring a profit margin of 30 % relative to the production cost. The sales expectation is 100 % of the quantity produced per year, 210 ton. Since the business approach is B2B, the resin is going to be sold in 20 kg barrels, which means 190 € per barrel.

7.3. Financial results

The economic analysis was performed using the business plan simulator provided by IAPMEI, 2020 in order to evaluate the viability of the project. After evaluation of different economic parameters, it was established that, since the profit margin is not very high, different investments would be made during the 6 years. The initial investments would be of 4 and 3 M€ for the first and second years, respectively, and of 2 M€ for the next four years.

Figure 5 presents the cash flow and accumulated cash flow through the first six years. Proceeding with the final calculations, the project’s NPV is 3.4 M€, the Payback time is 3.8 years, and the internal rate of return (IRR) is 36 %. It’s important to mention that these values are calculated based on the residual value after the six years.

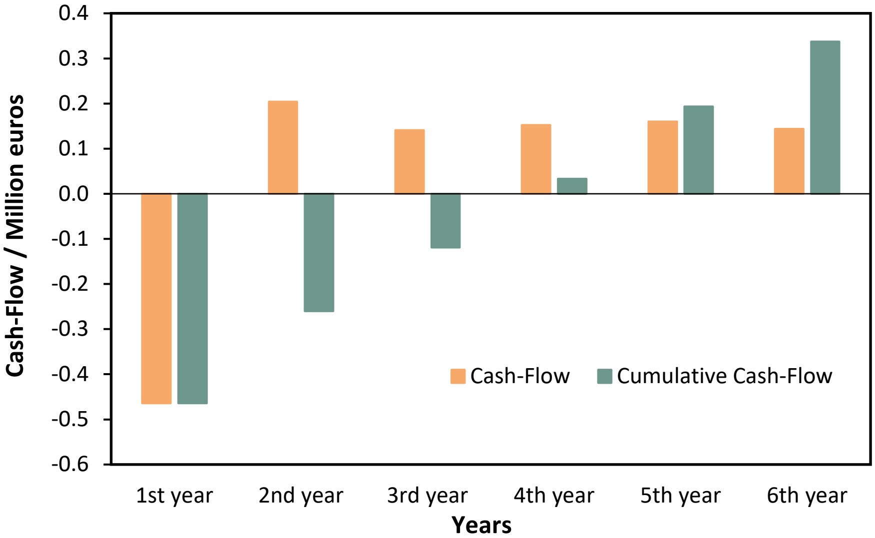


Figure 5: Cash-flow and cumulative cash-flow during the six years of the project.

To compare the company's costs with the predicted revenues, the total cumulative costs and cumulative revenues were calculated and shown in Figure 6. It is possible to notice how revenues surpass the costs, which is a positive indicator. Unfortunately, this difference is not as significant as expected.

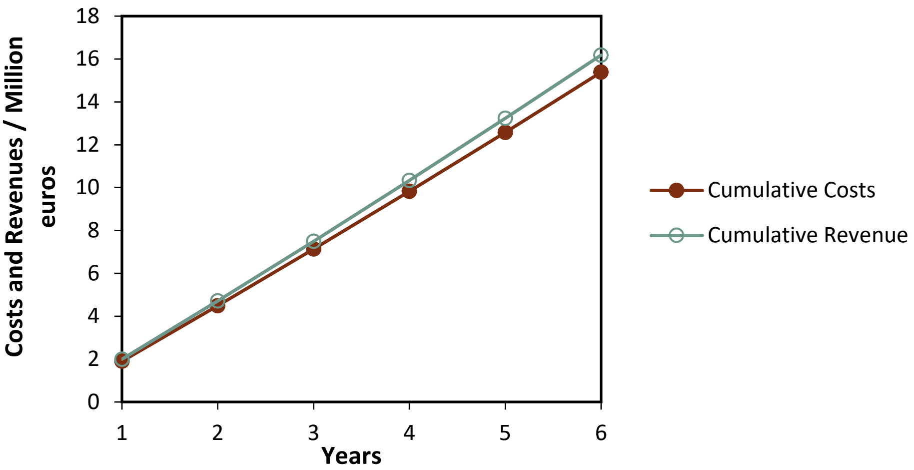


Figure 6: Predicted cumulative costs and revenues of the company during the six years of the project.

In conclusion, the project has a positive NPV and a feasible payback time. However, it is suggested the continuation of the study on how to produce more resin per year, since the low productivity results in a fluctuation of the cash-flow and, consequently, in the need for further investment and/or selling price increase.

8. Conclusions

The objective of this project was the production of a bio-PF resin with the use of chestnut shells. Considering the balance between environmental awareness and technological innovation, this project emerged as a way of reducing sustainability problems associated with the chestnut sector itself and serve as a response to market needs. Furthermore, this project appears as another useful alternative to the use of chestnut shells and a way to increase the chestnut sector, through innovation and increased fruit production.

Nowadays, PF resins are widely used, but the search for ecological options is increasingly gaining ground. These resins involve a significant percentage of phenol, a toxic substance that comes from fossil fuel sources. With the production of bio-PF resin, the global need for phenol in PF resin is reduced, by replacing a considerable percentage of phenol with a bio-oil obtained from chestnut shells, the resource to fossil fuels is reduced and one of the residues from chestnut processing, its shell, is used. This contributes to reducing the environmental impact of phenol and of the chestnut industry.

Bio resin, along with several secondary processes, is essentially produced from the pyrolysis of chestnut shells and the synthesis of phenol formaldehyde. Bio-oil is extracted through pyrolysis, which will replace part of the phenol that would be used in a common resin.

Due to its composition, bio-PF resin is easy to apply and versatile. Bio-PF adheres well to wood and polymers, protecting their surfaces and acting as a coating, including a waterproof coating. Furthermore, compared to bio resins already on the market, the bio-PF resin has UV protection properties from the lignin compound present in chestnut shells. Compared to common PF resins, it has a lower toxicity due to the incorporation of bio-oil and has a longer storage time due to the polyphenols present in the bio-oil that act as antioxidants.

It should be noted that the production of bio-PF resin has the main advantage of reducing the use of petrol, a non-renewable resource. On the other hand, in order to minimize waste in the process, an alternative needs to be studied in the laboratory to reduce the loss of water when discarding the water-soluble bio-oil and thus make more use of the raw material. Another suggested study would be the feasibility of producing secondary products such as biogas and bio char to feed the pyrolysis. This is in order to lower energy consumption and, if possible, make the process energy self-sustaining.

With 1500 ton/year of chestnut shells, it is expected to have a production of 111.2 ton/year of bio-oil and, consequently, 210.2 ton/year of bio-PF resin. If the final cost of the resin is 9.50 €/kg, the NPV of the project is 3.4 M€, leading to an IRR of 36 % and a payback time of 3.8 years. At a more advanced stage of our process, we could find more suppliers of raw materials so that we can increase production.

In conclusion, the project is feasible, however it is suggested the revision of how to increase the productivity of resin synthesis and the search for alternatives to reduce the waste of raw materials and further reduce energy consumption, for example, implementation of recycles of char and biogas.

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Supplementary Information

Selection Matrix

Product/Process	Scientific Maturity (10%)	Innovation (10%)	Engineering (25%)	Environmental impact (25%)	Market (15%)	Competition (15%)	Total
Bio-PF resin	7	8	9	9	8	5	8.0
Bio Leather	9	8	5	10	8	3	7.1
Ellagic Acid extraction	7	6	9	7	4	6	6.8
Food antioxidant	8	6	2	8	8	9	6.5
Agricultural Substrate	9	5	10	3	6	5	6.3
Activated charcoal	9	6	9	4	6	5	6.4
Biofuel	10	8	5	7	6	1	5.9
Composite panel with bio-PU resin	5	6	7	4	6	4	5.4
Film Packaging with UV protection	8	6	7	8	5	5	6.7
Tannin adhesive	5	7	8	7	7	2	6.3

Table S.1: Selection matrix, parameters and respective scores for the top 10 ideas.

Compositions of streams and products

Components	wt%	Components	wt%
1,2-Cyclopentanedione	0.0003	Guaiacylacetone	0.0048
2-Propanol	0.0001	Hexanoic Acid	0.0001
3-Methylcatechol	0.0020	HMW lignin	1.4559
4-Ethylguaiacol	0.0032	Hydroquinone	0.0041
4-Methylcatechol	0.0103	5-Hydroxymethylfurfural	0.0029
4-Methylsyringol	0.0002	Hydroxyphenylethanol	0.0101
5-Methylfurfural	0.0001	Isobutyric Acid	0.0001
Acetic acid	0.0006	Isoeugenol	0.0161
1-Hydroxy-2-propanone (acetol)	0.0004	Lactic Acid	0.0147
Acetylguaiacol	0.0047	Levoglucosan	0.0007
Bio-PF Resin	1.5032	Unidentified LMW compounds in LMW lignin	0.0428
n-Butanol	0.0597	Unidentified LMW compounds in sugar fraction	0.2120
Catechol	0.0103	3-Methylphenol (m-Cresol)	0.0001
Cellobiosan	0.0001	NaOH	1.0272
Cellobiose	0.0001	Nonadioic acid	0.0050
Coniferylaldehyde	0.0151	Oleic Acid	0.0101
4-Methylguaiacol	0.0103	4-Methylphenol (p-Cresol)	0.0001

2-Methylphenol (o-Cresol)	0.0001	Pentanoic acid	0.0001
Dihydroconiferyl alcohol	0.0050	Phenol	2.5561
Dilignols	0.0126	Pimaric acid	0.0731
Ethylene Glycol	0.0001	Primary Bio Res	92.7554
Eugenol	0.0067	Unidentified component (defined as cellulose)	0.0138
Formaldehyde	0.0380	Vanillic acid	0.0076
Glycolaldehyde (dimer)	0.0012	Vanillin	0.0125
Guaiacol	0.0044	Water	0.0857

Table S.2: Composition of the final bio-PF resin.

Products	wt%	Products	wt%
1,2-Cyclopentanedione	0.02	Coniferylaldehyde	0.06
1,4-Anhydro-3-deoxypentitol-2-carboxylic acids	0.10	HMW lignin	5.81
1-Hydroxy-2-butanone	0.13	Dihydroconiferyl alcohol	0.02
1-Hydroxy-2-propanone (acetol)	1.44	Dilignols	0.05
2,5-Dihydroxypentanoic acid	0.05	Ethyleneglycol	0.08
2-Acetylfuran	0.02	Eugenol	0.04
2-Butanone (metil etil cetona)	0.01	Furfural	0.11
2-Furanmethanol	0.02	Glycolaldehyde (dimer)	4.61
2-Methylphenol (o-Cresol)	0.01	Glycolic acid	0.11
2-Propanol	1.26	Guaiacol	0.11
2-Propanone (acetona)	0.05	Guaiacylacetone	0.02
3-Methyl-1,2-cyclopentanedione	0.10	H2	1.39
3-Methylcatechol	0.01	Hexanoic acid	0.02
3-Methylphenol (m-Cresol)	0.01	Hydroquinone	0.02
4-Ethylguaiacol	0.02	Hydroxyphenylethanol	0.04
4-Methylcatechol	0.05	Isobutyric acid	0.01
4-Methylguaiacol	0.11	Isoeugenol	0.14
4-Methylphenol (p-Cresol)	0.02	Lactic acid	25.40
4-Methylsyringol	0.01	Levoglucosan	1.25
5-Hydroxymethylfurfural	0.20	Methanol	0.36
5-Methylfurfural	0.01	Nonadioic acid	0.02
Acetaldehyde	0.11	Oleic acid	0.04
Acetic acid	3.68	Pentanoic acid	0.01
Acetylguaiacol	0.02	Phenol	0.02
Butyric acid	0.04	Pimaric acid	0.29
Catechol	0.05	Propionic acid	0.22
Cellobiosan	0.17	Syringol	0.04

Cellobiose	0.02	Unidentified LMW compounds in LMW lignin	0.17
Char	17.3	Unidentified LMW compounds in sugar fraction	0.84
CO	8.79	Vanillic acid	0.03
CO2	0.92	Vanillin	0.16
Unidentified component (defined as cellulose)	13.36	Water	11.70

Table S.3: Pyrolysis reaction (weight percentage) for 100 CSS biomass.

Components	**wt%**	**Components**	**wt%**
1,2-Cyclopentanedione	0.0006	Glycolaldehyde (dimer)	0.1342
1,4-Anhydro-3-deoxypentitol-2-carboxylic acids	0.0029	Glycolic acid	0.0032
1-Hydroxy-2-butanone	0.0038	Guaiacol	0.2322
2,5-Dihydroxypentanoic acid	0.0015	Guaiacylacetone	0.2484
2-Furanmethanol	0.0006	Hexanoic Acid	0.0006
2-Propanol	0.0367	HMW lignin	72.1589
3-Methylcatechol	0.1242	Hydroquinone	0.2484
3-Methyl-1,2-cyclopentanedione	0.0029	5-Hydroxymethylfurfural	0.0058
4-Ethylguaiacol	0.1664	Hydroxyphenylethanol	0.4968
4-Methylcatechol	0.6210	Isobutyric Acid	0.0003
4-Methylsyringol	0.0003	Isoeugenol	0.7998
5-Methylfurfural	0.0003	Lactic Acid	0.7394
Acetaldehyde	0.0032	Levoglucosan	0.0364
Acetic acid	0.1071	Unidentified LMW compounds in LMW lignin	2.1114
1-Hydroxy-2-propanone (acetol)	0.0419	Unidentified LMW compounds in sugar fraction	10.4326
2-Propanone (acetona)	0.0015	3-Methylphenol (m-Cresol)	0.0003
Acetylguaiacol	0.2484	2-Butanone (metil etil cetona)	0.0003
Butyric Acid	0.0012	Methanol	0.0105
Catechol	0.6210	Nonadioic acid	0.2484
Cellobiosan	0.0049	Oleic Acid	0.4968
Cellobiose	0.0006	4-Methylphenol (p-Cresol)	0.0006
Coniferylaldehyde	0.7452	Pentanoic acid	0.0003
4-Methylguaiacol	0.5328	Phenol	0.0006
2-Methylphenol (o-Cresol)	0.0003	Pimaric acid	3.6017
Dihydroconiferyl alcohol	0.2484	Propionic Acid	0.0064
Dilignols	0.6210	Syringol	0.0012

Ethylene Glycol	0.0023	Unidentified component (defined as cellulose)	0.3912
Eugenol	0.3328	Vanillic acid	0.3726
2-Acetylfuran	0.0006	Vanillin	0.6160
Furfural	0.0032	Water	2.1272

Table S.4: Lignin bio-oil stream composition after oil separation.