NEW WOOD FOAM-HEAT INSULATING MATERIAL OBTAINED THROUGH OAK WOOD-DELIGNIFICATION PROCESS

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ABSTRACT: A technique for manufacturing wood heat-insulating material for construction (known as wood delignification) without seriously affecting the cellulosic structure was inspired by the practices of the pulp and paper industry and adapted to the mentioned purpose. Among the numerous known methods of chemical treatment of wood for removing the lignin in the paper industry, the use of the suspension generated by mixing of NaOH, $Ca(OH)_2$, and distilled water at 260 °C in an electric oven was adopted. For the first time, oak wood (recycled in the form of sawdust) was chosen as the basic raw material in the wood delignification process due to its large availability in Romania's climatic conditions. Using 58 % oak wood, 23.3 % NaOH, 16.7 % $Ca(OH)_2$, and water addition, the best product had very low values of density (0,024 $g \cdot cm^{-3}$) and heat conductivity (0.031 $W \cdot m^{-1} \cdot K^{-1}$) as well as an acceptable value of compression resistance (0.9 MPa) for construction applications.
KEYWORDS: wood delignification, heat-insulating, oak wood, chemical treatment, density, heat conductivity.

1. INTRODUCTION

Natural cellulosic framework derived from wood through complete or partial removal of lignin without damage the initial wood structure is a process known as delignification of this plant [1]. Lignin, cellulose, and hemicellulose that make up the biomaterials structure, so including the wood of trees, are polymers with properties and behaviour similar to those of artificially made polymers. Among the three mentioned components, lignin has amorphous three-dimensional structure, with extremely branched form. It is known that the moist lignin of wood softens at approx. 100 °C, facilitating the molecule deformation in cell walls [2].

The old, well-known applications of wood (in construction as well as for the industrial manufacture of pulp and paper) are largely dependent on the behaviour of wood lignin. The lignin removal is the main operation of the pulp and paper manufacturing process, except for turning the biomass into liquid biofuels [1].

According to the forecasts issued in the work [3], biomaterial-based insulation could reach a global market value of US$ 229 million, representing an annual growth rate of 23.1 % starting from 2022. Due to CO_2 capture capacity, good durability and mechanical resistance, large availability in nature, and processing ability in the form of high-performance materials, wood is an attractive biomaterial [4]. In the form of by-product of some wood processing operations, sawdust is available in large amounts with low economic value and difficult methods for eliminating unused resources.

Recently, the manufacture of insulating materials based on biomass (in particular, wood waste) under ecological conditions and thermal efficiency has started to be carried out. According to [5], wood waste panels were made by hot pressing and assembly with vinyl and floor glue binder. Another method of manufacturing thermal insulation from wood waste by wet spraying and loose-fill methods without binder [6] was experimentally applied. The use of high proportions of binding materials or the low size of wood pores caused relatively high thermal conductivity values to be reached (up to 0.084 $W \cdot m^{-1} \cdot K^{-1}$). The creation of additional small voids through chemical treatment was proposed [7] to reduce the thermal conductivity (at 0.026 $W \cdot m^{-1} \cdot K^{-1}$).

The solution adopted and tested by Siciliano et al. [8] was based on the delignification of wood chips technique aiming at diminishing the density and implicitly heat conductivity of the material as an effective alternative to the usual thermal insulation in construction. Thermal conduction through the solid walls of wood cells represents the predominant type of heat transfer. By removing the lignin between the neighbouring channels of wood material, the conditions are created for the partial blocking of heat transfer. Thus, delignified wood shavings are adequate for diminished heat transfer. Additionally, the delignification creates a larger surface of the cellulose facilitating the formation of a stable froth. The density of delignified wood decreased compared to ordinary wood from 0.087 to 0.053 $g·cm^{-3}$. The heat conductivity was very low (0.038 $W·m^{-1}·K^{-1}$) and the compression strength had a satisfactory value (1.1 MPa). The manufacturing process consisted of mixing poplar wood chips with carboxymethyl cellulose (CMC) powder as an adhesive binder and deionized water. The mixture was heated at 100-150 ℃ in a hot plate stirrer for 8 hours.

Researchers from Fraunhofer Institute for Wood Research (Germany) have designed and tested a new froth material based on renewable resources replacing the traditional petroleum-oil based froths [9]. The new material has been achieved for heat insulation in lightweight construction. The manufacturing method involved the use of finely ground beech wood fibers and deionized water mixed together until a suspension was formed. This has been expanded by chemical or physical methods, dangerous emissions due to adhesives being excluded. As a result, a porous material with open pore structure and low density within the limits of 0.04-0.25 $g·cm^{-3}$ was obtained. Next, the product was processed in the form of hard froth panels or elastic froth. Building insulation materials manufactured of wood are already known in the world, but they have the disadvantage of low dimensional stability. The new type of wood-insulating material has compression strength (for 10 % compression amounted) in the range of 20-600 kPa, being influenced by the density value. Heat conductivity level was lowered below 0.04 $W·m^{-1}·K^{-1}$, the values being comparable to those of polystyrene insulation boards. The dimensional stability of this product was achieved. The fire resistance was experimentally determined, being similar to that of insulating materials made of natural wood fibers, but additives for fire protection can be easily added to the starting mixture.

Removing the lignin from wood-biomass known in the literature as delignification is one of the main fractionation methods used in the industrial manufacture of pulp and paper as well as in biorefineries. As also stated in other works [2], the main role of wood lignin is to hardening the material. Delignification-based fractionation was grouped into several delignification types: alkaline, acid, reductive catalytic fraction, etc. In the paper [1], the delignification processes used in present in the paper industry are presented. Alkaline delignification techniques include kraft, sulfite, and soda pulping, aqueous alkaline pretreatment, aqueous fiber & extraction, anhydrous ammonia pretreatment & extraction, and ammonia recycle percolation. The acidic delignification techniques are based on flow-through dilute acid preheating, flow-through hot water pretreatment, steam explosion pretreatment & extraction, organosolv pulping, and formaldehyde-assisted fractionation. The reductive catalytic techniques contain reductive catalytic fractionation. Other used techniques are ionic liquid dissolution organosolv pulping, and mechanical pretreatment & extraction. Alkaline techniques involve temperatures between 40-210 ℃ and the use mainly of NaOH (respectively, NH_3 in the case of ammonia pretreatment). Acid techniques require temperatures between 80-240 ℃ and use of H_2SO_4, HCl, water, organic solvents, etc. The reductive catalytic fractionation technique involves temperatures in the range of 180-250 ℃, redox catalyst, and organic solvents. Unlike the techniques mentioned above, the technique based on mechanical pretreatment and extraction is performed at room temperature and consists of extensive ball milling.

Delignification under alkaline conditions mentioned above is the most frequently used technique for removing lignin in biomass. The solubility of lignin increases significantly in the alkaline medium due to the deprotonation (removal of a proton such as H^+) of phenolic OH groups. The breaking of lignin-carbohydrate bonds is achieved in alkaline mediums, leading to increasing the fragmentation and degradation of lignin. In the current work, the aqueous alkaline pretreatment used in manufacturing process of paper was adopted for the oak delignification (temperature range of 40-160 ℃ and aqueous mixture including NaOH, $Ca(OH)_2$ and water).

The technique of improving the thermal insulation properties of biomaterials (such as wood) through delignification for construction applications is a new technique, although its basic principle is inspired by the technology of industrial paper manufacturing. The originality of the work presented below consists in the choice for the first time of oak wood as raw material and the adaptation of manufacturing recipe in an alkaline medium to this biomass type.

2. MATERIALS AND METHODS

2.1 Materials

Oak wood was chosen as woody material for experimental manufacturing the porous thermal insulation product through delignification. The reason for this choice was the high availability of this biomaterial as well as the fast growth of the tree.

In concordance with [10], the lignin contain of oak wood is between 22-29 %, while hemicellulose contain is in the range of 19-30 %, and cellulose reaches higher values (38-46 %). Raw material was recovered in form of sawdust from a wood-working workshop. Its mechanical processing was performed by fine grinding in a ball mill to sizes less than 80 µm.

The chemical treatment of wood-based raw material was performed using an aqueous mixture composed of NaOH, $Ca(OH)_2$ and distilled water. In general, the role of NaOH content is to reduce the material density and to increase the open porosity. Usually, NaOH, commercially available in form of solid pellets soluble in water, is used in foaming processes of solid powders dissolved in distilled water. The adopted concentration of NaOH solution was 1.6 $mol \cdot L^{-1}$.

$Ca(OH)_2$ contributes to form finer and more homogeneous porous structure. It is the most available (in form of fine powder or crystals) and lowest cost of the metal hydroxides. $Ca(OH)_2$ suspension resulted through mixing with the water releases Ca^{2+} ions forming an alkaline solution with pH of about 12.5.

Three experimental versions were chosen for production of oak wood delignified specimens using the material components mentioned above (Table 1).

Table 1. Composition of experimental versions

Composition	Version 1 (g)/(wt.%)	Version 2 (g)/(wt.%)	Version 3 (g)/(wt.%)
Oak wood	237/65.8	220/61.1	209/58.0
NaOH	91/25.3	91/25.3	91/25.3
$Ca(OH)_2$	32/8.9	49/13.6	60/16.7
Total	360/100	360/100	360/100
Added water	1000/-	1000/-	1000/-

Keeping constant the total value (360 g) of the solid components that includes oak wood, NaOH pellets, and $Ca(OH)_2$ as well as the concentration of the NaOH aqueous solution (91 $g \cdot L^{-1}$), the dosages corresponding to the three experimental versions have resulted according to Table 1. In percentage terms, the total amount of alkaline solution components used for the chemical treatment in order to remove the wood lignin increased between versions 1 and 3 from 34.2 to 42.0 wt. %.

2.2 Methods

The basic method applied for the manufacture of a new material with outstanding thermal insulating properties (extremely low density and thermal conductivity) through the oak wood delignification process consists in the chemical treatment of the biomaterial in an alkaline environment. It was created by using NaOH, $Ca(OH)_2$ and distilled water, separately prepared by stirring in a transparent glass vessel. After homogenization, the liquid mixture was poured over the previously processed fine wood powder and the mixing was continued until a suspension was formed, which was then cast into a parallelepiped metal mold of 85 x 100 mm, the height of its walls allowing the maximum thickness of 40 mm for the viscous material. Due to the high stable phenolic structure, the wood warming temperature had to be 260 °C to facilitate the lignin decomposition [10]. The heating was carried out in an electric laboratory oven where the mold was inserted. After reaching the required temperature, the warming process was stopped and the material was allowed to freely cool inside the oven (with the door open).

The method based on wood delignification allowed supplementing the porous structure with numerous very small pores, which allowed the increase of the total volume of voids in the wood structure, the significant decrease of density as well as heat conductivity (being well known that the air into the material pores is weak heat flow conductor).

According to known biochemical theories cited by Kumar et al. [1], lignin is formed by the addition of free internal secretions into the spaces between cellulose microfibrils in plant cell walls. The lignification process, which involves several stages, leads to the formation of heterogeneous macromolecules.

As mentioned above, the main role of lignin is hardening the vascular plants. Removing methods of lignin, especially through chemical processes, have already been studied previously, this process being extremely required in the paper and biorefining industries. Normally, chemical or thermal treatments influence the biopolymer (lignin) in the cell wall, therefore the physico-chemical properties of wood. The research to determine these influences was based on direct experiments regarding removing the lignin, being included in the work [1].

2.3 Methods for characterizing the wood specimens

Archimedes' method (ASTM D792-20) was adopted for measuring the density and porosity according to the literature recommendation [11]. For determining heat conductivity values the heat-flow method (ASTM E1225-04) [12] was used. The compression strength could be highlighted with the TA.XTplus C Texture analyzer. The absorbing water capacity of samples was measured by determining the amount of water absorbed in 24 hours by the wooden material in direct contact with standing water (ASTM D7433-19). Microstructural aspect of wood samples were investigated using Biological Microscope MT5000 model (1000 x magnification).

3. RESULTS AND DISCUSSION

3.1 Results

Using the methods of investigating the physical, mechanical, and thermal characteristics of delignified oak foam specimens, they were highlighted in Table 2.

Table 2. Characteristics of delignified oak foam specimens

Characteristic	Version 1	Version 2	Version 3
Density ($g \cdot cm^{-3}$)	0.102	0.056	0.024
Porosity (%)	78.2	85.7	90.5
Heat conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	0.050	0.039	0.031
Compression resistance (MPa)	1.1	0.8	0.9
Water uptake (wt.%)	3.0-3.5	2.8-3.5	2.2-3.1

Excellent thermal insulation performances of delignified oak wood specimens were obtained according to Table 2. The material density decreased from 0.102 $g \cdot cm^{-3}$ (version 1) to 0.024 $g \cdot cm^{-3}$ (version 3). These values are very small compared to those of the usual heat-insulating materials used in construction. According to [13], the density of natural oak wood is within the limits of 0.6-0.9 $g \cdot cm^{-3}$. Also, the heat conductivity reached very low values (up to 0.031 $W \cdot m^{-1} \cdot K^{-1}$) and as a consequence, the porosity increased up to 90.5 % due to the structural transformations of the wood after the chemical treatment applied for removing the lignin. The absorbing-water capacity of samples (after 24 hours) indicated values within the limits of 2.2-3.5 wt. %, where values corresponding to version 3 were the lowest (2.2-3.1 wt. %). This absorbing-water level is considered as adequate for the use of delignified wood as a heat-insulating material. The mechanical properties of the oak wood specimens are low, but acceptable for their use as thermal insulation panels of buildings (0.9 MPa in version 3).

Images of oak wood froth after the chemical treatment for removing the lignin are presented in Figure 1. The three images correspond to the manufacturing versions of delignified oak wood specimens.

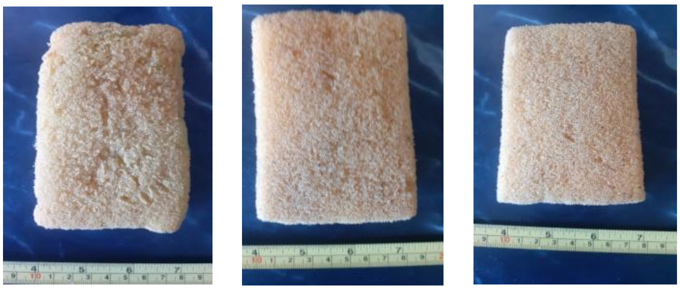

Figure 1. Oak wood froth after delignification
a – version 1; b – version 2; c – version 3.

Microstructural pictures of chemical treated oak wood specimens are presented in Figure 2. Version 3 (c) is the best version due to the agglomeration of very small pores (under 10 µm) through removing the lignin in the wood structure, visible in the magnified picture (right).

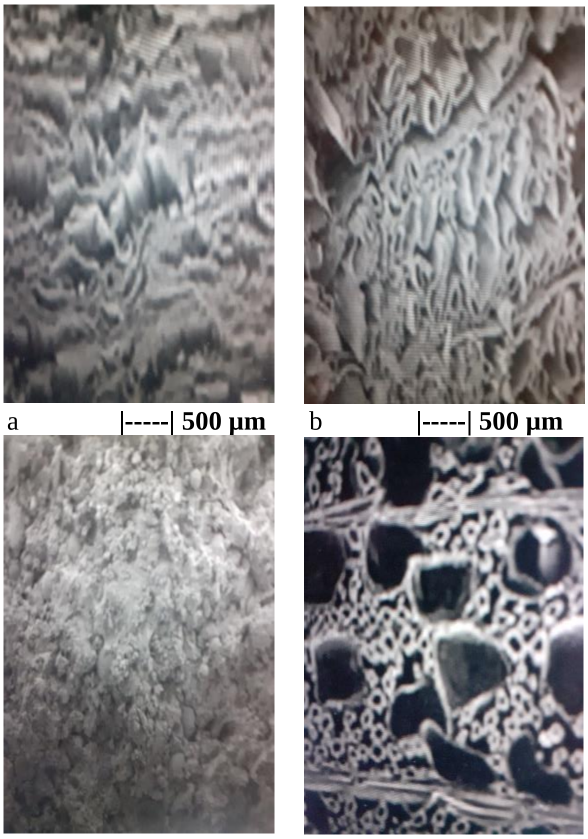

Figure 2. Microstructural images of wood specimens
a – version 1; b – version 2; c – version 3.

3.2 Discussion

The initial structural organization of wood containing lignin (22-29 %) is suitable for the heat transfer through heat conductivity. The application of chemical treatment (NaOH, $Ca(OH)_2$, and distilled water) and thermal treatment (heating to 260 °C) led to the large-scale replacement of lignin in the wood structure with a structure characterized by numerous extremely small pores (below 10 µm). The air inside the pores is a poor conductor of heat and thus, the heat conductivity of the woody material significantly decreases.

At the same time, the process of replacing a compact solid material (such is lignin) with a fine porous structure creates the conditions for decreasing the wood density value. The density reduction is sudden compared to the known initial values of oak wood (0.6-0.9 $g \cdot cm^{-3}$), reaching a minimum value of only 0.024 $g \cdot cm^{-3}$.

Obviously, the decrease in density to such low values influenced the mechanical properties of the new material. The compression resistance reached the value of 0.9 MPa, but this was considered acceptable for the use of oak wood foam in construction applications.

4. CONCLUSION

This work aimed at the experimental production of an environmentally friendly very porous heat-insulating material using oak wood as raw material for the first time. Applying a chemical wood treatment technique based on a suspension made of oak wood, NaOH, $Ca(OH)_2$, and distilled water, warmed to 260 °C, taken up from specific technologies of the paper industry, the lignin was largely removed from the typical structure of wood. As a result of the so-called delignification process, a structure characterized by numerous very small pores (under 10 μm) have substituted the lignite, contributing to the significant change in the physical and thermal features of the woody material (density of 0.024 $g \cdot cm^{-3}$, heat conductivity of 0.031 $W \cdot m^{-1} \cdot K^{-1}$, and porosity of 90.5 %). The delignification of oak wood froth performed in this experiment has proved that a residual wood in the form of sawdust chemically treated can be reused as an effective construction material with excellent heat-insulating properties.

5. REFERENCES

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