APPLICATION OF NON-EQUILIBRIUM THERMODYNAMICS TO THE ESTIMATION OF PHENOMENOLOGICAL TRANSFER COEFFICIENTS IN CONVECTIVE WOOD DRYING

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Abstract: *Convective drying is an important process within the wood industry since it improves the physical, mechanical and technological properties of wood. Starting from the critical moisture content, the evaporation surface gradually becomes deeper inside the wood board and thus the intensity of evaporation is different as compared to that one that occurs on the wood surface. The present study aimed to determine the heat and mass fluxes occurring during the falling-rate drying period in the boundary layer, based on the non-equilibrium thermodynamics, according to which the forms of molecular transfer (momentum, energy and mass) are coupled. The variation of the fluxes along the wood board was investigated and the influence of each flux component on the heat and mass fluxes was assessed. The phenomenological coefficients, as variables in the fluxes equations were also calculated.*
Keywords: *non-equilibrium thermodynamics, convective wood drying, phenomenological coefficients*

1. INTRODUCTION

A method for analyzing the process of convective wood drying process, where the coupled heat and mass transfer is influenced by the moisture evaporation that occurs between the surface of the wet wood material and the surrounding air is the non-equilibrium thermodynamics. It consists of phenomenological theories regarding simultaneous molecular transport of heat, mass and momentum in fluids and it is based on the laws of mass and energy conservation and Onsager's theorem of entropy increase [1], [2], [3]. According to Prigogine [4], the corresponding fluxes are linear relations of all thermodynamic forces involved in the process and the mutual and self phenomenological coefficients. There were a few attempts to determine the phenomenological coefficients specific to different irreversible heat and mass transfer processes. In his paper [5], Verros has determined the self diffusion and mutual diffusion coefficients by using the principles of non-equilibrium thermodynamics applied to diffusion (solvent evaporation from polymer solutions). Lewis and Malan [6] expressed liquid, vapor and energy fluxes based on phenomenological transfer coefficients and thermodynamic forces for the coupled heat and mass transfer processes in drying of non-hygroscopic and hygroscopic capillary particulate materials. They analyzed the mass transfer (molecular diffusion, thermal diffusion and capillary flow) and the heat transfer that occurred due to mass transfer, phase change and thermal conductivity. These transfer mechanisms are strongly coupled and non-linear functions of the thermodynamic state (temperature and moisture content). They cited Perrin and Javelas [7] and Fortes and Okos [8], according to which the phenomenological coefficients are typically highly non-linear functions of the thermodynamic state. They must be determined for each specific material by means of experimental and regression techniques. Stenholm [9] mentioned about the linear coefficient matrix from Onsager's formulation of irreversible thermodynamics that they can be measured experimentally or calculated by expanding around the thermal states. He named the fluxes "currents" and defined the forces as positive or negative deviations from equilibrium. The eigenvalues of the coefficient matrix are expressed in the paper. Based on the theory of non-equilibrium thermodynamics, transport equations for coupled mass and heat transport were derived by Kuhn et al. [10] for water pervaporation through a zeolite membrane. To model the paper drying process, Zvolinschi et al. [11] have used balance equations and common flux equations for heat and mass transfer in the paper drying process and comparative, flux equations based on the theory of non-equilibrium thermodynamics. They mentioned in the paper that the transfer coefficients for the

interface were evaluated by Bedeaux and Kjelstrup [12] in the absence of a parallel flow at the evaporation surface. The latter ones used non-equilibrium thermodynamics to obtain the appropriate boundary conditions at the evaporating surface of different liquids. Interfacial transfer coefficients, appearing in these boundary conditions, were determined from the experiments. They all were found as positive values.

Another method presented in previous works uses the theory of transport phenomena in porous materials developed by Luikov in order to analyze the conjugate problem of heat and moisture transport during thermal processes. In this regard, Kadem et al. [13] solved the three-dimensional Navier–Stokes equations along with the energy and concentration equations for the fluid coupled with the energy and mass conservation equations for the solid (wood) to study the transient heat and mass transfer during high thermal treatment of wood. A three-dimensional, unsteady-state model solving simultaneous heat and mass transfer in porous media was developed by Kocaefe et al. [14] The model took into account the variation of properties with temperature and/or moisture content and used Luikov's formulation. It was applied to the thermal treatment of wood at high temperature. Coles and Murio [15] introduced a stable numerical method for the determination of the temperature and moisture distribution in a Luikov system with space dependent diffusion coefficients during thermal drying in a porous medium. The mathematical model based on the set of coupled heat and mass transfer equations proposed by Luikov was applied to wood drying by several authors, for instance Irudayaraj et al. [16] and Younsi et al. [17], [18].

The study presented in this paper was focused on applying Onsager's coupled heat and mass transfer equations to convective wood drying. Heat and mass fluxes, thermodynamic forces and phenomenological coefficients were evaluated considering the retraction of the evaporation surface in wood.

2. MATERIALS AND METHODS

The convective heat and mass transfer process along a horizontal flat plate of moist wood located in a clear fluid, in this case heated air as drying agent, was considered in this study. The temperature and vapor concentration of the ambient medium are denoted 1 and $C_{1\infty}$, respectively. The flowing fluid has an incoming velocity u_∞. The flow regime is laminar, but this is monitored during the numerical runs, by computing the Reynolds number at each location of x. The x-coordinate is measured along the plate surface and the y-coordinate normal to it.

From the drying theory it is known that starting from the critical moisture content (which is about 30%) the evaporation surface gradually becomes deeper inside the wood [1]. Therefore, the evaporation occurs at a depth ξ below the wood surface (Fig. 1). This is also mentioned by Salin [19] who defines dry shell the wood thickness between the evaporation front and the wood surface, where there is no free water. Within the dry shell there is a moisture gradient which is the driving force for moisture migration from the evaporation front and a temperature gradient which is the driving force for the heat conduction to the evaporation front. Thus, an additional thermal resistance is developed in wood.
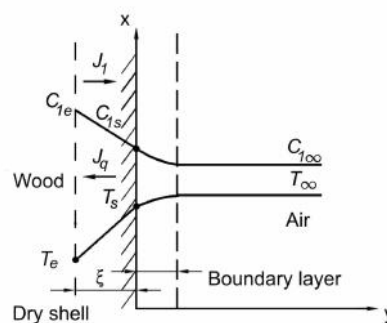

Figure 1: Temperature and moisture profiles across wood-air interface

Transfer of energy and mass is accompanied by an increase of entropy in a macroscopic system. According to the basic relation of irreversible processes thermodynamics, the entropy source is proportional to the sum of the products of fluxes and thermodynamic forces. Thus, the entropy production per unit time and unit fluid volume [20] can be written as

$$\dagger = \sum_i J_i X_i \tag{1}$$

where J_i are fluxes and X_i are thermodynamic forces.

Based on the phenomenological theories of irreversible processes, the irreversible fluxes are linear functions of the thermodynamic forces [20]

$$J_i = \sum_k L_{ik} X_k \tag{2}$$

The quantities L_{ik} are called phenomenological coefficients. Therefore, for a fluid volume unit located in the boundary layer, where molecular heat and mass transfer occurs, considering [3] and [20], the coupled heat and mass fluxes per unit of area can be written as follows:

$$J_q = -L_{TT}\frac{DT}{T^2} + L_{T1}\left[\frac{DT}{T^2}\left(r_0 + c_{p1}T - c_{p2}T\right) - \frac{R_1}{c_1 c_2}DC_1\right] - \frac{L_{TE_1}}{T}D\left(\frac{\rho_1 u^2}{2}\right) - \frac{L_{TE_2}}{T}D\left(\frac{\rho_2 u^2}{2}\right) \tag{3}$$

$$J_1 = L_{11}\left[\frac{DT}{T^2}\left(r_0 + c_{p1}T - c_{p2}T\right) - \frac{R_1}{c_1 c_2}DC_1\right] - L_{1T}\frac{DT}{T^2} - \frac{L_{1E_1}}{T}D\left(\frac{\rho_1 u^2}{2}\right) - \frac{L_{1E_2}}{T}D\left(\frac{\rho_2 u^2}{2}\right) \tag{4}$$

where L_{TT}, L_{T1}, L_{TE_1}, L_{TE_2}, L_{11}, L_{1T}, L_{1E_1}, L_{1E_2} are phenomenological transfer coefficients, T is the average air temperature, r_0 is the latent heat of vaporization of water at 273.15 K, c_{p1} and c_{p2} are constant-pressure specific heats of the air components - water vapor (index 1) and the dry air (index 2), R_1 is the gas constant of water vapor, c_1 and c_2 are mass fractions of the air components, ρ_1 and ρ_2 are the densities of the air components, u is the air velocity along the wood board, DT is the temperature gradient, DC_1 is the vapor concentration gradient, $D\left(\frac{\rho_1 u^2}{2}\right)$ and $D\left(\frac{\rho_2 u^2}{2}\right)$ are the kinetic energy gradients for the two air components, D stands for d/dy.

The phenomenological coefficients are in equations (3) and (4) unknown quantities. They can be determined if the fluxes and thermodynamic forces are known. Accordingly, they must determined by other methods. The thermodynamic forces can be expressed from the mediation theorem as

$$D\left(\frac{1}{2}\rho u^2\right) = \frac{\rho u_\infty^2}{2\delta_u(x)} \tag{5}$$

$$DT = \frac{T_\infty - T_s}{\delta_T(x)} \tag{6}$$

$$DC_1 = \frac{C_{1s} - C_{1\infty}}{\delta_C(x)} \tag{7}$$

where ρ is the density of air, u_∞, T_∞ and $C_{1\infty}$ are the air velocity, air temperature and water vapor concentration at the boundary layer outer edge, T_s and C_{1s} are the temperature and vapor concentration on the wood surface, δ_u, δ_T and δ_C are the thicknesses of the dynamic, thermal and concentration boundary layer.
According to Eckert and Drake [21] the dynamic boundary layer thickness and the thermal boundary layer thickness are

$$\delta_{u(x)} = 4.64\sqrt{\frac{\epsilon \cdot x}{u_\infty}} \tag{8}$$

$$\delta_{T(x)} = \delta_{u(x)}\frac{1}{1.026 \cdot \sqrt[3]{Pr}} \tag{9}$$

where ϵ is the coefficient of kinematic viscosity, Pr is Prandtl number.
By using the analogy between heat and mass transfer, the concentration boundary layer can be written as

$$\delta_{C(x)} = \delta_{u(x)}\frac{1}{1.026 \cdot \sqrt[3]{Sc}} \tag{10}$$

where Sc is Schmidt number.
If the heat and mass transfer includes both boundary layer and dry shell, the heat and mass flux equations are

$$J_q = h'\left(T_\infty - T_e\right) \tag{11}$$

$$J_1 = h_m'\left(\rho_{1e} - \rho_{1\infty}\right) \tag{12}$$

where h' and h_m' are the heat and mass transfer coefficients, ρ_{1e} and $\rho_{1\infty}$ are the vapor densities on the evaporation front and at the boundary layer outer edge. The heat transfer coefficient from the heated air to the evaporation surface is [1]

$$h' = \left(\frac{1}{h} + \frac{\varsigma}{k_s} \right)^{-1} \tag{13}$$

and the mass transfer coefficient from the evaporation surface to the heated air [19]

$$h_m' = \left(\frac{1}{h_m} + \frac{\varsigma}{D_s} \right)^{-1} \tag{14}$$

where h is the heat transfer coefficient for the corresponding case with a wet surface, ς is the effective thickness of the dry shell, k_s is the thermal conductivity within the dry shell, h_m is the mass transfer coefficient for the case with a wet surface, D_s is the diffusion coefficient within the dry shell.

From the conservation conditions of the heat and mass fluxes, the following balance equations can be written

$$h(T_\infty - T_s) = \frac{T_s - T_e}{\dfrac{\varsigma}{k_s}} \tag{15}$$

$$h_m(\rho_{1s} - \rho_{1\infty}) = \frac{\rho_{1e} - \rho_{1s}}{\dfrac{\varsigma}{D_s}} \tag{16}$$

where T_s and ρ_{1s} are the temperature and vapor density on the wood surface, T_e and ρ_{1e} are the temperature and vapor density on the evaporation surface.

By substituting equations (13) and (14) in (15) and (16), the next equalities between the two kinds of heat and mass transfer coefficients can be expressed

$$h' = h \frac{T_\infty - T_s}{T_\infty - T_e} \tag{17}$$

$$h_m' = h_m \frac{\rho_{1s} - \rho_{1\infty}}{\rho_{1e} - \rho_{1\infty}} \tag{18}$$

In order to determine h' and h_m', the heat and mass transfer coefficients h and h_m must be evaluated before. They can be obtained from criterial equations specific to the drying process. Nesterenko, cited by [1] developed the following relations for the heat and mass transfer in evaporation processes

$$Nu_x = 2 + A \cdot Pr^{0.33} \, Re_x^n \, Gu^m \tag{19}$$

$$Sh_x = 2 + A' \cdot Sc^{0.33} \, Re_x^{n'} \, Gu^{m'} \tag{20}$$

where $Gu = (T_\infty - T_s)/T_\infty$ is Gukhman number and

$A = 0.51$, $m = 0.175$, $n = 0.61$; $A' = 0.49$, $m' = 0.135$, $n' = 0.61$

are experimental coefficients, valid in the range $(3.15 \times 10^3, ..., 2.2 \times 10^4)$ of Reynolds number. We mention at this point that this range was encountered in the present analysis. The local Nusselt and Sherwood numbers are

$$Nu_x = hx/k_f \tag{21}$$

$$Sh_x = h_m x / D_f \tag{22}$$

where subscript f refers to the fluid (air).

The physical quantities were calculated by using data from thermodynamic tables [22] at the average temperature of air. The input data for numerical analysis were $T_\infty = 333.15\,\text{K}$, $u_\infty = 1.5\,\text{m/s}$ and the relative humidity of air at the boundary layer outer edge was $\{\varphi_\infty = 45\%$. The pressure was constant $p = 10^5\,\text{Pa}.\}$

3. RESULTS AND DISCUSSIONS

The phenomenological coefficients were calculated for a range of x-values between 0.1 and 0.25 m, the latter corresponding to the length of a wood board dried in a laboratory drier (wind tunnel). They are indicated in Table 1. According to Onsager's reciprocal relations [20], $L_{ik} = L_{ki}$. In the present paper the phenomenological coefficients were calculated based on the assumption that $L_{T1} = L_{1T}$. The phenomenological coefficients are physical constants, which are always positive. There is a condition mentioned by Prigogine [4] that the self coefficients L_{TT} and L_{11} are positive and the mutual coefficients L_{T1}, L_{TE1}, L_{TE2}, L_{1E1}, L_{1E2} can be either positive or negative. The negative values indicate that the gradients have opposite directions than those initially considered, since the heat and mass fluxes are also positive quantities. It also can be observed that L_{TE1} and L_{1E1} have opposite signs with respect to L_{TE2} and L_{1E2}, meaning that the air components, water vapor and dry air move in opposite directions during the drying process. Accordingly, a component separation occurs in the boundary layer

due to the influence of the kinetic energy of each component.

Table 1: Phenomenological coefficients

L_{TT} [WK/m]	$L_{T1} = L_{1T}$ [kgK/ms]	L_{TE1} [m²K/s]	L_{TE2} [m²K/s]	L_{11} [kgKs/m³]	L_{1E1} [Ks]	L_{1E2} [Ks]
1.238×10⁷	4.412	5.876×10¹¹	-3.59×10¹⁰	1.561×10⁻⁶	2.755×10⁶	-1.683×10⁵

The heat and mass flux equations (3) and (4) can be compared with those obtained from Fourier's law $J_q = -k_f DT$ and Fick's law $J_1 = -D_f \ DC_1$ expressed for the boundary layer if the other gradients become zero. There can be written therefore relationships between the phenomenological coefficients determined before and the thermal conductivity and coefficient of diffusion, respectively. From these considerations we obtained for the thermal conductivity of the fluid, k_f=0.37 W/mK (the value k_f=0.027 W/mK was used in equation (20)) and for the mass diffusion coefficient of the fluid, D_f=1.87×10⁻² m²/s (the value D_f=3.2×10⁻⁵ W/mK was used in equation (21)). The heat and mass fluxes per unit of area as functions of the x-coordinate are shown in Figures 2 and 3. There is a sensible decrease in the intensity of heat and mass transfer along the wood board.
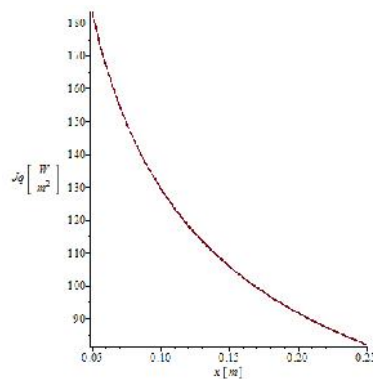

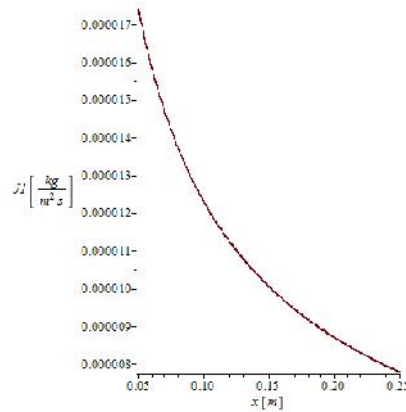**Figure 2:** Heat flux variation along the wood board

Figure 3: Mass flux variation along the wood board

Figure 4 shows the change of the dry shell thickness along the wood board. As can be seen, the thickness also decreases along the board being influenced by the heat and mass flux magnitudes.

4. CONCLUSION

Phenomenological equations for the coupled heat and mass transfer during wood drying that relate fluxes to thermodynamic forces were applied in the paper for the determination of the phenomenological coefficients. The fluxes were calculated from criterial equations and the thermodynamic forces from the mediation theorem. There was a decrease of both fluxes along the wood board, meaning that there is a non-uniformity of drying on the board length. The retraction of the evaporation front introduced an additional thermal resistance in wood that reduced the magnitude of the heat and mass transfer coefficients on the board length with respect to the same transfer coefficients if the evaporation front would have been on the wood surface. By using the method of non-

equilibrium thermodynamics the influence of each form of transfer (heat, mass and momentum) is pointed out in the heat and mass fluxes, showing that they are strongly coupled.
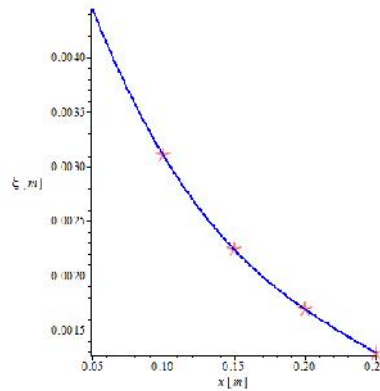

Figure 4: Dry shell thickness variation along the wood board

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