

BIOMASS DELIGNIFICATION CHEMICAL PROCEDURE FOR OBTAINING A ROMANIAN SPRUCE WOOD-INSULATING MATERIAL

Lucian Paunescu[1], Enikö Volceanov[2,3] and Bogdan Valentin Paunescu[4]
[1] Daily Sourcing & Research SRL Bucharest, Romania, lucianpaunescu16@gmail.com
[2] National University of Science and Technology POLITEHNICA, Faculty of Engineering in Foreign Language Bucharest, Romania, evolceanov@yahoo.com
[3] Metallurgical Research Institute SA Bucharest, Romania, evolceanov@yahoo.com
[4] Consitrans SA Bucharest, Romania, pnscbogdan@yahoo.com

ABSTRACT: A procedure for making a wooden heat-insulating product for construction applications through lignin removing is presented in this paper. The non-conventional procedure is almost similar to that known and used in the pulp and paper industry, but the technological purpose is clearly different. The type of tree wood chosen by authors (Romanian spruce wood) is a novelty compared to the rather large list of tree species tested so far and represents the originality of the work. The liquid alkaline environment was constituted of NaOH, $Ca(OH)_2$, and distilled water and this has activated the spruce wood waste. By removing lignin from the wood structure, heat conductance of the wooden material decreased by comparison with conductance of the same type of non-treated wood. The heat treatment temperature into an electric oven was 95 °C for 8 hours. The results showed the possibility to obtain a product with denseness value of 0.14 $g \cdot cm^{-3}$ and heat conductance of 0.030 $W \cdot m^{-1} \cdot K^{-1}$, i.e. very good insulation properties. Analyzing the material quality, this was almost identical to high-performance wooden materials.
KEYWORDS: biomass, removing lignin, spruce wood, alkaline environment, insulation properties.

1. INTRODUCTION

Biomass formation is naturally generated due to usual activities in agriculture, forestry, fishing, aquaculture, etc. [1]. Its properties recommend it as a potential source for producing newly created value materials. In the last time, the interest in the biomass valorization is clearly increasing. The consequence of this capitalization is also the reduction of greenhouse gas emissions in the terrestrial atmosphere due to diminishing the number of landfills for storage [2].

An important part of the biomass comes from the forestry and timber industry [1], that provides residual biomass. Sawdust coming from the timber industry represents a particular case chosen for the investigation carried out in this article.

Recently, it has been noticed that lignin represents an excellent source for new materials and bioenergy. According to [3], lignin can be considered as one of the most widespread polymers worldwide. A wide source of by-products (resin acids, fatty acids, aromatic compounds, carboxylic acids, etc.) comes from the pulp and paper industry. For technological causes, these by-products must be eliminated during the process, utilizing physical, chemical, thermal, or biological procedures.

By comparison with the other principal components of wood (cellulose and hemicellulose), lignin has the peculiarity of deforming its molecules from cellular walls of the wooden material as a result of moistening and warming at about 100 °C [4].

Natural cellulosic scaffolding coming from wood by lignin removal without affecting the original wood structure is known as wood delignification process [5]. Various types of tree wood (bamboo, Norway spruce, Chinese fir, balsa, basswood, hybrid poplar, birch, poplar wood) were tested in the world, according to [5], utilizing the lignin removal procedure.

Of the lignin removal procedures mentioned above in order to obtain the heat-insulating properties of biomass, the chemical procedures were chosen.

According to [1], effective tested techniques based on chemical procedures have used alkaline hydrolysis and acid hydrolysis, the first technique being more frequently applied. The pore-forming agents corresponding to alkaline hydrolysis were found to be sodium hydroxide (NaOH), calcium oxide (CaO), calcium hydroxide ($Ca(OH_2)$), and ammonia (NH_3). The ideal temperature experimentally found varied within 50-90 °C.

The literature mentions several articles on making materials with heat-insulating features by removing the lignin. Liu and Zhao [6] obtained wooden materials with very fine porous structure and heat conductivity of 0.026 $W \cdot m^{-1} \cdot K^{-1}$.

Using poplar wood chips as wooden raw material, Siciliano et al., [7] applied the delignification procedure to increase the cellulose surface in the wood mass by removing lignin and obtaining a foam with high stability. The delignified wood denseness decreased up to 0,053 $g \cdot cm^{-3}$ from 0,087 $g \cdot cm^{-3}$ corresponding to reference specimen (including lignin). The heat conductivity of this product had reduced values of 0.038 $W \cdot m^{-1} \cdot K^{-1}$. Normally, compression resistance was diminished, but remained at an acceptable value for application in construction. The manufacturing recipe also included carboxymethyl cellulose (CMC) as a binder with an adhesive role, and distilled water. The experimentally determined temperature for the heat treatment was between 100-150 °C for 8 hours.

An important contribution to obtaining excellent performances of foamed wood is revealed in the literature [8]. The team of researchers from the Fraunhofer Institute for Wood Research (Germany) used a mixture of finely ground beech wood in distilled water forming a suspension. Chemical and physical processes without added adhesives were applied to obtain a lightweight material with a structure containing open pores. Denseness of this material fell between 0.04-0.25 $g \cdot cm^{-3}$. Through further processing, the wooden material allowed to obtain hard expanded boards or elastic froth. The product had excellent physical stability. Heat conductivity had reduced values under 0.04 $W \cdot m^{-1} \cdot K^{-1}$, as well as the compression resistance (between 20-600 kPa). By comparison with the traditional commercially available polystyrene insulating boards, the characteristics of the product made at the Fraunhofer Institute were almost similar.

Authors of the current work [9] have recently tested the manufacture of an insulating wooden material through the delignification technique applied to oak wood recycled in the form of sawdust. The procedure consisted in generating the suspension by mixing wood waste with NaOH, $Ca(OH)_2$ and distilled water at 260 °C. The optimal product had low values of density (0.024 $g \cdot cm^{-3}$) and heat conductivity (0.031 $W \cdot m^{-1} \cdot K^{-1}$), while resistance to compression had satisfactory values (0.9 MPa) for construction applications.

Another experiment aiming at the production of insulating wood product through the same delignification technique applied to maple wood as sawdust was recently performed by the Romanian research team [10]. The adopted temperature of the process was much lower (90 °C) for 8 hours. The best product had a density of 0.21 $g \cdot cm^{-3}$ and a heat conductivity of 0.029 $W \cdot m^{-1} \cdot K^{-1}$. Qualitatively, the delignified wood properties were roughly similar to known expanded wood products.

The current work is focused on trying the manufacture insulating material from wood using Romanian spruce wood. According to data from the literature [11], the spruce is originated from the forests of Northern Europe, subalpine regions of Alps and Carpathian Mountains. In the Romanian area of Fagaras, this tree species is found at heights between 1500-1800 m. The use of Romanian spruce wood (in form of recycled sawdust) constitutes an originality element of the work, this material not having been tested until now.

2. MATERIALS AND METHODS

2.1 Materials

The wood composition as well as the structure of its cellular wall are decisive for the physio-chemical features of this biomaterial. According to the work [12], it is known that normally approximately 25 % of the wood composition is represented by lignin, 45 % by cellulose, and 25 % by hemicellulose. Lignin forms the hydrophobic surface through which water is transported to great heights (above 100 m) and, at the same time, ensures the tree resistance. On the other hand, lignin is an important obstacle in the technological process of extracting cellulosic fibers in the pulp and paper industry. The lignin composition can vary greatly. Basically, two categories of lignin are known: one from coniferyl alcohol monomers, which form the lignin for softwoods, and another from sinapyl alcohol monomer resulting after polymerization. A mixed lignin category, combining the two mentioned types, is specific to hardwoods.

According to the note above, the wooden material used as raw material in the current making process of insulating product adequate for application in construction was Romanian spruce wood tree as a hardwood.

The lignin removal procedure adopted in this experiment is of a chemical nature and is based on creating an alkaline environment composed of NaOH and $Ca(OH)_2$ in aqueous solution [13]. NaOH is available on the market in form of water-soluble solid pellets. $Ca(OH)_2$ is also commercially available as a fine powder soluble in water. Mixing the two mentioned solid components in distilled water, a sludge is formed. Experimentally, the concentration of the NaOH aqueous solution was chosen at 90 $g \cdot L^{-1}$.

2.2 Methods

The wood delignification by chemical treatment in an alkaline environment at relatively low temperature (around 100 °C) is the method used in this experiment. In principle, the partial elimination of lignin and hemicellulose due to the alkaline treatment increases the matrix/fiber interface and allows an excellent adhesion between matrix and natural fiber. By eliminating lignin and hemicellulose as non-cellulosic components with lower densities, the fiber density increases due to the alkaline treatment. Also, fibers are separated from each to other, the crystallinity as well as the cellular structure and fiber orientation changes [13].

In particular, the wood delignification through the alkaline treatment contributes to the formation of a porous structure characterized by the existence of numerous low pores, favouring the increase in the volume of voids into the wood mass and the increase in the heat conductance of this material, whose air voids are poorly conductive to heat flow [5].

As noted above, one of the basic roles of lignin is to increase the tree resistance. Lignin removal procedures have been previously studied according to [5] with a technological interest in the paper and biorefining industries, but completely different from the one developed in the current work.

As a conclusion of its previous use, the chemical procedure of wood delignification is not an unknown technique, but represents a successful takeover of this technique in a certain relatively close domain, the purpose being however clearly different.

The preparation of the mix containing the waste biomass (Romanian spruce wood) and the liquid alkaline solution was performed according to basic principles of this preparing type. Thus, the liquid component (NaOH, $Ca(OH)_2$, and distilled water) and respectively, the solid component (wooden waste in the form of sawdust) of the mixture were processed separately.

The adopted NaOH concentration in distilled water was 90 $g \cdot L^{-1}$, kept constant for all experimental versions. The weight proportion of $Ca(OH)_2$ was modified in the range of 8.8-17.4 %.

The biomass waste was finely ground to particle size below 80 µm and homogenized separately from the liquid mixture. Next, the liquid mixture was gently poured over the solid powder and stirred until the suspension was formed. This suspension was loaded into a matrix with dimensions of 80 x 80 mm and a maximum height of 60 mm. The thermal treatment adopted consisted of heating the mix at 95 °C for 8 hours, according to the recommendation in the work [14].

Experimentally, three testing versions for manufacturing porous wood material through delignification procedure were tried (Table 1), compared with a reference version of the same type of un-treated wood.

Table 1. The composition of testing versions

Composition	Version (g/ wt. %)		
	No. 1	No. 2	No. 3
Romanian spruce wood	239.2/ 66.3	224.1/ 62.1	208.2/ 57.7
NaOH	90/ 24.9	90/ 24.9	90/ 24.9
$Ca(OH)_2$	31.8/ 8.8	46.9/ 13.0	62.8/ 17.4
Total	361/ 100	361/ 100	361/ 100
Water addition	1000/ -	1000/ -	1000/ -

Adopting the total quantity of solid component materials at 361 g, the Romanian spruce wood values corresponding to each testing version resulted between 208.2-239.2 g (or 57.7-66.3 wt. %), decreasing from version 1 to version 3.

2.3 Methods for determining the sample features

Archimedes' procedure (ASTM D792-20) was used for denseness and porousness measurement also taking into account the information from the literature [15]. Applying the guarded-comparative-longitudinal heat flow technique (ASTM E1225-04), heat conductance was determined [16]. The compression resistance was highlighted within the analyzer TA.XTplus C Texture type. For the water uptake identification, the procedure developed at Växjö University (Sweden) [17] adequate for hardwoods was chosen. The wood samples were let float in deionized water for maximum 72 hours. Biological Microscope MT5000 model, 1000 x magnification was utilized to examine the microstructural particularities of samples.

3. RESULTS AND DISCUSSION

3.1 Results

The investigation methods of physio-mechanical and heat characteristics of porous delignified spruce wood (versions 1-3) and the reference non-treated wood (noted R) allowed the comparation of these values (Table 2).

Table 2. Features of porous delignified woods and reference wood sample

Feature	Reference wood	Version 1	Version 2	Version 3
Denseness ($g \cdot cm^{-3}$)	0.77	0.21	0.19	0.14
Porousness (%)	39.6	73.5	78.0	83.1
Heat conductance ($W \cdot m^{-1} \cdot K^{-1}$)	0.112	0.062	0.040	0.030

Compression resistance (MPa)	1.3	1.0	0.8	0.6
Water uptake (wt. %)	2.7	2.8	3.0	3.1

Examining the experimental results in Table 2, large differences can be observed between those of products obtained by removing lignin and those of the non-treated reference wood. Denseness of reference product having the value of 0.77 $g \cdot cm^{-3}$ decreased significantly in the case of products subjected to removing lignin, falling within the limits of 0.14-0.21 $g \cdot cm^{-3}$. The heat conductance was thus influenced in direction of diminishing their values from 0.112 $W \cdot m^{-1} \cdot K^{-1}$ (reference wood) to the range of 0.062-0.030 $W \cdot m^{-1} \cdot K^{-1}$ (in the case of products made in versions 1-3. Compression resistance was in the range of 0.6-1 MPa, being still quite close to the resistance value corresponding to the reference wood (1.3 MPa). The same conclusion resulted from the comparison of the water uptake values of the samples treated in alkaline environment and those non-treated, being relatively similar (2.8-3.1 wt. % in the first case and respectively, 2.7 wt. % in the case of the reference wood).

The apparent aspect of delignified Romanian spruce wood samples (noted with V1-V3) by comparison with the aspect of the non-treated reference wood sample (noted with R) are shown in Figure 1.

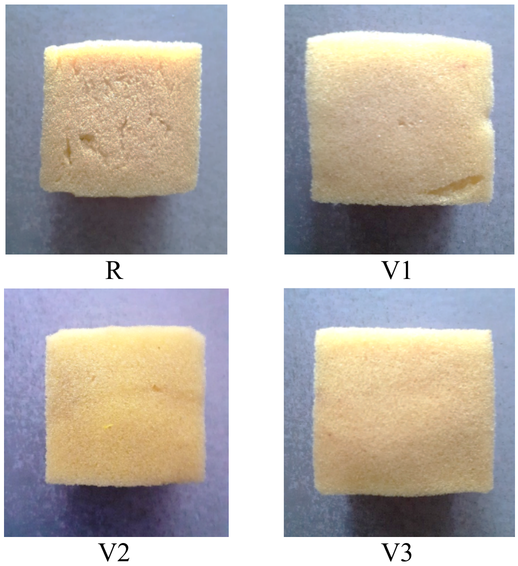

Figure 1. Comparative aspect of delignified wood (V1-3) and reference wood (R)

V1 – version 1; V2 – version 2; V3 – version 3;
R – reference wood version.

The images show a significant increase in the level of porosity fineness of the analyzed samples surface (V1-3) by comparison with the non-treated wood sample of the same type (R version). Also, the increase of the total amount of $Ca(OH)_2$ and NaOH, i.e. the alkaline environment, contributed to the progressive improvement of the porosity fineness of the treated samples. This trend was much more clearly highlighted by the pictures representing their microscopic appearance presented in Figure 2.

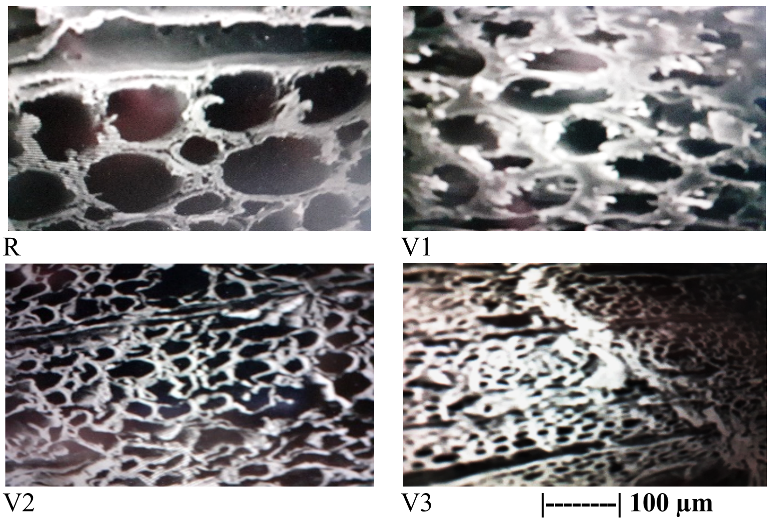

Figure 2. Images of microstructural aspect of delignified wood samples (V1-3) and reference wood sample (R)

V1 – version 1; V2 – version 2; V3 – version 3;
R – reference wood version.

3.2 Discussion

Although the chemical procedure of biomass delignification is not in itself an original method, this technique nevertheless represents a model of borrowing a procedure successfully used in one field of industrial activity in another relatively close one.

The well-known delignification technique applied in the pulp and paper industry has a clearly different technological purpose than that of creating an adequate cellular structure for thermal insulation in the construction sector. However, both purposes have in mind the lignin elimination from the structure of the wooden material.

According to the knowledge accumulated in this field of research, only a delignification procedure without the removal of hemicellulose has the capacity for ensuring a more economical effect and a higher thermal insulation effectiveness for the biomass.

Alkaline hydrolysis procedures applied in biomass delignification are most frequently used to remove lignin from the wood mass. The alkaline environment has a proven capacity to significantly improve the solubility of lignin due to the elimination of a proton (for example H^+) or phenolic OH^- groups. Thus, carbohydrate-lignin bonds in an alkaline environment are broken, leading to disintegration, destruction, and removing lignin.

The method of removing lignin applied in this work included both the effect of the alkaline environment on activating the chosen wood type (Romanian spruce wood) and the heat treatment of the suspension poured into moulds at a temperature of 95 °C for 8 hours.

The experiment had as the main purpose testing a wood tree type (Romanian spruce wood) unused until now in the process of removing lignin to obtain the appropriate properties of heat-insulating material. The results of this test were more than promising, indicating the achievement of thermal insulating performances at the level of those reported in the literature by different research teams in the world.

4. CONCLUSION

The recent concern of the research team that authored the current work was focused on testing several wood species aiming at the possibility of obtaining construction materials with excellent insulating properties through lignin delignification. In this work, a type of wood unused until now was tested under laboratory conditions, despite the long list of wood species analyzed in the world. In the present case, Romanian spruce wood was subjected to tests using the already well-known alkaline treatment. The chemical procedure of wood delignification was adopted in this paper by using the alkaline environment formed from NaOH, $Ca(OH)_2$, and distilled water. The thermal process temperature, to which the suspension poured in moulds was subjected, was 95 °C for 8 hours. The samples of products experimentally obtained as a result of applying the mentioned chemical treatment for the removal of lignin were characterized by very low values of denseness (0.14-0.21 $g \cdot cm^{-3}$) as well as heat conductance (0.030-0.062 $W \cdot m^{-1} \cdot K^{-1}$), while the compression resistance had small values, but satisfactory (between 0.6-1.0 MPa). By comparison with characteristics of the non-treated reference wood, denseness value of this sample was much higher (0.77 $g \cdot cm^{-3}$) and also the heat conductance value reached 0.112 $W \cdot m^{-1} \cdot K^{-1}$, i.e. clearly greater to the experimental samples. The comparison with traditional polystyrene materials used in construction as insulating boards, shows that the performances of the wooden specimens obtained in this experiment are almost similar to those of polystyrene.

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