Promoting advances in understanding water vapor sorption in wood: relegating popular models and misconceptions

S V Glass[1,*], **S L Zelinka**[1], **C R Boardman**[1] **and E E Thybring**[2]

[1] Building and Fire Sciences, US Forest Service Forest Products Laboratory, 1 Gifford Pinchot Drive, Madison, WI 53726, USA

[2] Bioresource Chemistry & Technology, Department of Geosciences and Natural Resource Management, University of Copenhagen, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark

*Correspondence: samuel.v.glass@usda.gov

Abstract. Water vapor sorption is a fundamental characteristic of wood as a building material. Apart from empirical prediction, models are often used to interpret the time-dependent process of water vapor uptake (sorption kinetics) and equilibrium states of water in wood (sorption isotherms). This paper summarizes our recent investigations into measurement methods and popular models that are widely used for interpreting these physical phenomena. Commonly used criteria for determining equilibrium moisture content with the dynamic vapor sorption technique yield much larger errors than previously thought. A more rigorous equilibrium criterion and a method to reduce data acquisition time are proposed. Evaluation of the parallel exponential kinetics model with improved data and multi-exponential decay analysis indicates that this model is unable to characterize the full sorption kinetic response following a step change in relative humidity. Fitting of common sorption isotherm models to high-quality equilibrium data for wood gives model predicted physical quantities such as monolayer capacity and enthalpy of sorption that are far from agreement with independently measured data. Thus, these models are not valid for water vapor sorption in wood. New theoretical models are needed that correctly describe the physical phenomena.

1. Introduction

The performance of wood as a building material is highly influenced by its interaction with water. Physical properties (dimensions, heat capacity, thermal conductivity) and mechanical properties (strength, stiffness, creep) depend strongly on moisture content. In addition, water is a critical factor in mold growth and fungal decay.

Models are commonly used for empirical prediction of wood moisture content (MC) as a response to environmental conditions, i.e., relative humidity (RH) and temperature. Additionally, theoretical models are used for interpretation of sorption kinetics as well as sorption isotherms. Such interpretation relies on the assumption that the idealized physical system for which the model is derived is an adequate representation of the real physical system. Here we summarize recent work on this topic and highlight three main concerns: the need for reliable measurements and stringency in defining equilibrium (Section 2); the inadequacy of a popular model for sorption kinetics (Section 3); and the failure of well-known sorption isotherm models to accurately predict physical quantities for water in wood (Section 4). The paper concludes with recommendations for advancing the state of the art.

2. Promoting reliable sorption measurements

Experimental measurements provide a foundation for validating sorption models and relating equilibrium states to other physical properties. Several criteria affect the reliability of the data, including the operational definition of equilibrium, the calibration accuracy of mass, temperature, and RH measurements, and the stability of the environmental conditions (temperature and RH) [1]. A mass stability criterion is often used for identifying equilibrium, meaning that the moisture content is assumed to be sufficiently close to equilibrium when the rate of change in mass with time under constant environmental conditions becomes arbitrarily small. Surprisingly, our evaluation of sorption data for wood found that the more reliable measurements were made in the 1960s and 1970s [1].

In the past 15 years, automated sorption balances, also known as dynamic vapor sorption (DVS) analyzers, have become widely used. A commonly reported mass stability criterion for this technique is a rate of change in moisture content less than 0.002% min^{-1}, or 20 micrograms of water per gram of dry material per minute (20 µg g^{-1} min^{-1}) over a 10-min period. Although this criterion reduces data acquisition time, it yields much larger errors than previously thought [2], as illustrated for loblolly pine in Figure 1 using our recent DVS data [3] for a solid specimen 1.2 mm thick (longitudinal) with dry mass of ~20 mg. These errors in MC are more significant than measurement errors in temperature or RH using DVS analyzers. We defined equilibrium operationally as the point at which the change in mass over 24 hours was within the inherent mass stability of the instrument (2 µg). Furthermore, we developed a correction method to account for systematic error from interrupting data collection prior to equilibrium; this method improves data quality while reducing acquisition time [3].

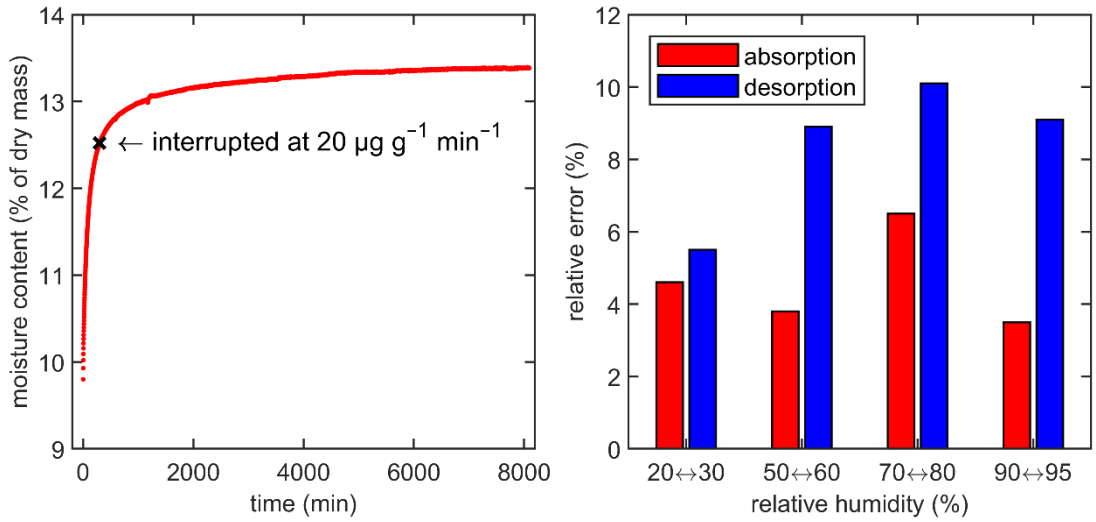

Figure 1. Water vapor absorption in loblolly pine from 70% to 80% RH as moisture content vs. time (left). Relative error in equilibrium moisture content of loblolly pine using the 20 µg g^{-1} min^{-1} stability criterion for various relative humidity conditions (right). Data replotted from [3].

3. Relegating the parallel exponential kinetics model

The most widely adopted model to interpret the rate of water vapor sorption in wood is the parallel exponential kinetics (PEK) model. Mathematically, this model is the sum of two independent exponential functions, each having a moisture component and a characteristic time constant corresponding to "fast" and "slow" sorption processes [4–6]. Many papers have ascribed physical significance to the model parameters. Although the PEK model yields good curve-fitting statistics, we found that this was an artifact of interrupting the measurements prior to equilibrium (i.e., stopping data acquisition prematurely) [7], as illustrated in Figure 2. When the model was fitted to data collected to

equilibrium (given by the operational definition described above), the parameters changed drastically, the residuals became nonrandom, and the fitting statistics became worse (e.g., Figure 2, right column).

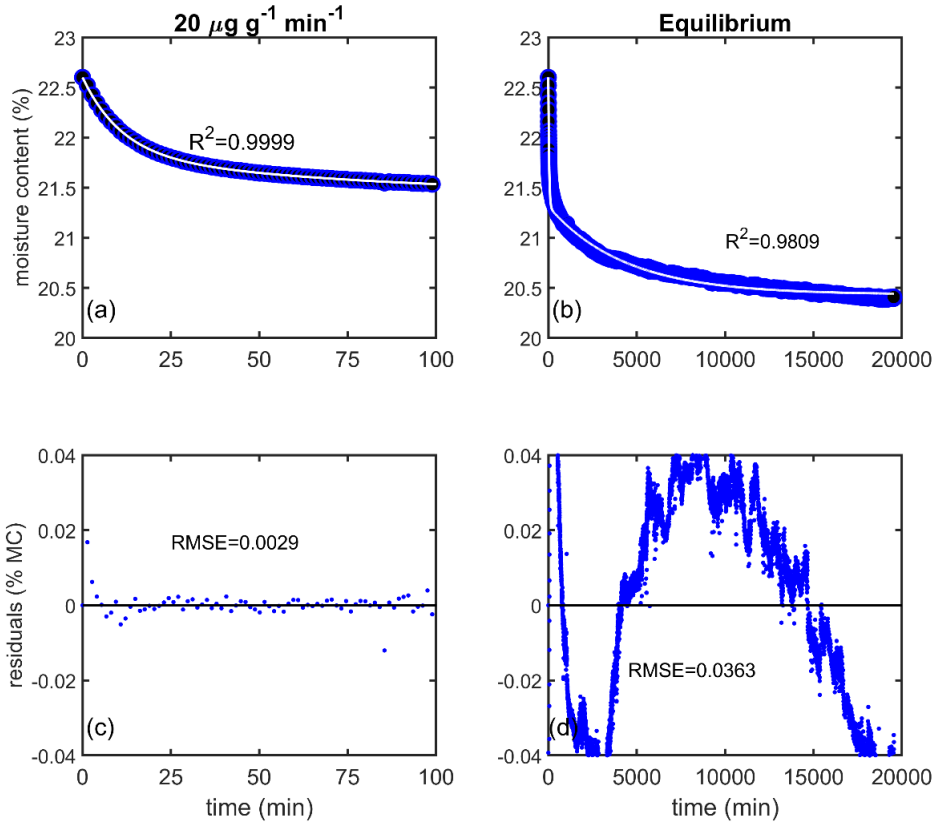

Figure 2. (Top) PEK model (white curve) fitted to scanning desorption data (blue points) from 95% to 90% RH in loblolly pine, for interrupted sorption (left) based on the common mass stability criterion of 20 μg g^{-1} min^{-1} over 10 min and for sorption until equilibrium (right). (Bottom) Residuals from PEK model fits. Data replotted from [7] for solid specimen 1.2 mm thick (longitudinal) with dry mass of ~20 mg.

We introduced a new approach for analyzing sorption kinetic data known as multi-exponential decay analysis (MEDEA), which involves fitting a series of hundreds of exponentially decaying functions to normalized sorption data [6–8]. This approach generates spectra indicating the dominant time scales of sorption kinetics after a change in RH until equilibrium is reached. The spectra exhibit between two and six distinct peaks or components, as shown in Figure 3. Most cases have four or more components. This analysis confirms that the PEK model does not capture the full sorption process, and the model parameters cannot be physically meaningful.

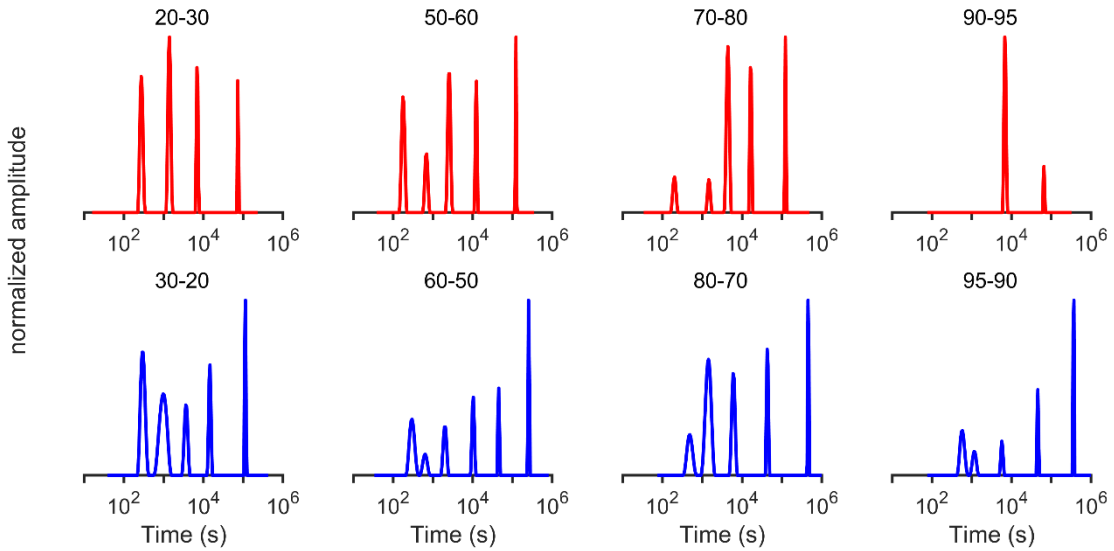

Figure 3. MEDEA spectra for loblolly pine absorption steps (top row) and desorption steps (bottom row). Peaks indicate dominant relaxation times. Numbers above each spectrum indicate the initial and final RH. Data replotted from [8] for solid specimen 1.2 mm thick (longitudinal) with dry mass of ~20 mg.

4. Relegating popular sorption isotherm models

Several sorption isotherm models, including the Brunauer-Emmett-Teller (BET) [9], Dent [10], Guggenheim-Anderson-de Boer (GAB) [11–14], and Hailwood-Horrobin (HH) [15] models, have been widely applied to water vapor sorption in wood. However, these models do not correctly predict the enthalpy of sorption, a key thermodynamic quantity for wood–water interactions [16]. Despite this and further critiques [17–18], the models are often used in the scientific literature to predict properties such as the monolayer capacity, which is a representation of the number of available sorption sites in the material. After identifying high-quality sorption isotherm data for wood at multiple temperatures [1, 19], we fitted the models mentioned above and compared the physical properties predicted by the models with independently measured values [20]. None of the models accurately predicted any of the physical properties. The discrepancy between model predictions of monolayer capacity and measured values of hydroxyl (-OH) groups accessible for water sorption is illustrated in Figure 4. Uncertainty analysis showed that the disagreement between predicted values and experimental measurements could not be attributed to experimental error. These findings demonstrate that the models cannot be considered valid or meaningful for describing wood–water interactions.

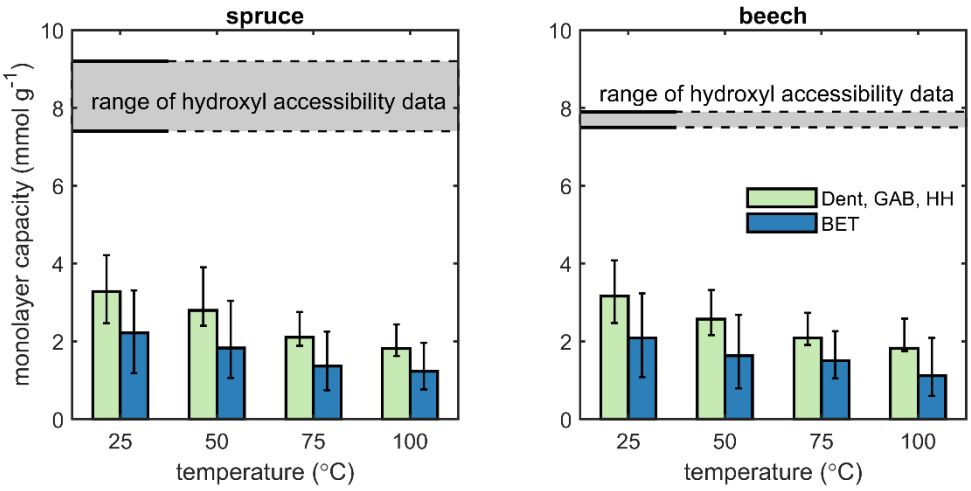

Figure 4. Predicted monolayer capacity from models fitted to sorption data for spruce and beech [19] as a function of temperature, compared to experimental hydroxyl accessibility data. Data replotted from [20] for models mentioned in the body of the paper.

5. Recommendations

This paper highlights the importance of reliable sorption measurements and the invalidity of the parallel exponential kinetics model and popular sorption isotherm models for understanding wood–water interactions. New and improved experimental methods that can probe smaller length scales and refined computational methods are needed to elucidate the complex interactions between water and wood [21]. New modeling approaches are needed that correctly describe the complex physical phenomena involved in the sorption process, including the heat of interaction, moisture-induced swelling, internal stresses, and changes in polymer mobility [6]. Finally, equilibrium models are needed that explain the distinct populations of absorbed water in the cell wall and the origin of sorption hysteresis [20].

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