EXCELLENT HEAT-INSULATING PROPERTIES OF MAPLE WOOD FOAM OBTAINED BY REMOVING THE LIGNIN

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ABSTRACT: *A new method for making wood heat-insulating material for building (known as wood delignification) without serious disturbing the cellulosic structure was borrowed from the pulp and paper manufacturing technology and adapted to the new objectives. The use of a suspension obtained by mixing NaOH and Ca(OH)2 in distilled water, heated at 90 ℃ in an electric oven, as one of known techniques of chemical treatment of wood for removing the lignin was adopted. As an original wooden raw material, recycled maple wood was chosen in the wood delignification process due to its high natural availability. Using 56.9 % maple wood, 26.0 % NaOH, 17.1 % Ca(OH)2, and added water, the optimal product had very low values of density (0.023 g·cm-3) and heat conductivity (0.030 W·m-1·K-1) as well as an acceptable value of compression strength (0.9 MPa) for building applications.*

KEYWORDS*: wood delignification, maple wood, chemical treatment, heat-insulating, heat conductivity.*

1 INTRODUCTION

In the last decades, the industrial interest for valorization of biomass properties in the form of wide variety of products registered a significant increase. Biomass is the result of activities in the fields of agriculture, forestry, fishing, and aquaculture as well as the storage of biodegradable industrial or municipal waste. (Diaz-Montaño, 2022). In general, the biomass as a residual material negatively influences the environmental quality (soil and water), so that its using for making new products is beneficial avoiding the storage of biomass waste in the environment, reducing the greenhouse gases (CO2) emission by eliminating some manufacturing processes that have become unnecessary and also brings important economic benefits (Tripathi et al., 2019). The large availability of biomass in nature as well as the economic advantage of its using have contributed to the increase of manufacturers' interest in the application of biomass as a valuable natural resource (Diaz-Montaño, 2022).

The current paper is focused on the biomass coming from forestry industry. According to Diaz-Montaño, forestry waste resulted from the forestry treatment is considered into primary biomass group, while forestry industry residues coming from lumber industry take place from secondary biomass group. Both groups mentioned above provide residual biomass, whose valorization is available and necessary in ecological terms. In particular, the sawdust resulting from the lumber industry constituted the type of waste whose recovery was the focus of the authors' team.

Except for water and organic impurities existing in low ratios, the main components of the wood structure are: cellulose as a polymer which has the ability to crystallize in the form of very strong fibers, lignin also as a polymer, but in amorphous form, which acts as a binder or matrix for the cellulose as well as hemicellulose as a partial crystalline polymer, which also acts as a binder or matrix (Wood composition, 2022). Of the three components mentioned above, lignin has a very branched three-dimensional structure. Softening the lignin by wetting occurs at about 100 ℃ allowing the molecule deformation in cell walls (Börcsök & Pásztory, 2021).

In terms of its microstructure, the wood has long cells (in axial direction) and low cells (in radial direction). Groups of cellulose chains (called microfibrils) first covered by hemicellulose and then by the lignin are structural components previously discovered by researchers. Several microfibril layers compose the long axial wood cells. The microfibril layers are separated and variably oriented. Modifying the position of the layers inside the structure ensures to the wood cells higher resistance in several directions. However, the wood structure remains very anisotropic (Wood composition, 2022).

Natural cellulosic skeleton resulting from wood through removing the lignin (partial or total), without negatively affecting the initial wood structure, is a process known as wood delignification. This process, in numerous technological and compositional versions, is usually applied in the manufacturing industry of pulp and paper aiming at removing the lignin for technological reasons. Several wood species were tested in the removing process of lignin: Chinese fir, balsa, basswood, Norway spruce, birch, bamboo, poplar wood, hybrid poplar, and poplar wood flour (Kumar et al., 2021).

The known technologies for improving biomass properties are classified into several groups: thermochemical, chemical, biological, and physical processes (Diaz-Montaño, 2022). In this experiment, we were interested in chemical processes capable of removing the lignin favouring the improvement of heat-insulating properties of wood, of which alkaline hydrolysis and acid hydrolysis are the most effective. Alkaline hydrolysis proved to be effective for removing the lignin, without degrading the sugars. The most important reagents used in alkaline hydrolysis are: NaOH, NH3, CaO, and Ca(OH)2, and the temperatures are within the limits of 50-90 °C (Diaz-Montaño, 2022). The wood species chosen for the first time as raw material in the experiment was maple wood (Norwegian maple), the most widespread tree of this type in Europe. Wide geographical areas between Greece and the Ural Mountains (Russia) are suitable for the development of this tree used on a large scale in the field of wooden furniture.

Some methods of removing the lignin in the wooden structure, having as a secondary result the significant loss of its strength, was considered attractive by researchers for the manufacture of building materials with excellent heat-insulating properties. The formation of additional voids with very small dimensions (of micron order) in the material structure was investigated by a Chinese team (Liu & Zhao, 2022) leading to the decrease of heat conductivity up to 0.026 W·m-1·K-1.

The work of Siciliano et al. (2022) was based on one of the wood delignification methods aiming at decreasing the density and the heat conductivity of material. Such a wooden material could be an effective alternative to the current thermal insulation solutions in the building construction. Normally, the preponderant type of thermal transfer through the solid walls of wood is the thermal conduction. Removing the lignin in the wooden structure ensures the conditions for disturbing and partially blocking this heat transfer, significantly increasing the thermal insulation properties of the material. In addition, the delignification process generates a more extensive surface of cellulose, allowing the formation of a stable foam. By comparison with the density of untreated wood (0.087 g·cm-3), that of delignified wood decreased to 0.053 g·cm-3. Very small values of heat conductivity (around 0.038 W·m-1·K-1) were obtained, while the compression resistance reached low but satisfactory values (up to 1.1 MPa). The component materials of the making recipe were poplar wood chips, carboxymethyl cellulose powder (also known as CMC) as an adhesive binder, and deionized water. The heating temperature in a hot plate stirrer of this mixture reached 100-150 ℃ for 8 hours.

A new foamed wood material with excellent heat-insulating properties for the construction sector based on renewable resources (Wood foam, 2021) was reported by the research team from the Fraunhofer Institute for Wood Research (Germany). The manufacture of this product involved the use of finely ground beech wood and deionized water mixed together to obtain a suspension. Chemical and physical methods were applied without the addition of adhesives. The treatment favoured the production of a porous material with open pore structure and very low density in the range of 0.04-0.25 g·cm-3. Then, the porous material was processed as hard foamed panels or elastic froth. Unlike the usual wooden insulating materials with low dimensional stability, the new material has achieved a good physical stability. The compression resistance (for 10 % compression amounted) fell within the limits of 20-600 kPa and heat conductivity had values less than 0.04 W·m-1·K-1, being comparable in value to those of traditional polystyrene insulation panels.

The alkaline processes used in delignification (as mentioned above) are the most often applied processes for removing the lignin into biomass. The alkaline medium has the role of greatly increasing the lignin solubility due to the removal of a proton (such as H+) of phenolic OH- groups. Thus, in the alkaline medium, lignin-carbohydrate bonds are broken, leading to increasing the fragmentation and destruction of lignin. In this paper, the pretreatment in an aqueous alkaline medium, practiced in the pulp and paper manufacturing process, was chosen for the delignification of maple wood. The mixture included NaOH, Ca(OH)2, and distilled water.

Although the principle of the method for improving the heat-insulating characteristics of wood is sequentially inspired by the technological process of pulp and paper manufacturing, it is considered a technical innovation that involves the creation of a new wood product intended for building construction. In the case of the industrial manufacture of pulp and paper, the removal of lignin aims to favour the capture of cellulose, while in the case of the current experiment, the same technical objective favours the physico-thermal properties of a new product, so that the goal pursued is completely different in the two cases. The work originality consists in choosing and testing for the first time the maple wood for the manufacture of the new type of material as well as adopting the peculiarities of the making technique.

2 MATERIALS AND METHODS

2.1 Materials

Maple wood was adopted as wooden material in the current experiment. The wide availability of this tree type in the European territory, including also Romania, contributed to its choice as a raw material. The wood of trees represents an organic tissue that ensures the transport of water and nutrients. The structure of cell wall and the composition of wood are the main factors that influence its physical and chemical properties. Usually, 25 % lignin and 70 % cellulosic carbohydrates (of which 45 % cellulose and 25 % hemicellulose) compose the wood structure (Novaes et al., 2010).

The maple wood was recycled in the form of sawdust from a Romanian wood-working workshop. For use in this experiment, the wood was very finely ground in a ball mill to sizes under 90 µm. For the chemical treatment of ground wood, the option of using an aqueous mixture including sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)2) mixed in distilled water for obtaining a suspension was adopted. Usually, the role of the NaOH content is to decrease the density value and increase the proportion of open porosity of material. NaOH is available on the market in the form of water-soluble pellets, which are used dissolved in distilled water, having the role of alkaline activator in the manufacture of geopolymer concrete from alumino-silicate waste (Paunescu et al., 2023; Davidovits et al., 1994). The concentration of the NaOH solution was experimentally adopted at 2.2 mol·L-1 (i.e. 88 g·L-1). Experimentally, it was found that Ca(OH)2 favours the formation of finer and more homogeneous porous structures. This material is most commercially available in the form of fine powder or crystals and has the lowest price among metal hydroxides. In chemical terms, mixing Ca(OH)2 with water results in an alkaline suspension (pH of about 12.5) containing Ca2+ ions.

Three experimental versions (2-4) were adopted (Table 1) for making the maple wood foam delignified samples, while version 1 was prepared without removing the lignin as the reference natural specimen.

Table 1. Composition of experimental versions

Composition	**Version 2**	**Version 3**	**Version 4**
Maple wood (g/wt. %)	232/ 66.3	217/ 62.0	202/ 57.7
NaOH (g/wt.%)	88/25.1	88/25.1	88/25.1
Ca(OH)2 (g/wt. %)	30/8.6	45/12.9	60/17.1
Total (g/wt. %)	350/100	350/100	350/100
Added water (g)	1000	1000	1000

Keeping constant the total value (350 g) of the solid components including maple wood, NaOH pellets, and Ca(OH)2 as well as the concentration of the NaOH aqueous solution (88 g·L-1), the amounts 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 2 and 4 from 33.7 to 42.2 wt. %.

2.2 Methods

The main method applied for making a new material with remarkable thermal insulation properties (extremely low values of density and thermal conductivity) through the maple wood delignification process consists in the chemical treatment of the biomass in an alkaline medium. It was created by using NaOH, Ca(OH)2 and distilled water, separately prepared by stirring in a 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. According to (Law et al., 2022), the highest delignification efficiency can be reached through chemical treatment carried out at temperatures around 90 °C, with delignification efficiency of 31 %. At higher temperatures (100-120 °C) the efficiency decreases up to 4 %. In the case of high stable phenolic structure (e.g.: the oak wood) the optimal temperature can even exceed 200 °C. The heating was performed in an electric laboratory oven (at 90 °C) shown in Fig. 1, where the mold was inserted. After reaching the required temperature, the heating process was stopped and the material was freely cooled inside the oven.

Fig. 1. 1.5 kW-laboratory electric heating oven of 60 L

and maximum temperature of 500 °C

The method based on wood delignification allowed supplementing the porous structure with numerous very low pores, which has facilitated the increase of the total volume of voids in the wood structure, the significant decrease of density value as well as heat conductivity value (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. (2021), 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 treatments, 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 (Diaz-Montaño, 2022).

2.3 Methods of investigating the sample features

Archimedes' method (ASTM D792-20) was adopted for measuring the density and porosity according to the literature recommendation (Density, 2014). For determining heat conductivity values the heat-flow method (ASTM E1225-04) (Yüksel, 2016) was used. The compression strength could be determined with the TA.XTplus C Texture analyzer. The water uptake 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 appearance of wood samples was investigated using Biological Microscope MT5000 model (1000 x magnification).

3 RESULTS AND DISCUSSION

3.1 Results

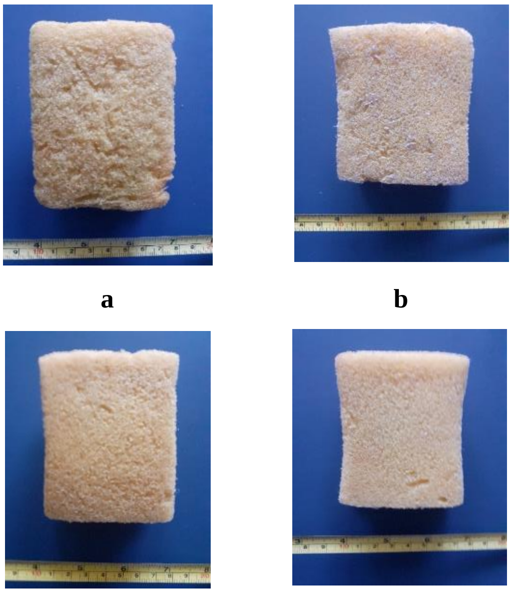
Applying the methods of investigating the physical, mechanical, and thermal features of delignified maple foam specimens led to obtaining the following results presented in Table 2.

Table 2. Features of maple foam specimens

Feature	Version			
	No. 1	No. 2	No. 3	No. 4
Density (g·cm-3)	0.70	0.088	0.054	0.023
Porosity (%)	11.4	80.6	85.0	90.9
Heat conductivity (W·m-1·K-1)	0.297	0.045	0.038	0.030
Compression strength (MPa)	3.8	1.0	0.9	0.9
Water uptake (wt.%)	5.0	3.1	2.9	2.6

Remarkable heat-insulating performances of delignified maple wood samples were obtained in accordance with Table 2. The density registered significant decreasing from 0.70 g·cm-3 corresponding to the reference natural wood (version 1) to 0.088 g·cm-3 (version 2), 0.054 g·cm-3 (version 3), and 0.023 g·cm-3 (version 4). These values are much below the level of traditional insulation material densities used in building construction. Also, the density value range of natural maple wood (untreated) according to the literature (Wood species, 2015) is between 0.62-0.75 g·cm-3. Also, very low thermal conductivity values were reached for the delignified specimens, versions 2-4 registering 0.045, 0.038, and 0.030 W·m-1·K-1, respectively. By comparison, these heat conductivity values are excellent for the low transfer of heat flow through the mentioned samples, compared to the high level of heat conductivity corresponding to the natural wood (0.297 W·m-1·K-1). The porosity of wood specimens subjected to the delignification treatment had very high values (over 80 %), while the reference sample had extremely low porosity (only 11.4 %). According to the measurement results, the amount of water absorbed by delignified wood is lower (2.6-3.1 wt. %) compared to that of untreated natural wood (5 wt. %). As mentioned above, lignin plays an important role in the plant wood, ensuring good mechanical strength. Thus, it was found that the reference sample reached a compression strength of 3.8 MPa, while the delignified samples had strengths between 0.9-1 MPa. However, for applications in building construction in the form of insulation boards, these values are considered acceptable.

Images of maple wood foam after the chemical treatment for removing the lignin are shown in Fig. 2. The pictures noted (b)-(d) correspond to the manufacturing versions (2-4) of delignified maple wood samples, while the image (a) represents the appearance of the reference sample (untreated).

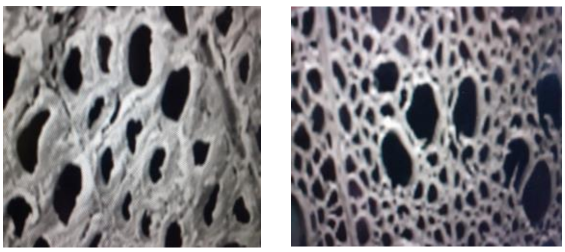


a **b** **c** **d**

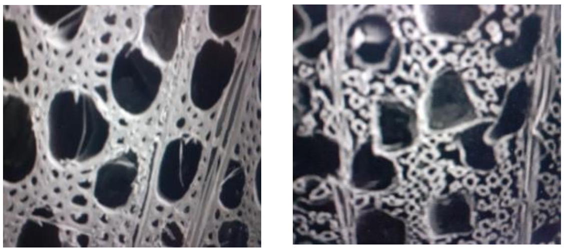
Fig. 2 Images of natural and delignified maple wood

a – version 1 (natural wood); b – version 2 (delignified wood); c – version 3 (delignified wood); d – version 4 (delignified wood).

The microstructural appearance of the chemically and thermally treated maple wood specimens as well as that of the natural maple wood specimen (untreated) representing the reference sample are shown in Fig. 3.



a **b**



c **d |-------| 100 µm**

Fig. 3 Microstructural appearance of natural and delignified maple wood

a – version 1 (natural wood); b – version 2 (delignified wood); c – version 3 (delignified wood); d – version 4 (delignified wood).

Increasing the total weight proportion of the chemical treatment components (NaOH and Ca(OH)2) up to 42.2 % (in the case of version 4) contributed to major changes in the structural tissue of the wood. As mentioned above in this paper, the destruction of lignin allows the formation of micron cells, whose decreasing dimensions and increasing degree of crowding between the vertical channels through which water and nutrients circulate are visible in the case of versions 2-4. Except the mentioned channels, the structure of untreated natural wood (version 1) is practically compact, keeping the basic characteristics of this biomass (good strength and very low porosity).

3.2 Discussion

The experimental results have shown that in the case of maple wood, the application of chemical treatment (with the alkaline solution containing NaOH and Ca(OH)2) and thermal treatment (heating to 90 °C of the suspension) in order to obtain a heat-insulating material with excellent properties applicable in building construction is appropriate. The optimal delignified wood specimen was obtained in the version of using 57.7 % maple wood, 25.1 % NaOH, 17.1 % Ca(OH)2 and added water. The physical, mechanical, and thermal characteristics of this specimen were: density of 0.023 g·cm-3, porosity of 90.9 %, heat conductivity of 0.030 W·m-1·K-1, compression strength of 0.9 MPa, and 2.6 wt. % water uptake.

The natural cellular tissue of wood containing 25 % lignin is adequate for the heat transfer through heat conductivity. The application of chemical treatment (NaOH, Ca(OH)2, and distilled water) and thermal treatment (heating to 90 °C) led to the large-scale replacement of lignin in the wood structure with one characterized by numerous extremely low pores (below 10 µm). The air inside the pores is a poor conductor of heat and thus, the heat conductivity of the wooden material significantly decreases.

Simultaneously, the process of replacing a compact solid material (such is lignin) with a fine porous structure favours decreasing the wood density value. The density reduction is sudden compared to the initial value of the maple wood (0.70 g·cm-3), reaching a minimum value of only 0.023 g·cm-3.

Obviously, the density decreasing to such low values influenced the mechanical properties of the new building material. The compression strength reached the value of 0.9 MPa, but this is considered acceptable for the use of maple wood foam in construction applications.

The experimental results presented in this paper confirmed that the biomass coming from sawdust recycling as a waste of mechanical processing the wooden material (in this case, maple wood) is suitable for the manufacture of new heat-insulating materials as a result of the chemical and thermal treatment for removing the lignin.

4 CONCLUDING REMARKS

The work aimed at experimentally making an experimentally friendly very porous thermal insulation material using recycled maple wood as raw material. This wooden material was used for the first time, according to the information from the international literature, representing the main originality of the work. The basic principle of chemical treatment of wood with the help of an alkaline suspension obtained by mixing with NaOH, Ca(OH2) and distilled water as well as heating to 90 °C, was borrowed from some techniques industrially applied in the manufacture of pulp and paper. If in the case of the mentioned industrial procedure (known as wood delignification), the purpose of the chemical treatment applied to wood is to recover the cellulose by removing the lignin from the wooden structure, in the case of the experiment presented in the paper, the technical objective was removing the lignin to obtain a cellular tissue with numerous very small pores (on the order of microns) and excellent thermal insulation properties. Three experimental versions of the making recipe were tested and a version of untreated maple wood as a reference version for comparing the results. The total proportion of the alkaline mixture components (NaOH and Ca(OH)2) was increased in the experimental variants from 33.7 to 42.2 %. Using the highest component proportion (42.2 %), the optimal delignified wood specimen had the following physical, mechanical, and thermal characteristics: density of 0.023 g·cm-3, porosity of 90.9 %, heat conductivity of 0.030 W·m-1·K-1, compression strength of 0.9 MPa, and water uptake of 2.6 wt. %. Considering the wide natural availability of wood, environmentally friendly character, the low cost of the process, and the excellent heat-insulating characteristics of the product, we consider that its realization on a large scale and its application in construction are viable.

5 REFERENCES

Börcsök, Z., Pásztory, Z. (2021). The role of lignin in wood working processes using elevated temperatures: an abbreviated literature survey, European Journal of Wood and Wood Products, Springer, vol. 79, pp. 511-524.

Davidovits, J., Davidovits, M., Davidovits, N. (1994). Process for obtaining a geopolymeric alumino-silicate and products thus obtained, US Patent no. 5342595.

Density and porosity measurement of solid materials, Anderson Materials Evaluation Inc. (2014), available at: https://andersonmaterials.com/density-and-porosity-measurement-of-solid-materials/ Accessed: 2023-04-11.

Diaz-Montaño, D. M. (2022). Valorization of biomass as a raw material to obtain products of industrial interest, in Biomass, Biorefineries and Bioeconomy, Samer, M. (ed.), available at: https://doi.org/10.5772/intechopen.104108 Accessed: 2023-04-17.

Kumar, A., Iyske, T., Petrić, M. (2021). Delignified wood from understanding the hierarchically aligned cellulosic structures to creating novel functional materials: A review, Advanced Sustainable Systems, Wiley Online Library, Hoboken, New Jersey, USA, vol. 5, no. 5.

Law, K. W., Chew, J. J., Yiin, C. L., Lock, S. S. M. (2022). Thermal degradation behavior and kinetic modelling of green solvents-delignified biomass: a sustainable biomass-to-energy approach, in Value-Chain of Biofuels: Fundamentals, Technology, and Standardization, Elsevier, pp. 89-103.

Liu, H., Zhao, X. (2022). Thermal conductivity analysis of high porosity structures with open and closed pores, International Journal of Heat and Mass Transfer, Elsevier, Amsterdam, Netherlands, vol. 183, Part A.

Novaes, E., Kirst, M., Chiang, V., Winter-Sederoff, H., Sederoff, R. (2010). Lignin and biomass: A negative correlation for wood formation and lignin content in trees, Plant Physiology, National Library of Medicine, vol. 154, no. 2, pp. 555-561, available at: https://doi.org/10.1104/pp.110.1611281 Accessed: 2023-08-03.

Paunescu, L., Paunescu, B.V., Volceanov, E. (2023). High mechanical strength-geopolymer concrete based on coal fly ash and ground recycled residual glass added in the fine aggregate, Buletinul Institutului Politehnic Iasi-Chimie si Inginerie Chimica, vol. 69 (73), no. 2, pp. 81-93.

Tripathi, N., Hills, C. D., Singh, R. S., Atkinson, C. J. (2019). Biomass waste utilisation in low-carbon products: harnessing a major potential resource, NPJ Climate and Atmospheric Science, vol. 2, no. 1, pp. 1-10, available at: https://doi.org/10.1038/s41612-019-0093-5 Accessed: 2023-03-10.

Wood composition. (2022). Materials Science & Engineering, University of New South Wales, Sydney, Australia, available at: https://www.unsw.edu.au/science/our-schools/materials/engage-with-us/high-school-students-and-teachers/online-tutorials/composites/wood/wood-composition Accessed: 2023-06-12.

Wood foam from tree to foam. (2021). Fraunhofer Institute for Wood Research, Braunschweig, Germany, available at: https://www.wki.fraunhofer.de Accessed: 2023-05-22.

Wood species-Densities, The Engineering ToolBox. (2015), available at: https://www.engineeringtoolbox.com/wood-density-d_40.html Accessed: 2023-07-02.

Yüksel, N. (2016). The review of some commonly used methods and techniques to measure the thermal conductivity of insulation materials, in Insulation Materials in Context of Sustainability, Almusaed, A. and Almssad, A. (eds.), ISBN 978-953-51-2625-6, available at: https://doi.org/10.5772/64157 Accessed: 2023-07-13.