

MATHEMATICAL DESCRIPTION OF THE SPECIFIC HEAT CAPACITY OF THE WOOD ABOVE THE HYGROSCOPIC RANGE DURING WOOD FREEZING

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ABSTRACT

A mathematical description of the specific heat capacity c of wood above the hygroscopic range during wood freezing has been suggested. The description takes into account the physics of the freezing process of both the free and the hygroscopically bound water in the wood. It reflects also the influence of the fiber saturation point of wood species on the value of their c during wood freezing and the influence of the temperature on the fiber saturation point of the wood during its freezing. A software program has been prepared for the computation of c according to the suggested mathematical description. With the help of the program, computations have been done for the determination of c of often used in veneer and plywood production beech and poplar wood with moisture content $0.4 \text{ kg}\cdot\text{kg}^{-1} \leq u \leq 1.2 \text{ kg}\cdot\text{kg}^{-1}$ at the temperature range between $0 \text{ }^\circ\text{C}$ and $-60 \text{ }^\circ\text{C}$ during freezing of the wood.

Key words: wood, freezing, specific heat capacity, mathematical description, bound water, free water, computation.

INTRODUCTION

During technological and other engineering calculation connected with thermal and hydrothermal treatment of wood materials it is necessary to have information about thermo-physical characteristics of wood and about the impact of numerous factors on them. One of the most important such characteristic is the specific heat capacity of the wood.

The main influencing factors on the specific heat capacity are the temperature T and the wood moisture content u , including the aggregate condition of the water in the wood. The impact of these factors has been reflected in the suggested earlier by us mathematical description of the specific heat capacity of frozen and non-frozen wood and also of frozen wood during its defrosting (Deliiski 1990). Our further studies have shown (Deliiski 2003), that most precise mathematical description of c must include also the impact of the fiber saturation point of wood species u_{fsp} and the dependence of u_{fsp} from T .

The aim of the present work is to suggest a mathematical description of the specific heat capacity of the wood above the hygroscopic range during freezing of both the free and the bound water in the wood.

For achieving of this aim experimental data of different authors and the mathematical descriptions of the specific heat capacity of the wood during wood defrosting, made earlier by the first co-author (Deliiski 1990, 2003, 2011, 2013) were used, with taking into account for the first time the influence of the fiber saturation point of wood species on the value of their c during water freezing in the wood and the influence of the temperature on the fiber saturation point of the wood during its freezing.

MATHEMATICAL DESCRIPTION OF THE WATER FREEZING TEMPERATURE IN THE WOOD

According to Chudinov (1966, 1968) and Topgaard and Söderman (2002), if the wood has a significant quantity of free water, i.e. if the cell holes and the gaps among the

cells are almost completely filled with water, the centres of crystallization during the cooling arose in the water at temperatures around $-5\text{ }^{\circ}\text{C} \div -6\text{ }^{\circ}\text{C}$. If the wood moisture content is slightly larger than u_{fsp} , i.e. a small quantity of free water is present in the wood, then the centres of crystallization in it arose at temperatures around $-12\text{ }^{\circ}\text{C} \div -15\text{ }^{\circ}\text{C}$. However, when there is only bound water in the wood, i.e. $u \leq u_{\text{fsp}}$, then the centres of crystallization arose at even lower temperatures.

Based on the results from personal experimental studies in his DSc. dissertation, Chudinov (1966, 1968) suggests a graph for the change of the temperature of freezing of the water in birch wood with fiber saturation point at $T = 293.15\text{ K}$ (i.e. at $t = 20\text{ }^{\circ}\text{C}$) $u_{\text{fsp}}^{293.15} = 0.3\text{ kg}\cdot\text{kg}^{-1}$ depending on u . Accord-

$$T_{\text{fr}} = 268.15 - 118.85 \exp[-9.9(0.3 + u - u_{\text{fsp}}^{293.15})^{1.3}] \quad @ \quad 0.12\text{ kg}\cdot\text{kg}^{-1} \leq u \leq u_{\text{max}} \quad (1)$$

With the help of the expression $(0.3 + u - u_{\text{fsp}}^{293.15})$ in equation (1) the determined by Chudinov (1966) relationship's character of the influence of u on T_{fr} for birch wood with $u_{\text{fsp}}^{293.15} = 0.30\text{ kg}\cdot\text{kg}^{-1}$ is accepted as valid for all wood species taking into account the concrete value of their $u_{\text{fsp}}^{293.15}$. It is only possible to make a future clarification of equation (1) when having extensive experimental data for the change in T_{fr} depending on u for wood species with different value of $u_{\text{fsp}}^{293.15}$.

The calculated according to equation (1) change in t_{fr} for birch wood with $u_{\text{fsp}}^{293.15} = 0.30\text{ kg}\cdot\text{kg}^{-1}$, beech wood with $u_{\text{fsp}}^{293.15} = 0.31\text{ kg}\cdot\text{kg}^{-1}$, and poplar wood with $u_{\text{fsp}}^{293.15} = 0.35\text{ kg}\cdot\text{kg}^{-1}$ (Nikolov and Vidolov 1987, Deliiski 2013) depending on u

ding to this graph the water freezing temperature in the wood t_{fr} is equal to the following: $t_{\text{fr}} \approx -20\text{ }^{\circ}\text{C}$ at $u = 0.3\text{ kg}\cdot\text{kg}^{-1}$, $t_{\text{fr}} \approx -10\text{ }^{\circ}\text{C}$ at $u = 0.4\text{ kg}\cdot\text{kg}^{-1}$, $t_{\text{fr}} \approx -7.5\text{ }^{\circ}\text{C}$ at $u = 0.5\text{ kg}\cdot\text{kg}^{-1}$, $t_{\text{fr}} \approx -6.5\text{ }^{\circ}\text{C}$ at $u = 0.6\text{ kg}\cdot\text{kg}^{-1}$, and for $u \geq 0.8\text{ kg}\cdot\text{kg}^{-1}$ the temperature t_{fr} asymptotically comes close to $t_{\text{fr}} \approx -5\text{ }^{\circ}\text{C}$. Due to the lack of other published data for the water freezing temperature in the wood, for the mathematical description of t_{fr} below, the quoted above data obtained by this author for the change of t_{fr} depending on u at $u_{\text{fsp}}^{293.15} = 0.3\text{ kg}\cdot\text{kg}^{-1}$ has been used.

Taking into account the influence of u_{fsp} on t_{fr} , the shown in (Chudinov 1966, 1968) graphical dependency $t_{\text{fr}}(u)$ can be approximated with the help of the following equation:

in the range $0.2\text{ kg}\cdot\text{kg}^{-1} \leq u \leq 1.0\text{ kg}\cdot\text{kg}^{-1}$ is shown on Fig. 1. The graph for birch wood shown on this figure coincides completely with the suggested by Chudinov (1966, 1968) graph.

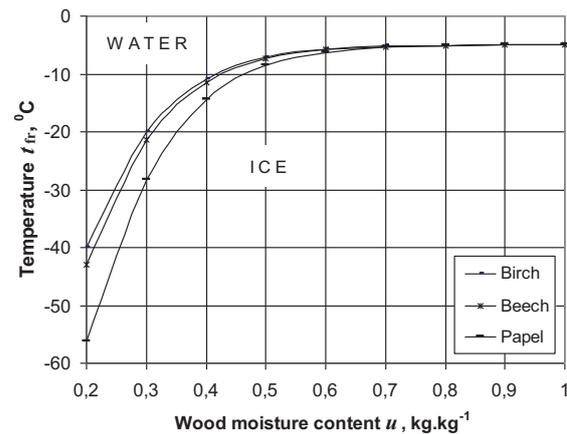


Figure 1: Change in t_{fr} for birch, beech and poplar wood, depending on u

The equation (1) is used below for the determination of T_{fr} in the mathematical description of the fiber saturation point and the

specific heat capacity during the freezing of both the free and the bound water in the wood.

MATHEMATICAL DESCRIPTION OF THE SPECIFIC HEAT CAPACITY OF THE WOOD DURING FREEZING OF THE FREE AND BOUND WATER IN THE WOOD

The mathematical description of the specific heat capacity of the wood during wood freezing has been done using the experimentally determined in the dissertations by Kanter (1955) and Chudinov (1966, 1968) data for its change as a function of t and u . This data for $c(t, u)$ finds a wide use in both the European (Shubin 1990, Trebula and Klement 2002, Videlov 2003) and the American specialized literature (Steinhagen 1986,

1991, Khattaby and Steinhagen 1993) when calculating various processes of the thermal processing of frozen and non-frozen wood.

The approach used in the mathematical description of c is analogous to this, which has been used earlier in the description of $c(t, u)$ of non-frozen wood and of frozen wood during its defrosting (Deliiski 1990) without taking into account the influence of the fiber saturation point of wood species on the value of its c and the influence of the temperature on u_{fsp} .

The specific heat capacity of the wood during its freezing can be calculated with the help of the following equations for $c(T, u, u_{nfw}, u_{fsp})$:

$$c = K_c \frac{526 + 2.95T + 0.0022T^2 + 226u + 1976u_{nfw}}{1 + u} \quad @ \quad u > u_{nfw} \quad \& \quad 213.15 \text{ K} \leq T \leq T_{fr}, \quad (2)$$

where

$$K_c = 1.06 + 0.04u + \frac{0.00075(T - 271.15)}{u_{nfw}}, \quad (3)$$

$$u_{nfw} = 0.12 + (u_{fsp} - 0.12) \exp[0.0567(T - 271.15)] \quad @ \quad 213.15 \text{ K} \leq T \leq T_{fr}. \quad (4)$$

After the freezing of the free and during the freezing of the bound water in the wood, a constant value of u_{fsp} is used in the mathematical description of c , which the wood has at the temperature of the beginning of its freezing T_{fr} (Deliiski 2013), i. e.:

$$u_{fsp} = u_{fsp}^{293.15} - 0.001(T_{fr} - 293.15) \quad @ \quad 213.15 \text{ K} \leq T \leq T_{fr}. \quad (5)$$

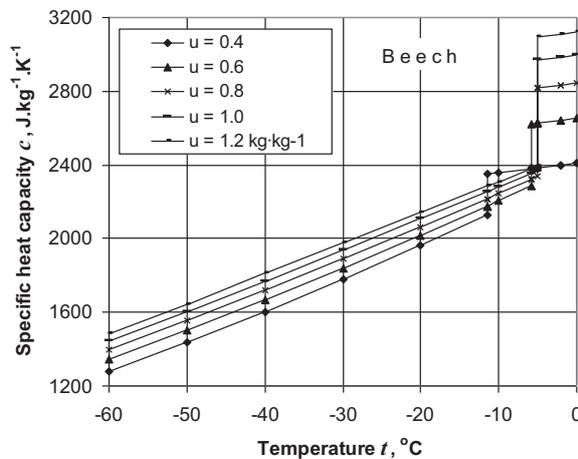
Due to the lack of published data on the influence of t on u_{fsp} for wood containing ice, in the derived below mathematical description of c at $T < T_{fr}$ constant values of u_{fsp} are obtained for each wood specie according to equation (5).

The values of c of non-frozen wood above the hygroscopic range at $T_{fr} < T \leq 273.15 \text{ K}$ (i.e. at $t_{fr} < t \leq 0 \text{ }^\circ\text{C}$) can be calculated according to the following equation (Deliiski 2011, 2013):

$$c = \frac{2862u + 555}{1 + u} + \frac{5.49u + 2.95}{1 + u} T + \frac{0.0036}{1 + u} T^2 \quad @ \quad u > u_{fsp} \quad \& \quad T_{fr} < T \leq 413.25 \text{ K}. \quad (6)$$

RESULTS AND DISCUSSION

For the computation of c according to equations (1) ÷ (6) a software program has been prepared in FORTRAN (Dorn and McCracken 1972), which has been input in the calculation environment of Visual Fortran Professional. With the help of the program computations have been made for the determination of c of often used in the veneer and plywood production beech (*Fagus Silvatica* L.) and poplar (*Populus alba* L.) wood in the ranges $0.4 \text{ kg}\cdot\text{kg}^{-1} \leq u \leq 1.2$



$\text{kg}\cdot\text{kg}^{-1}$ and $213.15 \text{ K} \leq T \leq 273.15 \text{ K}$, i.e. $-60 \text{ }^\circ\text{C} \leq t \leq 0 \text{ }^\circ\text{C}$.

During the computations of $c(t,u)$ the values of $u_{\text{fsp}}^{293.15} = 0.31 \text{ kg}\cdot\text{kg}^{-1}$ for the beech wood and $u_{\text{fsp}}^{293.15} = 0.35 \text{ kg}\cdot\text{kg}^{-1}$ for the poplar wood were used (Nikolov and Videlov 1987).

On Fig. 2 the calculated change in c of beech and poplar wood respectively during the freezing of the water in the wood, depending on t and u is shown.

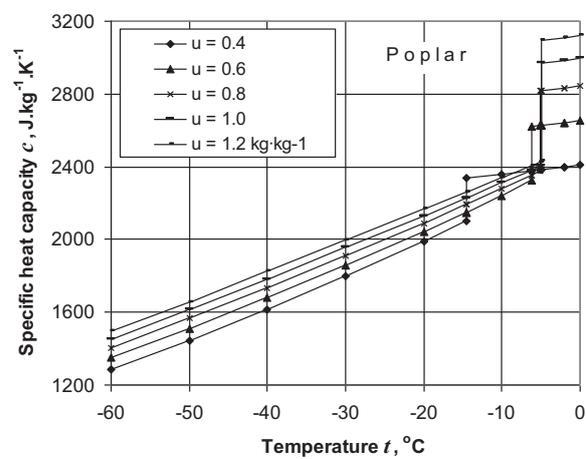


Figure 2: Change in c of beech (left) and poplar (right) wood during freezing of the water in the wood, depending on t and $u > u_{\text{fsp}}$.

On the graphs of Fig. 2 it can be seen that the decrease in t at a given value for u leads to decrease in c both for wood containing and non-containing ice.

The change in c of frozen and non-frozen wood depending on t , calculated according to equations (2) and (6) is very close to being linear. From the analysis on Fig. 2 and Fig. 3 it can also be seen that at a given value of t an increase in u both for wood containing and not containing ice, causes non-linear increase in c .

On the graphs of Fig. 2 it can also be seen that at $t = t_{\text{fr}}$ jumps take place in c for wood with given $u > u_{\text{fsp}}$ from the larger value of c of the non-frozen wood to the lower value of c of the frozen wood. These

jumps are explained by the phase transition into ice of the extra cooled part of the free water in the wood at $t = t_{\text{fr}}$ during wood cooling. Namely, at the values of $t = t_{\text{fr}}$ the influence on c of a significant difference in the specific heat capacity of the water in a liquid and hard aggregate state occurs. According to Chudinov (1966, 1968) the specific heat capacities of the water and the ice are equal to $c = 4237 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and $c = 2261 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ respectively.

Because of the increase of the ice quantity from the free water in the wood with increasing of u and also because of the increasing of the extra cooled part of free water at t_{fr} with increasing of u , the change Δc in the

specific heat capacity during these jumps increases non-linearly depending on u : from $\Delta c = 223 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $u = 0.4 \text{ kg}\cdot\text{kg}^{-1}$ and $t_{\text{fr}} = -11.47 \text{ }^\circ\text{C}$ to $\Delta c = 702 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $u = 1.2 \text{ kg}\cdot\text{kg}^{-1}$ and $t_{\text{fr}} = -5 \text{ }^\circ\text{C}$ for the beech wood and from $\Delta c = 234 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $u = 0.4 \text{ kg}\cdot\text{kg}^{-1}$ and $t_{\text{fr}} = -14.49 \text{ }^\circ\text{C}$ to $\Delta c = 666 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $u = 1.2 \text{ kg}\cdot\text{kg}^{-1}$ and $t_{\text{fr}} = -5 \text{ }^\circ\text{C}$ for poplar wood. The larger value of $u_{\text{fsp}}^{293.15} = 0.35 \text{ kg}\cdot\text{kg}^{-1}$ of poplar wood in comparison with $u_{\text{fsp}}^{293.15} = 0.31 \text{ kg}\cdot\text{kg}^{-1}$ of beech wood causes larger values of c of the frozen poplar wood than c of the frozen beech wood at given values of t and u (refer to eqs. (5), (4), and (2)). The difference Δc between c of frozen poplar and frozen beech wood increases with increasing of u and at $u = 1.2 \text{ kg}\cdot\text{kg}^{-1}$ it varies from $8 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $t = -60 \text{ }^\circ\text{C}$ to $36 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at $t = -5 \text{ }^\circ\text{C}$.

CONCLUSIONS

The present paper presents the mathematical description of the specific heat capacity of frozen and non-frozen wood above the hygroscopic range, which takes into account to a maximum degree the physics of the process of freezing of both the free and the bound water in the wood. It reflects the influence of the temperature, wood moisture content, and for the first time the influence of the fiber saturation point of wood species on the value of their c during water freezing in the wood and the influence of the temperature on the fiber saturation point of the wood during its freezing.

An equation for the determination of the temperature of the beginning of the water freezing in the wood, t_{fr} , has been derived depending on the wood moisture content u and on the standardized fiber saturation point of the wood at temperature $T = 293.15 \text{ K}$, i.e. at $t = 20 \text{ }^\circ\text{C}$.

For the computation of the specific heat capacity of the wood during its freezing, equations have been presented as well.

For the computation of the specific heat capacity of the wood during wood freezing according to the suggested mathematical description of c a software program has been prepared in the calculation environment of Visual Fortran Professional. With the help of the program computations have been carried out for determination of c of beech and poplar wood above the hygroscopic range with moisture content $0.4 \text{ kg}\cdot\text{kg}^{-1} \leq u \leq 1.2 \text{ kg}\cdot\text{kg}^{-1}$ at a temperature range from 213.15 K to 273.15 K , i.e. from $-60 \text{ }^\circ\text{C}$ to $0 \text{ }^\circ\text{C}$.

The obtained results show that a decrease in t at a given value for u leads to decrease in c both for wood containing and non-containing ice. The change in c depending on t is almost linear. The results show also that at a given value of t an increase in u both for non-frozen wood and for wood containing ice causes non-linear increase in c .

If non-frozen wood with given $u > u_{\text{fsp}}$ is subjected to cooling and the wood temperature decreases and reaches a temperature $t = t_{\text{fr}}$, a jump take place in c from the larger value of c of the non-frozen wood to the lower value of c of the frozen wood. This jump is explained by the phase transition into ice of the extra cooled part of the free water in the wood at $t = t_{\text{fr}}$ during wood cooling because of the almost twice lower value of the specific heat capacity of the ice in comparison to the value of specific heat capacity of the liquid water. Because of the increase of the ice quantity from the free water in the wood with increasing of u and also because of the increasing of the extra cooled part of free water at t_{fr} with increasing of u , the change in the specific heat capacity during these jumps increases non-linearly depending on u .

The larger value of $u_{\text{fsp}}^{293.15} = 0.35 \text{ kg}\cdot\text{kg}^{-1}$ of poplar wood in comparison with $u_{\text{fsp}}^{293.15} = 0.31 \text{ kg}\cdot\text{kg}^{-1}$ of beech wood causes larger values of c of the frozen poplar wood than c of the frozen beech wood at given values of t and u .

Symbols:

- c – specific heat capacity ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$);
 exp – exponent;
 t – temperature ($^{\circ}\text{C}$): $t = T - 273.15$;
 T – temperature (K): $T = t + 273.15$;
 u – moisture content ($\text{kg}\cdot\text{kg}^{-1} = \%/100$);
 Δ – difference (for the change in c);
 & – and simultaneously with this;
 @ – at.

Subscripts and superscripts:

- c – specific heat capacity;
 fr – freezing;
 fsp – fiber saturation point;
 max – maximum possible value;
 nfw – non-frozen water;
 293.15 – at 293.15 K, i.e. at 20 $^{\circ}\text{C}$ (for the standard values of the wood fiber saturation point).

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UNIVERSITY OF FORESTRY

FACULTY OF FOREST INDUSTRY

INNOVATION IN WOODWORKING INDUSTRY AND ENGINEERING DESIGN

2/2016

INNO vol. V Sofia

ISSN 1314-6149
e-ISSN 2367-6663

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