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Effect of enzymatic treatment (endo-glucanases) of fiber and mechanical lignocellulose nanofibers addition on physical and mechanical properties of binderless high-density fiberboards made from wheat straw

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ABSTRACT

Fiberboards are used in a variety of applications that can be for interior as well as for exterior. However, their production involves the consumption of virgin wood fibers and the use and production of formaldehyde-based adhesives, with the consequent impact on the environment and health. The removal of these adhesives results in a significant loss of physico-mechanical properties. To confront these major problems, the use of wheat straw, an agricultural waste, as raw material for the production of binderless fiberboards has been explored. As an alternative to synthetic adhesive, enzymatic treatment of fiber and lignocellulose nanofibers (LCNFs) addition, as well as their combination, have been studied. The different treatments produce an important increase in the mechanical properties in front of the untreated fiber and commercial fiberboard, being the combination of both which presents the best results. Separately, the enzymatic treatment produces a greater strengthening effect than the addition of LCNF. In terms of structural stability, the addition of LCNFs and treatment combinations shows the best results for water absorption and thickness swelling. The results obtained show the possibility to obtain fiberboards without synthetic adhesives with mechanical properties far superior to commercial fiberboardsas as such as bending strengths higher than 100 MPa, flexural modulus 5.5 GPa, internal bond 1.6 MPa, and 122.52 kJ/m^2 of impact strength with an estimated added cost of 1 €/m^3.

1. Introduction

The production of fiberboard is usually based on wood or other lignocellulosic fibers combined with an adhesive, bonded together under heat and pressure to form panels [1]. The role of adhesives is the transfer and distribution of loads between components, increasing the strength and modulus of the final material. The effectiveness of the stress transfer between the components depends of the strength and number of bonds generated [2]. The adhesion system is generated by two mechanisms, mechanical and chemical. This mechanical adhesion increases when the adhesive can penetrate the fibers. On the other hand, the bonds formed between adhesive and fibers, although they can be covalent, are mostly from van der Waals's forces, dipole-dipole forces, and hydrogen bonds. In this sense, the generation of bonds is conditioned by the surface chemical composition of the fibers. The presence of extractives on the surface of the fibers interferes with the formation of these bonds, generating poorly bonded areas [2]. During the 20th century, adhesives for fiberboard production were developed from synthetic organic polymers obtained from petrochemicals and natural gas. Synthetic thermoset adhesives such as phenol-formaldehyde, resorcinol-formaldehyde, melamine-formaldehyde, urea-formaldehyde, isocyanate, and epoxy adhesives have been traditionally used. The presence of synthetic adhesives in the fiberboard production process is intended to give these materials optimal mechanical and physical properties for their final application [3]. Formaldehyde-based resins are the most widely used adhesive in the industry due to their low cost, water-solubility, ease of use, thermal properties, low cure temperature, and high performance [4,5]. About 90% or more of the world's fiberboard production is produced with these resins [6]. The implementation of the REACH regulation (EC N° 1907/2006) in 2007, obliges countries

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to evaluate the possible health and environmental consequences of certain substances. In 2012, formaldehyde is included in the community rolling action plan (CoRAP), which prioritizes and plans the evaluation of substances over 3 years. Its inclusion was due to its effect on human health (CMR properties), exposure/wide dispersive use, worker exposure, and high aggregate tonnage. Finally, in 2014, after its evaluation, formaldehyde has been classified as carcinogenic category 1B according to the CLP Regulation (N° 605/2014). It shows that the exposure of the human body to large doses of formaldehyde can result in a high risk of poisoning, and exposure for prolonged periods in the occurrence of cancer [7]. The use of these resins not only harms workers during the production and curing process but also produces formaldehyde emission to the atmosphere and the environment during the exposure of these fiberboards in their final application, especially in high moisture and high-temperature conditions [8,9]. It results in the reversibility of amino-methylene bonds, the instability of the methylene ether bridges, and their hydrolysis during panel production and lifetime use. Therefore, the use of some chemicals such as formaldehyde resins in building materials has been shown to be harmful to the environment and human health [10].

This regulation under the global approach of sustainability that the current society must take requires the development of boards free of these synthetic adhesives that are not bio-based, not biodegradable, and that are also dangerous for the environment and human health. In this sense, the development of formaldehyde-free adhesives from renewable sources such as lignin, soy protein, wheat protein, and starch has been investigated during the last years [11–14]. However, their high cost and limited performance limit their industrial application at present [15,16]. In the last years, the use of the wet-forming process has gained attention to develop products that do not require binders or that reduce their need considerably [17–21]. Fiberboards produced with this process have certain disadvantages compared to the conventional dry-forming process, such as low density and limited strength [22]. It is due to the low adhesion between fibers during the formation process. Therefore, for the production of self-bonded and all-lignocellulosic fiberboard, several pretreatments techniques have been developed to increase the fiber-fiber bonding capacity for the fiberboard production [9], such as steam explosion [23], electromagnetic radiation [24], chemical pretreatments, or enzymatic pretreatment [25]. The enzymatic pre-treatment is especially important among these pre-treatments. Its greater selectivity leads to a soft treatment, with less damage to the fibers and less generation of residues and by-products. The action of these enzymes on the fibers depends mainly on their nature (laccases, pectinases, cellulases, etc.), the accessibility of the fibers, and the pre-treatment conditions (temperature, pH, concentration, time, and enzyme dose) [18,20,26]. The use of endoglucanases as an enzymatic pre-treatment, which has been practically unexplored in the manufacture of fiberboard, has been shown to be effective in paper production. This treatment increases the bonding capacity of the fibers, increasing the mechanical strength of the final material [27]. On the other hand, during the last few years, nanotechnology has developed rapidly in many fields. In this sense, the use of cellulose nanofibers in the manufacture of fiberboards is presented as an alternative to the future. Specifically, lignocellulose nanofibers have the great advantages of being derived from renewable sources, being biodegradable and having a high specific surface area, and therefore a high bonding capacity. Therefore, the incorporation of these nanofibers should allow to significantly increase the mechanical properties of the fiberboards, without synthetic adhesives [28–30]. The increase in the bonding capacity of the fiber surface by the assisted action of enzymes and the high specific surface and mechanical properties of cellulose nanofibers, allow the partial or total replacement of synthetic adhesives maintaining or even increasing the properties of the fiberboards [17,19,20,28]. The use of synthetic adhesives is not the only problem facing the industry. The use of fiberboard is increasing annually due to the demand for fiber-based products rather than products coming from plastics or non-renewable sources [31]. Therefore, the increase in demand for fiber products has generated a higher demand for virgin fibers which can cause deforestation. For this reason, it is necessary to find alternative sources to produce fiberboard, as a substitute for wood fiber [32,33]. Alternative raw materials can be found due to its similar properties, in the agricultural residues [13]. To date, most of these agricultural residues are burned. This action is economically inefficient and environmentally dangerous due to the large number of greenhouse gases emitted, in addition to the non-use of these residues which have also cost resources to grow. Some of the main advantages of using this type of biomass are its easy renewal, recyclability, accessibility, biodegradability, and ecological compatibility. The transformation of these residues into different products with higher added value can lead to an improvement in the competitiveness of the agricultural and industrial sectors. The cost of fiberboards manufacture using waste biomass can reduce by half compared to those made from wood [34]. One of the most widely produced crops in the world, also in Europe, is wheat. In 2018, Europe produced 242 M tons of wheat, representing almost 50% of the total cereal production [31]. It is estimated that for the production of one wheat grain kg, between 0.8 and 1 kg of waste, like straw, is generated. Considering this relationship, it is estimated that approximately more than 200 million tons of wheat straw residue is generated annually in Europe. The medium and high-density fiberboard (MDF/HDF) production has increased over the last years (2010–2018) by approximately 59%, reaching 17.7 M m^3 [31]. Assuming an average density for MDF/HDF fiberboards of 800 kg/m^3, the demand for MDF/HDF in Europe could be fulfilled satisfied using wheat straw as raw material. An additional benefit of this is that the production of fiberboards from wheat straw contributes positively to reducing CO_2 pollution in the air.

The motivation for this work was the use of wheat straw as raw material to produce binderless high-density fiberboards (HDF) by applying two treatments. Enzymatic action (biobeating) and the addition of cellulose nanofibers (separately and in combination) have been studied to improve the intrinsic fiber-fiber bonding capacity and enhance the product properties in comparison with commercial fiberboard containing synthetic adhesives. The use of these two treatments on the same substrate allows a direct comparison of the suitability of each of them in fiberboard production according to the final properties of the product (physical and mechanical), as well as the advantages of their joint use. The use of this type of treatment in comparison with the industrial use of synthetic resins as compared from a technical and economic point of view. The effectiveness of the different treatments was analyzed according to their effect on the physical and mechanical properties as well as their water absorption and swelling capacity. The study carried out has shown how the use of cellulose nanofibers and enzymatic treatment allows achieving mechanical properties higher than the commercial fiberboards.

2. Materials and methods

2.1. Materials

The raw material used in this research was wheat straw (*Triticum* spp.). Wheat straws were provided by an independent farmer from Écija (Seville, Spain). Once collected, it was manually screened to remove unwanted objects and dried at a constant temperature. Subsequently, it was stored in plastic bags to maintain a constant humidity of around 9%. The reagents used in this work were: acetic acid (CH_3COOH); acetone (C_3H_6O); hydrochloric acid (HCl); sulfuric acid (H_2SO_4); sodium chloride (NaCl); sodium hydroxide (NaOH); sodium chlorite ($NaClO_2$), all of them provided by Sigma-Aldrich and used without further purification. The enzymatic cocktail used was Novozym 476, kindly provided by Novozymes A/S (Denmark), which contains 2% endo-β-1,4-glucanases with an activity factor of 4500 CNF-CA/g cellulose (tested over a CMC substrate).

2.2. Methods

The general flowchart of the experimental work is summarized in Fig. 1. Wheat straw was used as raw material to obtain cellulosic fiber. From these, lignocellulose nanofibers (LCNFs) were obtained to be used as a reinforcing agent on binderless fiberboards made from the cellulosic fiber themselves. In addition, the process of biobeating through the action of enzymes was also analyzed as a fiber treatment to produce binderless fiberboards. The joint action of both treatments, LCNF addition and biobeating, and their effects on the final properties of the fiberboards were also analyzed.

2.2.1. Wheat straw cellulosic pulp production

Wheat straw was subjected to a pulping process, optimized in previous works, suitable for the production of lignocellulose nanofibers (LCNFs) [35]. The pulping process consists of a soda pulping at 100 °C, for 150 min, 7% NaOH (over dry matter), and a liquid: solid ratio of 10:1. The pulp was washed with tap water, filtered, passed one time through a Sprout-Waldron refiner (model 105-A, Andritz, USA), and sieved to separate the uncooked material. The characterization of raw material and wheat straw pulp was determined according to the following standards: beating degree (TAPPI T-227), pulping yield (gravimetric method), α-cellulose (T-9m54), lignin (T-203os61), holocellulose (T-222), ash (T-211), ethanol extractables (T-204) and viscosity (ISO 5351:2010). The morphological analysis of the cellulosic fiber was carried out using a Morfi. About 30,000 fibers of a 1 wt% fiber suspension were analyzed by the software MorFi v.9.2. to determine the average fiber length and diameter, and fines percentage (fines limit detection of 76 μm).

2.2.2. Lignocellulose nanofiber (LCNF) production

Lignocellulose nanofibers were produced using exclusively mechanical processes. These processes consist of the combination of pretreatment using mechanical refining (PFI beater) until a Schopper-Riegler degree of 90 °SR is obtained, and subjecting a 1.5 wt% fiber suspension to mechanical treatment of high-pressure homogenization (GEA Panda 2000) following the sequence: 4 passes at 300 bars, 3 passes at 600 bars and 3 passes at 900 bars. The obtained LCNF suspension was stored in a refrigerator at 4 °C for its adequate conversation until use.

2.2.3. Characterization of the LCNFs

The obtained LCNFs were characterized in terms of their nanofibrillation yield, cationic demand, carboxyl content, specific surface, diameter, and length. The nanofibrillation yield was determined by centrifugation to isolate the nanofibrillated fraction, which remains in the supernatant, from the non-nanofibrillated or partially nanofibrillated fraction, which sediments. The sedimented fraction was dried to constant weight and weighted, and the yield was calculated according to the methodology reported by Besbes et al. [36]. The cationic demand was determined using a Mütek PCD 05 particle charge detector using the methodology described by Ref. [37]. The carboxyl content of the LCNFs was determined using conductometric titration. The titration curve showed three characteristic regions, the first one corresponds to the excess of acid, the second one to the neutralization of carboxylic groups, and finally the third region to the NaOH excess. The intersection point was calculated, and their values were used to determine the carboxyl content following the protocol described by Besbes et al. [36]. The cationic demand and carboxyl content values were used for the theoretical specific surface and diameter estimation. It was calculated assuming the two possible interaction mechanisms between the surface of LCNFs and the poly-DADMAC molecule. Estimating the surface area of a single molecule of poly-DADMAC is possible to calculate the surface of the LCNFs, and considering the cylindrical geometry of the fiber, it is possible to calculate their average diameter [37]. The intrinsic viscosity value determined according to the ISO 5351:2010, was used to calculate the degree of polymerization (DP) according to the methodology described by Marx-Figini [38]. The degree of polymerization was related to the length of the LCNFs by the relation established by Shinoda et al. [39].

2.2.4. Enzymatic treatment of cellulosic fibers

The enzymatic treatment (biobeating) of the cellulosic fibers was carried out by adapting the methodology described by Delgado-Aguilar et al., 2015 [40]. The process was conducted at a temperature of 65 °C, enzyme dosage of 350 g/Tn, pH 4.8, and pulp consistency of 8 wt%. The enzyme used in this work was a β-1,4-endoglucanase (Serzym 50) supplied by SERTEC-20 S.L. (Spain) and the treatment time was set at 30 min, 1 h, and 2 h. Once the treatment was completed, a 10% NaOH solution was added dropwise to increase the pH of the suspension, and

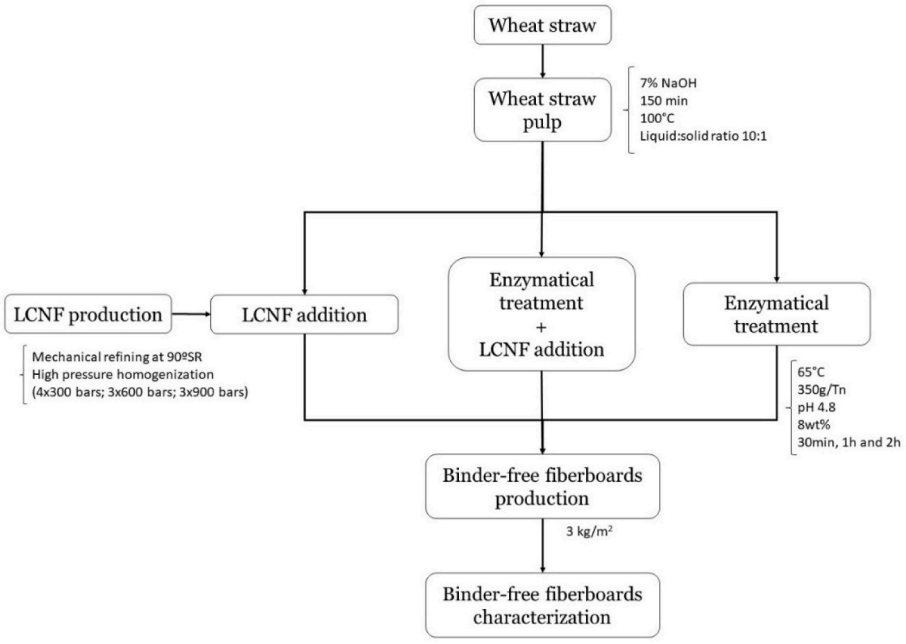

Fig. 1. General flowchart of the experimental process.

the temperature was increased to 80 °C to inactivate the action of the enzyme. Then, fibers were washed several times with water and stored at 4 °C.

2.2.5. Fiberboard production

The untreated wheat straw cellulosic fiber and enzymatic-treated fiber were used directly in the production of the fiberboards. The fibers were dispersed in a 50 L capacity pulper equipped with a helical rotor at 1100 rpm for a time of 10 min to ensure the proper fiber disintegration and distribution in water. The fiber suspension was filtered through a paper sheet former with a diameter of 30 cm to remove the excess water and retain the fiber material. The amount of fiber suspension was calculated to obtain a fiber web with a dry weight of 3 kg/m^2 based on commercial fiberboard density and mold dimensions. The fiberboards reinforced by cellulose nanofibers were prepared to add 5 wt% of LCNFs over the amount of fiber used (dry weight). Based on previous studies, the use of 5% LCNF has been used to obtain mechanical increases without compromising the technical and economic feasibility of the fiberboards. The specified amount of LCNFs (from the initial gel-like form) were added to the different fiber (untreated and enzymatic-treated) and dispersed in water in a disintegrator for 180,000 revolutions. Once fiber and LCNFs were dispersed together, 0.5 wt% of cationic starch and 0.8 wt% of colloidal silica were added to the suspension and stirred at 300 rpm for 20 min. These reagents were added as retention agents to ensure proper LCNF-fiber interaction and prevent losses of the nanometric materials during the fiberboard formation. After the process was completed, the suspension was filtered following the method explained above for fiberboard formation. The identification and treatment conditions of the different samples are summarized in Table 1.

The fiber web obtained was introduced into a stainless-steel mold and hot-pressed in a hot press machine Lab-Econ 300 (Fontijne Presses, Netherland). The pressing process was carried out following the conditions described by Dominguez-Robles et al. [21]. At first, the specimens were pressed for 3 min at 75 °C and a pressure of 8 MPa, reducing the humidity of the material to 50–60 wt%. Subsequently, the pressure was increased to 14 MPa for a further 5-min period to remove much of the remaining moisture. Once this point was reached, the pressure was decreased to initial levels (8 MPa) and the temperature was increased to 150 °C for 60 min. Thereafter, the temperature was gradually increased to 230 °C. The most efficient process to produce binderless fiberboards and have found that increasing the temperature to 230 °C allows a higher cohesion of the board. Although it is known that this temperature is above the cellulose degradation temperature, it has been found that there is no such degradation during the process, as its shown in Fig. 2a. Once the temperature was reached, the pressure was increased to 14 MPa and a decompression-compression-decompression cycle was performed for 5 min under the same conditions. The final product moisture was approximately 6–8 wt%. Fig. 2b shows the evolution of pressure and temperature during the fiberboard formation process.

Table 1
Overview of sample identification and treatments.

Sample identification	Treatment conditions
Commercial fiberboard	Commercial high-density fiberboard (HDF) containing synthetic adhesives [17]
Untreated	HDF from 100% untreated cellulosic fiber from wheat straw
5% LCNF	Addition of 5% LCNFs on untreated HDF
30′ Enz	HDF produced from enzymatic-treated fiber for 30′
30′ Enz + 5% LCNF	HDF produced from the combination of enzymatic (30′) and LCNF addition (5%) treatments.
1 h Enz	HDF produced from enzymatic-treated fiber for 1 h
1 h Enz +5% LCNF	HDF produced from the combination of enzymatic (1 h) and LCNF addition (5%) treatments.
2 h Enz	HDF produced from enzymatic-treated fiber for 2 h
2 h Enz +5% LCNF	HDF produced from the combination of enzymatic (2 h) and LCNF addition (5%) treatments.

2.2.6. Fiberboard characterization

The fiberboard was cut into 150 × 50 mm specimens with approximately 4 mm of thickness (80–85% moisture content) and were conditioned at 20 °C and 65% relative humidity (RH) before any physical or mechanical test were conducted, and the dimensions of the test pieces were determined according to the standards ISO 27769–1:2009 and ISO 27769–2:2009. The fiberboard specimens were characterized according to International Organization for Standardization. The apparent density was determined according to the standard ISO 9427:2003. The mechanical properties of the fiberboard were measured according to ISO 16978:2003 for the impact strength, flexural modulus, and flexural strength; and according to ISO 12466–1:2007 for the internal bonding. The water absorption and thickness swelling were determined according to the standards ISO 16979:2003 and ISO 16983:2003, respectively. The one-way ANOVA test was made with R. A confidence interval of 95% was used in order to compare the variables. Tukey test was used to evaluate the differences between groups.

3. Results and discussion

3.1. Wheat straw and fiber characterization

Table 2 shows the chemical composition of wheat straw raw material and cellulosic pulp obtained after the pulping process in comparison with other agriculture residues used for fiberboard production. Wheat straw shows a higher carbohydrate content (sum of hemicellulose and cellulose) than other agricultural residues previously used for HDF production such as banana brunch, sugarcane bagasse, canola straw, rice straw, and vine shoots. However, it shows a lower carbohydrate content compared to corn stalk. Concerning lignin content, all the agriculture residues compared in this work present a similar value (14–18%), except for the vine shoot which presents a higher lignin amount (24%).

To remove non-structural elements and to purify and improve the fiber-fiber bonding capacity of the lignocellulosic elements (lignin-lignin, lignin-carbohydrate, and carbohydrate-carbohydrate), wheat straw was subjected to soft conditions pulping process for remaining a residual lignin content and a great amount of carbohydrate content. A comparison of these chemical compositions revealed that the extractives and ash content decrease after the pulping process due to the partial solubilization of these non-structural components. Therefore, the carbohydrate fraction increased from 63.16% to 75.83% compared to the initial raw material. This is due to the purification of the α-cellulose fraction in the fiber, the remaining of a large part of the hemicelluloses, and the slight reduction of the lignin content. A high hemicellulose content and a residual lignin content is key to the use of a cellulosic fiber for obtaining lignocellulose nanofibers, as well as for use in fiberboards [45]. The use in this work of pulping process with soft conditions allows the obtaining of high process yield and the ideal chemical composition for these uses in comparison with other processes such as organosolv and kraft [35].

Fig. 3 shows the morphological distribution (length and width) for the untreated wheat straw cellulosic pulp. The obtained fiber shows a fiber length of 502 μm, higher than others cereal straws, such as oat and barley [46], and similar values than vine stems, corn stalk, and kraft Eucalyptus wood fiber [21]. Regarding fiber width (20.1 μm), it shows a similar range in comparison with other agricultural residues and hardwoods [17,41]. The fines content was 36.9%, in concordance of other agricultural residues, and higher than the industrial pulps used in the papermaking industry [13]. A high fines content can result in the production of fiberboards with high mechanical properties. The presence of virgin fines, with a good bonding capacity and a smaller size than fibers, allows greater interaction between fibers [20].

The action of the enzymes β-1,4-endoglucanases takes place on the

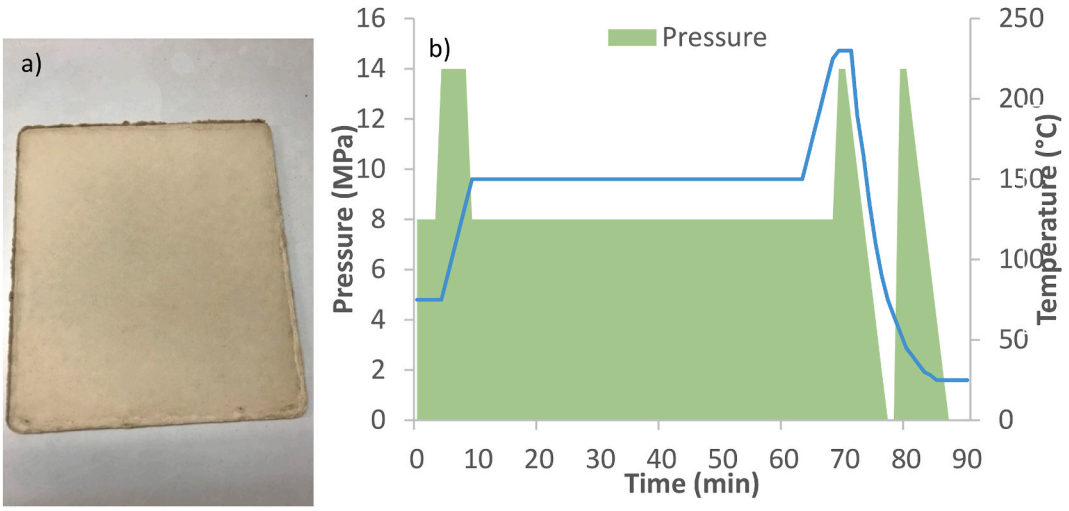

Fig. 2. A) Binderless fiberboard. B) Pressure and temperature evolution during the fiberboard formation process.

Table 2
Chemical compositions of different agriculture residues used for fiberboard production.

	EtOH Ext (%)	AQ Ext (%)	Ash (%)	α-cellulose (%)	Hemicelluloses (%)	Lignin (%)	Reference
Wheat straw	12.65	7.17	7.22	33.35	29.81	15.68	This work
Wheat straw pulp	6.22	4.83	3.72	50.88	24.95	9.91	This work
Banana brunch	2.76	14.81	12.36	51.01	17.10	14.28	[23]
Sugarcane bagasse	2.2	16.20	–	30.90	28.40	18.90	[41]
Corn stalk	3.1	–	3.2	44.00	33.00	16.00	[17]
Canola straw	8.12	–	6.21	41.10	–	17.16	[42]
Rice straw	3.72	–	22.19	39.63	20.54	13.92	[43]
Vine shoots	13.10	–	3.70	43.60	19.10	24.00	[44]

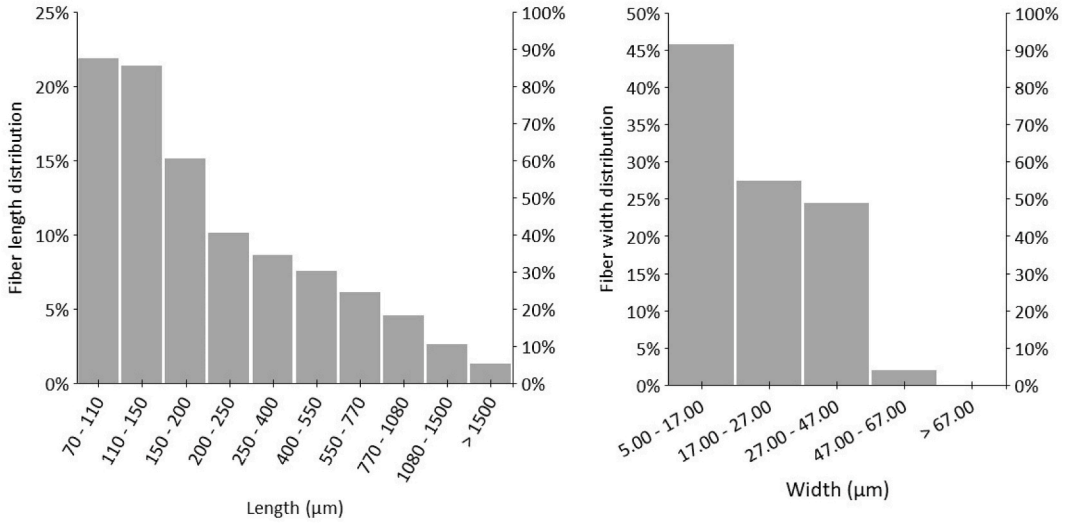

Fig. 3. Wheat straw fibers length and width distribution.

β-1,4 linkages of the cellulose chain, especially in the cellulose amorphous region. This enzymatic treatment (biobeating) produces the delamination of the cellulosic fibers producing its fibrillation, in a similar way to what mechanical beaters can produce. However, enzymes can lead to a gentler and more specific beating. An important concern with mechanical beating is the damage to the fiber if it is too severe, which can influence its physical properties. The use of enzymes facilitates the balance between the positive and negative aspects of beating. Mechanical beating requires a large energy requirement in comparison with the use of enzymes. For this reason, the enzymatic treatment for produce fibrillation and improve the fiber-fiber bonding capacity is gaining attention in the last years. After the enzymatic treatment, it is observed that the morphology of the fibers in terms of length and width does not vary significantly. However, if we considered the fines content, it shows how it increases to about 45.9% and 48.2% for the 1 h and 2 h treatments, respectively.

3.2. *Lignocellulose nanofiber characterization*

The high shear forces produced during the high-pressure

homogenization process, allow the destruction of the molecular hydrogen bonds between the cellulose chains and the delamination of the fibers to nanometric sizes. For instance, the mechanical pretreatment differs in its low cost, efficiency in nanofibrillation, the length of the resulting nanofibers, and the low size achieved. The high content of hemicelluloses present in wheat straw cellulosic pulp (24.95%) and the residual lignin content (9.91%) causes the hemicelluloses to inhibit the coalescence of cellulose fiber favoring the nanofibrillation process, and the lignin acts as an antioxidant preventing the union of previously broken bonds [47].

The yield of nanofibrillation of the lignocellulose nanofibers (LCNFs) obtained from the wheat straw cellulosic pulp (40.20%) was higher than other LCNFs obtained by mechanical treatments from agricultural residues (15–20%) [48]. However, the cellulose nanofibers obtained by TEMPO-mediated oxidation (TO-CNF) show values above 95% due to the greater nanofibrillation efficiency of this pretreatment [49]. The cationic demand and carboxyl content can be used to estimate the specific surface area and diameter of the lignocellulose nanofibers according to the methodology proposed by Espinosa et al. [37]. The cationic demand and the carboxyl content of the LCNFs were 338.97 μeq/g and 58.60 μeq/g, resulting in a specific surface area of 136.54 m^2/g. Assuming that LCNFs have a cylindrical geometry it is possible to calculate the diameter value from the specific surface area. In this case, the LCNFs present a value of 18.30 nm, lower than diameters reached by other cellulose nanofibers obtained by mechanical treatments and close to the nanometric values shown by the TO-CNF (17-5 nm) [50,51]. The use of mechanical pretreatment as opposed to the use of TEMPO-mediated oxidation or even enzymatic hydrolysis allows obtaining longer nanofibers. Molecular segments broken from amorphous regions are degraded by the strong oxidative effect during the TEMPO-mediated oxidation, degrading these cellulose regions into gluconic acid or small dissolved fragments by depolymerization and β-elimination. The length of the nanofibers is strongly related to the mechanical properties of the final composites made of cellulose or cellulose nanofibers [52]. The high specific surface area of the nanofibers obtained (136.54 m^2/g), allows the creation of a greater number of links between fibers and nanofibers. This high binding capacity results in an improvement of the physical and mechanical properties of the final products.

3.3. Mechanical properties of the binderless fiberboards

To study the suitability of the binderless fiberboard production from wheat straw, the mechanical properties of the untreated fiber and the different treatments, LCNF addition, enzymatic treatment, and their combination, were studied. The results of the mechanical properties of binderless fiberboards compared with commercial fiberboards are specified in Fig. 4. The flexural strength (FS), flexural modulus (FM), internal bond (IB), and Izod impact (IZ) of the untreated fiberboards show values of 52.79 MPa, 1850 MPa, 0.83 MPa, and 76.13 J/m, respectively. In comparison with commercial HDF with synthetic resins, the values obtained for untreated fibers show higher values for FS and IB. Nevertheless, the values of FM and IZ no longer show the values achieved by commercial HDF. Despite not using synthetic resins, the values achieved by wheat straw are quite close to those presented by commercial HDF. This is partly due to its high carbohydrate content, its residual lignin content, and its high content of fines compared to wood fibers used in industry [20]. These characteristics combined with the high pressures generated during the fiberboard formation, lead to the formation of covalent bonds between the lignin-carbohydrate, carbohydrate-carbohydrate, and lignin-lignin at fiber interfaces.

As can be seen in Fig. 4, regardless of the treatment used, the mechanical properties were improved concerning the fiberboard made of untreated fiber, and even to the values presented by commercial fiberboard using synthetic resin as a binder. Regarding FS, it is especially interesting to observe how the use of wheat straw with enzymatic treatment at 30 min reaches 68.46 MPa and produces a gradual increase until reaching 95.60 MPa for a 2 h treatment, representing 81.09% and 129.26% more than the values shown by untreated fiber and commercial HDF, respectively. On the other hand, the addition of 5% LCNFs also produces a significant increase in FS, reaching 62.93 MPa, being in this case also higher than those shown by untreated fiber (19.21%) and commercial HDF (50.91%). A similar trend is observed for FM and IZ, increasing these properties in each treatment. For the addition of LCNFs, a value of 2999 MPa and 95.75 kJ/m^2 is achieved for flexural modulus and Izod impact, respectively.

In the case of enzymatic treatment, the increase of FM and IZ, were more pronounced, reaching 3879 MPa and 113.68 kJ/m^2, with a treatment of 30 min. On the other hand, this increase is more pronounced in the 2-h treatment, reaching an increase of 158.20% and 82.63% for flexural modulus; and 97.04% and 73.76% for Izod impact,

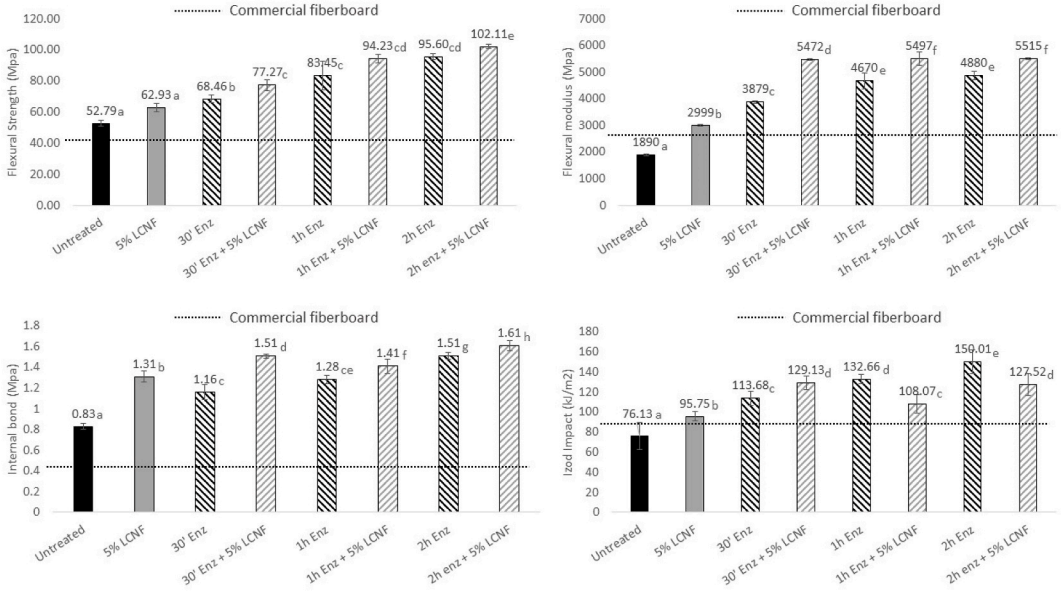

Fig. 4. Mechanical properties of wheat straw fiberboards (The commercial data were extracted from Theng et al. [17]).

to the untreated and commercial HDF, respectively. However, in the 2-h enzymatic treatment, it is possible to observe the stabilization of FM and IZ compared to the 1-h treatment. On the contrary, the addition of nanofibers allows a greater increase in the IB of the fiberboards (1.31 MPa) than by enzymatic treatment at 30 min and 1 h (1.16 and 1.28 MPA, respectively). This phenomenon is due to the smaller size of the cellulose nanofibers, which can be placed between the different layers of the filtering cake. In general, it is observed that the addition of small amounts of LCNFs (5%) produces a large increase in the mechanical properties of the fiberboards. On the other hand, the enzymatic treatment produces a gradual increase until reaching its maximum for the longest treatment (2 h). The maximum values reached for both treatments are higher than commercial fiberboards, so it is concluded that they are effective in improving the production of fiberboards. The combination of both treatments produces a significant improvement compared to the addition of LCNFs or enzymatic treatment separately. The improvement produced by the addition of LCNFs is due to several factors, such as their high intrinsic mechanical properties, their high specific surface resulting in enhanced formation of hydrogen bonds with adjacent fibers, the reduction of voids gaps between fibers due to tension forces, and LCNF contraction, and the homogeneous distribution of fibers. The optimal content of LCNFs was defined as 5%, since from this value there is a saturation phenomenon of the binding capacity between the LCNFs and the fibers of the fiberboards, decreasing the mechanical properties for higher contents [17]. With the enzymatic treatment, it can be seen noticed how the hydrolysis of the fiber, its higher exposure, and the generation of fines produce an improvement in the final properties of the fiberboards. However, when the enzymatic treatment is carried out for more than 2 h, it is observed how excessive hydrolysis is produced, causing a significant decrease in the degree of polymerization of cellulose, and therefore producing a negative effect on the mechanical properties [20].

When the combination of both treatments was analyzed it was obtained that for the resistance to flexion the increase produced practically linear reaching 102,11 MPa for the enzymatic treatment of 2 h and the addition of a 5% of LCNFs. This value means that the FS of the binderless fiberboards obtained is 144.86% higher than the commercial ones. These values would allow the incorporation of mineral fillers, reducing the consumption of fibers, while maintaining properties higher than commercial fiberboards [53]. In contrast, the values obtained by combining an enzymatic treatment of only 30 min and the addition of 5% LCNFs are practically at the same level as in the combination of both treatments for longer enzymatic treatment times. This seems to indicate that the stabilization of these values observed during the increased biorefining time is accentuated by the addition of LCNFs. In general terms, it can be concluded that the combination of both treatments leads to the highest mechanical properties of fiberboards.

Table 3 shows how there are differences in the density of the fiberboards produced, especially by the increase when LCNFs are added. It was determined that the density has a direct relation with the mechanical properties that materials show, therefore, to eliminate this variable in the analysis of the properties of the fiberboards. The determination of the density allows the calculation of the specific mechanical properties of the fiberboards produced. The similarity of the densities of all samples (850–920 kg/m^3) does not show trends contrary to those observed in the analysis of the absolute mechanical properties, so the effect of each of the treatments on the improvement of these properties is confirmed.

3.4. Physical properties of the binderless fiberboards

Water absorption (WA) and thickness swelling (TS) are two fundamental parameters to analyze the dimensional stability of the fiberboards. Fig. 5 shows the evolution of water absorption for the different fiberboards as a function of immersion time. Two data of special interest can be extracted from this analysis, the short water absorption (2 h) and the long water absorption (24 h). It is observed that for untreated fiber a value of 87.59% is reached for a short period and a value of 102.93%. The values shown for wheat straw fiberboards are higher than those shown for commercial fiberboards containing synthetic resins, which attain a water absorption value of 80% for 24 h [17]. For fiberboards produced from enzymatic-treated fiber, there is a similar trend as fiberboards from the untreated fiber. However, a decrease in water absorption is observed when LCNFs are added or when both treatments are combined. For boards reinforced with LCNFs, it is observed as the water absorption is 72.24% and 101.26% for 2 h and 24 h, respectively. It is therefore concluded that the addition of LCNFs to the fiberboard composition, in addition to improving the mechanical properties, slowed down the water absorption of the material but did not reduce it over long periods. This fact is observed to a greater extent when both treatments are combined, regardless of the time used, reaching values around 65% and 85% for 2 h and 24 h, respectively, slowing down and decreasing in this case the absorption of water.

Fig. 6 shows the thickness swelling values of the different samples of fiberboards for different periods. The fiberboards from untreated fibers show an increase of the thickness after the immersion of 44.36% and 54.98% for 2 h and 24, respectively. Contrary to what was observed for water absorption, the swelling values presented by commercial HDF (66%) are higher than those presented by untreated fiber [13]. The production from enzymatic-treated fiber produces a decrease in the swelling capacity of the fiberboards showing a value for 24 h around 45%. In addition, it is observed that this behavior does not improve or worsen when the time of the enzymatic treatment is increased. The addition of LCNFs does not lead to a decrease in the swelling of the fiberboards, showing values like the obtained for the untreated fiber. However, the combination of both treatments produces a similar decrease in this parameter than that produced by the enzymatic treatment. These values not only show a better behavior than commercial HDF but also lower values than many others described in the literature by several authors [17,44,54–57].

Table 3
Results of the mechanical properties of fiberboards. Different letters a, b, c, d, and e represent the statistical difference (ANOVA, $P < 0.05$) between the properties of the materials.

Samples	ρ (kg/m^3)	FS/ρ (MPa·m^3/kg)	FM/ρ (MPa·m^3/kg)	IB/ρ (MPa·m^3/kg)	Izod/ρ (J·m^2/kg)	Elong (mm)
Commercial*	893.10 ± 19.00	0.047 ± 0.001	2.99 ± 0.03	$5.26{\cdot}10^{-4} \pm 2.47{\cdot}10^{-5}$	$9.6{\cdot}10^{-2} \pm 0.2{\cdot}10^{-3}$	–
Untreated	849.25 ± 12.16a	0.062 ± 0.002a	2.23 ± 0.04a	$9.77{\cdot}10^{-4} \pm 3.53{\cdot}10^{-5}$a	$8.9{\cdot}10^{-2} \pm 1.6{\cdot}10^{-3}$a	2.94 ± 0.06a
5% LCNF	896.64 ± 9.33b	0.070 ± 0.003a	3.34 ± 0.05b	$14.6{\cdot}10^{-4} \pm 5.58{\cdot}10^{-5}$bc	$10.7{\cdot}10^{-2} \pm 4.9{\cdot}10^{-3}$e	2.69 ± 0.03a
30′ Enz	851.03 ± 5.12a	0.080 ± 0.003b	4.56 ± 0.06c	$13.6{\cdot}10^{-4} \pm 8.23{\cdot}10^{-5}$b	$13.3{\cdot}10^{-2} \pm 8.2{\cdot}10^{-3}$c	3.34 ± 0.20ac
30′ Enz + 5% LCNF	902.58 ± 3.67bc	0.086 ± 0.004bc	6.06 ± 0.03e	$16.7{\cdot}10^{-4} \pm 2.22{\cdot}10^{-5}$d	$14.3{\cdot}10^{-2} \pm 7.3{\cdot}10^{-3}$c	3.29 ± 0.04 ab
1 h Enz	891.28 ± 8.11b	0.094 ± 0.011cd	5.24 ± 0.34d	$14.4{\cdot}10^{-4} \pm 4.49{\cdot}10^{-5}$bc	$14.9{\cdot}10^{-2} \pm 5.2{\cdot}10^{-3}$d	3.18 ± 0.43a
1 h Enz + 5% LCNF	913.38 ± 1.9cd	0.103 ± 0.003de	6.02 ± 0.27e	$15.4{\cdot}10^{-4} \pm 7.66{\cdot}10^{-5}$c	$11.8{\cdot}10^{-2} \pm 1.9{\cdot}10^{-3}$b	2.98 ± 0.05a
2 h Enz	897.01 ± 4.71b	0.107 ± 0.002e	5.44 ± 0.17d	$16.8{\cdot}10^{-4} \pm 3.34{\cdot}10^{-5}$d	$16.7{\cdot}10^{-2} \pm 1.3{\cdot}10^{-3}$e	4.06 ± 0.83c
2 h Enz + 5% LCNF	918.48 ± 3.68d	0.111 ± 0.001e	6.00 ± 0.03e	$17.5{\cdot}10^{-4} \pm 5.44{\cdot}10^{-5}$b	$13.8{\cdot}10^{-2} \pm 1.2{\cdot}10^{-3}$c	3.94 ± 0.32bc

FS: Flexural strength; FM: Flexural modulus; IB: Internal bonding; Izod: Impact test; Elong: Elongation at break. The commercial data were extracted from Theng et al. [17].

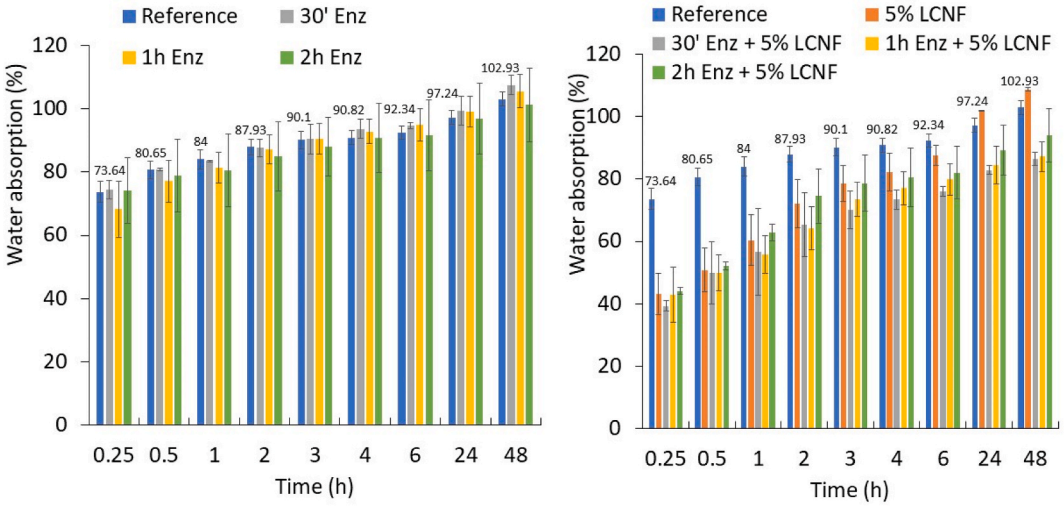

Fig. 5. Water absorption evolution of fiberboards. The reference data were extracted from Theng et al. [17].

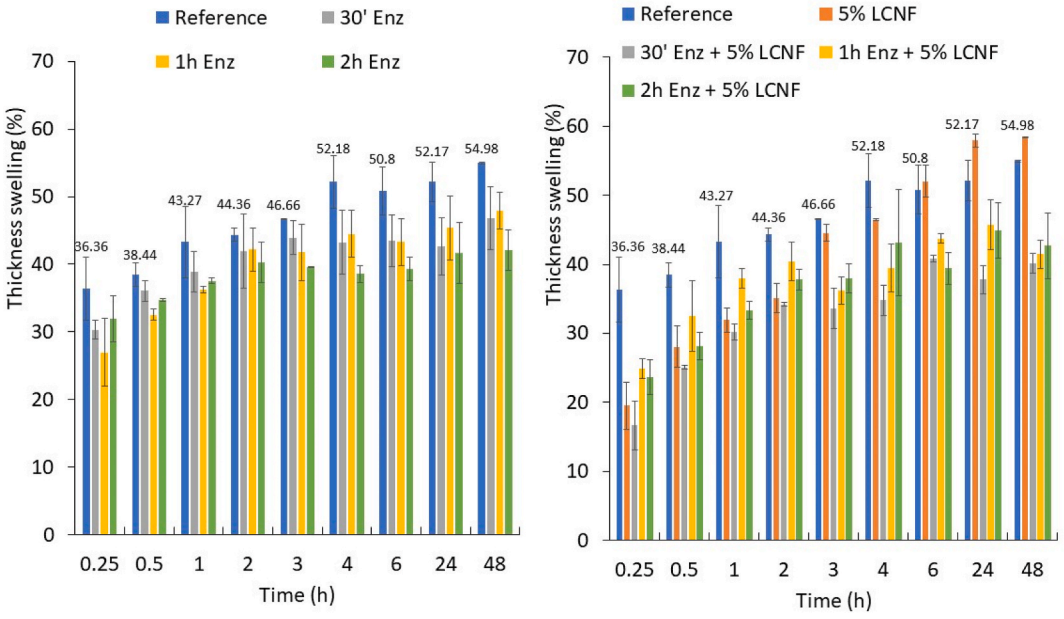

Fig. 6. Thickness swelling evolution of wheat straw fiberboards The reference data were extracted from Theng et al. [17].

3.5. Economics and sustainability considerations

The estimation of cost and environmental impact should be key elements in the evaluation of the manufacturing processes of any product.

The approach of the economic study of binderless fiberboard manufacturing technologies found in the literature focuses mainly on the profitability of using alternative resources to wood; however, no studies have been found that rigorously analyze the substitution of synthetic adhesvies by enzymatic treatments and/or the addition of cellulose nanofibers. The economic feasibility of using agricultural residues as a fiber source for binderless fiberboard was reported by Uitterhaegen et al. [58], who reported that the use of coriander straw for the production of binderless fiberboard using the twin-screw extrusion process resulted in a low total cost ranging from 0.44 to 0.46 €/kg. This highlights a possible competitiveness of these raw materials against commercial fibers (hardwood and softwood) that are typically around 0.50 €/kg [58].

To evaluate the economic viability of the incorporation of these treatments, the added cost for their manufacture has been estimated. In the absence of industrial data, laboratory prices have been taken as a reference, assuming an energy cost of 0.08 €/kWh.

Table 4 shows the production cost for 1 kg of fiber for enzymatic treatment (1.07 €/kg) and the production of 1 kg of LCNF (2.24 €/kg). The application of both treatments would therefore lead to an increase of 1.03 €/m^3. However, the current cost of urea-formaldehyde resin of approximately 0.3 €/m^3 should be discounted for an addition of 18% [4]. This leads to an increase in the production cost of fiberboard of approximately 0.74 €/m^3. Assuming an approximate cost of 3.01 €/m^2 of commercial fiberboard, the use of these treatments as a replacement for synthetic adhesives would represent 0.17% of the final cost. It is therefore feasible in advance to incorporate these treatments for the production of fully bio-based, biodegradable, and environmentally sustainable fiberboards.

The environmental impact of panel manufacturing is mainly due to its high energy consumption and environmental pollution through the emission of formaldehyde and volatile organic compounds, in addition

Table 4
Enzymatic treatment and LCNF addition cost for a fiberboard production.

Treatment	Chemicals (€/kg of fiber)	Enzymes (€/kg of fiber)	Energy (€/kg of fiber)	Price (€/kg of fiber)	Fiberboard added cost (€/m^3)	Fiberboard added cost (€/m^2)
Enzymatic treatment	0.12	0.71	0.24	1.07	0.93	0.0047
LCNF addition	–	–	2.24	2.24	0.10	0.0005
TOTAL					1.03	0.0052

to the subsequent disposal of the product. In addition, the construction sector plays a very important role in the global environmental scenario and can reduce its environmental impact considerably with the introduction of more sustainable materials.

Life Cycle Assessment (LCA) is a methodology capable of assessing the environmental impact of products, covering raw material procurement, processing, product manufacturing, marketing and end-of-life. Some authors have studied the environmental impact related to the manufacture of fiberboard without binders. González-García et al. developed binderless fiberboard by means of an enzymatic treatment using laccase, demonstrating their industrial viability [59]. Freire et al. evaluated the environmental impact of binderless MDF and HDF and compared their results with commercial boards using urea-formaldehyde binder [60]. They demonstrated the superiority of binderless fiberboards in most environmental impact categories (climate change, acidification, land use, particulate matter, water depletion and freshwater eutrophication). However, the study also shows the need for improvements in the production system of these binder-free boards when mass allocation is the criterion applied in the product modeling system. The analysis carried out by Freire et al. highlights the need to reduce the impacts of fiber transportation and processing.

In this regard, the literature is still too limited to draw adequate conclusions. For this reason, more studies are needed that take into account environmental impact and circular economy principles.

Despite their potential, there are few examples of the application of binderless fiberboards in the building materials market. The lack of information from economic and environmental studies of the manufacturing processes of these products makes it difficult to have a clear idea of the competitiveness of these products in the market. To break this gap, future studies should be aimed at improving the physical characteristics of binderless fiberboards, finding new ways of sustainable use of these products, studying the economic competitiveness of these materials in the construction market (including the influence of raw material and production technology), and studying the environmental impact and benefits compared to current commercial fbierboards.

4. Conclusions

Wheat straw cellulose pulp was used for high-density fiberboard (HDF) production. The replacement of formaldehyde-based resins was explored by the use of different enzymatic treatments and lignocellulose nanofibers (LCNFs) addition. Compared to commercial HDF with synthetic resins, the values obtained for untreated fibers show higher values for Flexural strength (52.79 Mpa) and Internal bond (0.83 MPa). However, the values for Flexural modulus (1890 Mpa) and Izod impact (76.13 kJ/m^2) do not reach the values obtained for commercial HDF (2697 Mpa and 85.74 kJ/m^2, respectively). The different treatments produce an increase in the mechanical properties, however, the effect produced by enzymatic treatment is more intense, reaching the maximum values for 2 h treatment. The combination of both treatments was found to produce a significant improvement compared to each treatment separately. The increase in properties obtained, mainly bending strength (102 MPa) indicates that it is possible to reduce the grammage of the fiberboards produced to obtain the same properties as a commercial board. In this sense, the reduction in grammage would lead to lighter fibreboards with the same properties. The water absorption is higher for untreated (97%) and enzymatic treated (96–99%) wheat straw fiberboard than for commercial fiberboard containing synthetic resins (80%). On the other hand, the addition of LCNF slows down the water absorption but it does not decrease over long periods, reaching similar values to untreated fiber at 24 and 48 h. However, when treatments are combined, water absorption for the short and long periods is observed, showing values (82–89% of water absorption) close to the ones shown by commercial boards. The thickness swelling showed by untreated fiberboards (55%) was lower than that of commercial HDF (66%). In addition, enzyme-treated fiber leads to a decrease in this property, similar to the produced by the treatment combination (37–44%). The analysis of the physical and mechanical properties shown by the boards manufactured by the different technologies studied reveals that the combination of both treatments (30 minutes of enzymatic and 5% addition of cellulose nanofibers) results in fiberboards with better mechanical properties and greater structural stability, even surpassing current commercial boards. Despite their potential, more in-depth studies of the economic and environmental approach to the production processes of binderless fiberboards are required to analyze their competitiveness in the market.

Credit author statement

Eduardo Espinosa: Investigation and Methodology **Quim Tarrés:** Investigation, data curation, and Writing – original draft**, Dyna Theng:** Investigation, methodology, formal análisis, and writing-review**, Marc Delgado-Aguilar:** Supervision, resources, project administration, and writing-review**, Alejandro Rodríguez:** Supervision, validation, Writing – original draft, Writing – review & editing.**, Pere Mutjé:** Supervision, resources, project administration, and writing-review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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