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Acquisition of sorption isotherms for modified woods by the use of dynamic vapour sorption instrumentation. Principles and Practice

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ABSTRACT

The complex wood-water relationship has been the topic of numerous studies. Sorption isotherms – in particular – have been derived for hundreds of wood species, their sap- and heartwood sections as well as for decayed, engineered and modified wood materials. However, the traditional methods for obtaining sorption isotherms are very time consuming. With new dynamic vapour sorption (DVS) instrumentation, the acquisition of data for constructing sorption isotherms is suddenly dramatically lowered. Where the traditional methods often required months, data can now be obtained in a matter of days depending on the number of data points required.

The fast data acquisition makes DVS a useful tool in studying the sorption properties of wood, and especially in studying the effect of different modification treatments on these properties. This study includes an investigation of the sorption properties of heat treated and acetylated softwood. The results of both are compared with results for untreated softwood, and general remarks regarding the acquisition and interpretation of sorption data are made. It is pointed out that care must be taken when interpreting results such as desorption isotherms not commencing from full water saturation.

The sorption properties of heat treated Scots pine (Celloc) and acetylated Radiata pine (Accoya) showed a greater hysteresis effect for the previous than both acetylated and untreated softwood. Furthermore, the effectiveness of the different modification treatments was quantified by the reduction in moisture content relative to untreated Scots pine sapwood. This may be used in future documentation of the resistance of modified wood to fungal decay.

Keywords: dynamic vapour sorption, sorption isotherms, modified wood.

1. INTRODUCTION

The complex wood-water relationship has been the topic of numerous studies. Sorption isotherms – in particular – have been derived for hundreds of wood species, their sap- and heartwood sections as well as for decayed, engineered and modified wood materials. Traditionally, sorption isotherms have been acquired by using a number of different saturated salt solutions each reflecting a target relative humidity (RH). The material to be investigated is positioned close to the saturated salt solution surface to equilibrate. The equilibrium moisture content is obtained when the mass change of the investigated material is below a certain threshold per time unit (a dm/dt requirement). For screening purposes, chambers with controlled climates (‘air-conditioning’) have also been used. Both methods, however, are time and labour consuming since all samples need to be manually transported and registered a number of times in each chamber. This also introduces a considerable room for error.

The availability of dynamic vapour sorption (DVS) instrumentation has reduced the amount of work needed to obtain sorption isotherms for wood materials. The basic assumptions for all three methods are, however, identical since equilibrium is defined based on dm/dt requirements, e.g. 0.001 %/min. Using automated equipment reduces time and labour intensity, but the operator still needs to understand the basic assumptions. Most DVS instruments are inaccurate when target RH is set $> 96\%$. Therefore this value is often set as maximum target. This means that the subsequent desorption is a scanning curve in the highest RH region – not the true desorption curve. This paper focuses on the importance of understanding the basic wood-water relationship when applying DVS instrumentation. Both untreated and modified softwood species are employed and adsorption as well as scanning and true desorption curves derived.

2. EXPERIMENTAL METHODS

The investigation of sorption properties reported in this study was performed using dynamic vapour sorption (DVS) instrumentation of the type DVS Advantage 2 from Surface Measurement Systems, London, UK. The basic principle of the equipment is shown in Fig. 1.

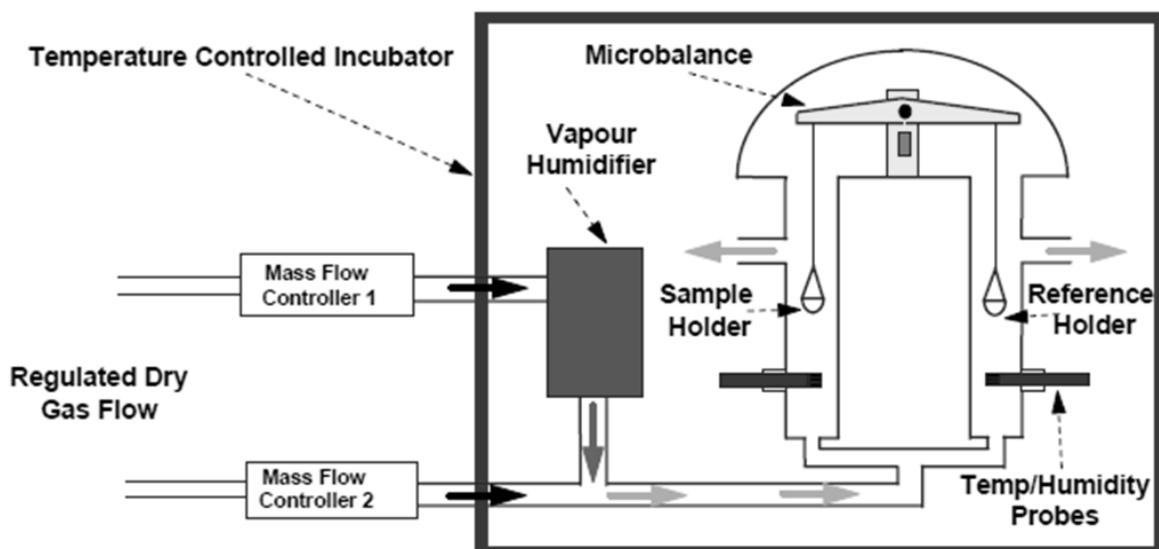


Figure 1: Schematic illustration of the basic principle behind the DVS Advantage. Reproduced with kind permission of Surface Measurement Systems, London, UK.

The cantilever of the microbalance is continuously held in horizontal position by an applied moment. The electrical current used to uphold this moment is therefore an indirect measure of the mass loaded in the sample holder. The equipment is capable of keeping a stable temperature in the range 5-60 °C. The relative humidity (RH) of the air surrounding the loaded sample in the sample holder is controlled by mixing dry and water saturated air to a mixed air with a specified RH. Thus, in the range 0-96 % RH all levels of RH are possible. This is an advantage over the traditional method with saturated salt solutions, where the levels of RH were limited by the different available salt solutions.

This type of DVS Advantage is capable of handling up to 5 g sample mass; however, for a highly hygroscopic material like wood, a sample mass of around 20-50 mg is enough. The smaller the sample mass, the faster the data acquisition. However, in order to secure accuracy of the obtained results, sample masses below 20 mg should be avoided. Using the DVS introduces another parameter – the time-out. This parameter sets the maximum time spent at each RH level before moving up or down. Some wood materials equilibrate quickly while others – in particular some modified woods – require longer time at each sorption step to arrive at the true equilibrium. Some knowledge on the sorption properties of the material is therefore needed to set the parameters correctly.

2.1 Material and preparation

The sample material used in this study covers both untreated Scots pine sapwood as well as two types of modified softwood: heat treated Scots pine (Celloc) and acetylated Radiata pine (Accoya). Since only a very small amount of material is necessary for the sorption experiments, measures must be taken in order to secure a representative sample. Therefore, the different types of sample material were grinded down to a powder with a maximal particle size of 1 mm. This does not change the sorption properties of the wood (Seborg and Stamm 1931). Samples were taken from the powders, and the sample mass varied between 20-45 mg (dry weight).

2.2 Experimental procedure

All experiments in this study were performed at 20 °C. In order for the software to automatically change the surrounding RH when moisture equilibrium for the sample is obtained, a dm/dt stability criterion must be met. The dm/dt stability criterion selected for the experiments in the present study was in the range 0.001-0.002 %/min and based on previous findings for a sample range of 20-45 mg of wood.

Two types of experiments were undertaken. First, adsorption-desorption cycles were run in the range 0-90 % RH starting and finishing at 0 % RH. Secondly, the samples were subjected to desorption from water saturation. In order to water saturate the samples they were held in filter paper and submerged in demineralised water in a dessiccator. Hereafter, vacuum (0.1 bar) was applied for 1 hour followed by a pressure (8 bar) for 1 hour. After this, the desorption experiment was run starting at 80 % RH and ending at 0 % RH in steps of 20 % RH.

3. RESULTS AND DISCUSSION

The basic results obtained from the sorption isotherm experiment are shown in Fig. 2. The mass as function of time is illustrated along with the relative humidity (RH) surrounding the wood sample.

Due to the small sample amount used, i.e. only 35 mg dry weight, the entire experiment is completed within 2.5 days.

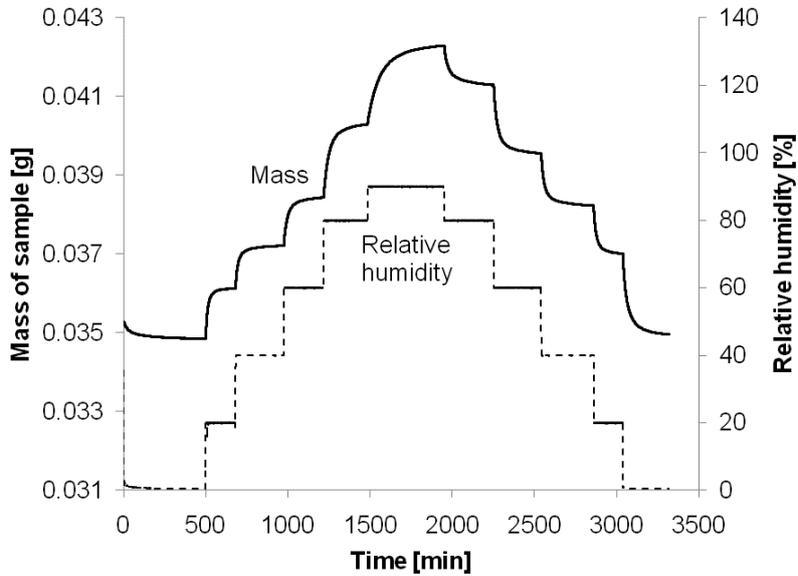


Figure 2: Mass of untreated Scots pine sapwood sample (solid line) and relative humidity (dashed line) in the DVS equipment as function of time.

The change in mass over time can also be illustrated as the dm/dt over time in Fig. 3. As can be seen, the software automatically moves to the next RH step upon meeting the dm/dt stability criterion set by the operator. From Figs. 2 and 3 it is clear that the chosen criterion was satisfactory in securing a sample mass sufficiently close to the true equilibrium mass at the different RH levels. Thus, in the following the sample mass at the end of each RH step is referred to as the mass in equilibrium with the given climate conditions. This mass can be used for calculating the moisture content of the sample on the basis of the acquired dry mass of the sample. This was found after completing the first step of the test run at 0 % RH, see Fig. 2.

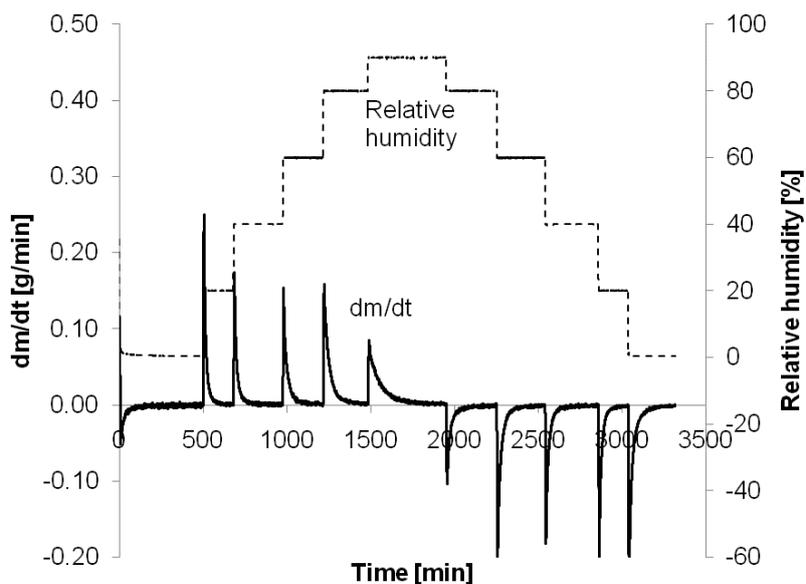


Figure 3: Mass change over time, dm/dt along with the relative humidity illustrated as function of time for the untreated Scots pine sapwood sample.

3.1 Sorption isotherms and hysteresis

The moisture content in equilibrium with the different RH levels can be used to construct sorption isotherms as those depicted in Fig. 4. In this figure curves for the two different types of modified wood are illustrated along with the curve for the untreated Scots pine sapwood sample. The sorption isotherms for all three types of samples have a sigmoidal shape. As expected, the modified woods have sorption isotherms below that for the untreated Scots pine sapwood.

It is evident that there is a significant hysteresis, i.e. the curves obtained from desorption and adsorption do not coincide. This is due to the changing hygroscopicity of the wooden samples during adsorption and desorption (Urquhart 1929; Watt 1980). The hygroscopicity is a measure of the number of available sorption sites in the material. During desorption internal bonds between sorption sites are created by the formation of hydrogen bonds (Papadopoulos and Hill 2003; Weatherwax 1977). Urquhart and Eckersall (1930) suggest that the sorption hysteresis of wood might be due to this mechanism where the sorption sites are brought together during desorption to satisfy each other rather than forming hydrogen bonds to water molecules. Upon a subsequent adsorption, the hygroscopicity has been lowered since a number of sorption sites have been saturated by each other in a favourable way. Hereby, the amount of available sorption sites is lowered resulting in a lower hygroscopicity and lower moisture content for a given humidity. As the adsorption proceeds, the structure is gradually opened up again due to swelling of the cell wall, hereby increasing the number of available sorption sites.

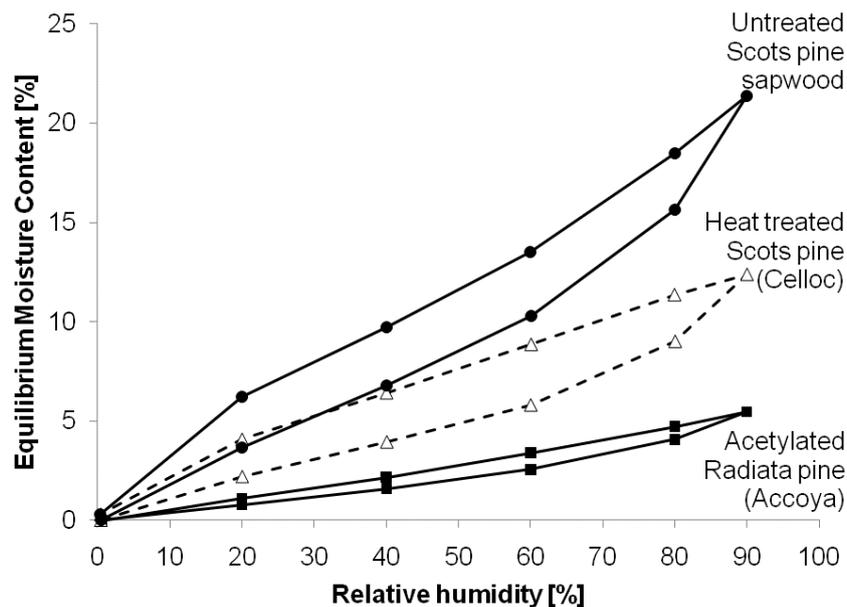


Figure 4: Sorption isotherms for untreated Scots pine sapwood, heat treated Scots pine (Cello), and acetylated Radiata pine (Accoya).

The sorption isotherm curves with 11 points each have been obtained from data for three types of samples in just over 4.5 days in total. However, one must bear in mind, that the desorption curves for the three samples are *not* true desorption boundary curves. This is because the maximal hygroscopicity can only be reached by complete water saturation of the wood. Such cannot be reached just through exposure to saturated water vapour, e.g. over a liquid water surface (Hill et al. 2009). It can only happen by vacuum saturation where the liquid water is forced into the wood.

In order to illustrate the significant difference between desorption curves from water saturation and desorption curves obtained from conditioning in humid air, desorption curves from saturation were acquired for the two types of modified wood, see Figs. 5 and 6. This was done by vacuum saturating samples and then starting the experiment in the DVS instrument at 80 % RH followed by decreasing RH in steps of 20 % RH.

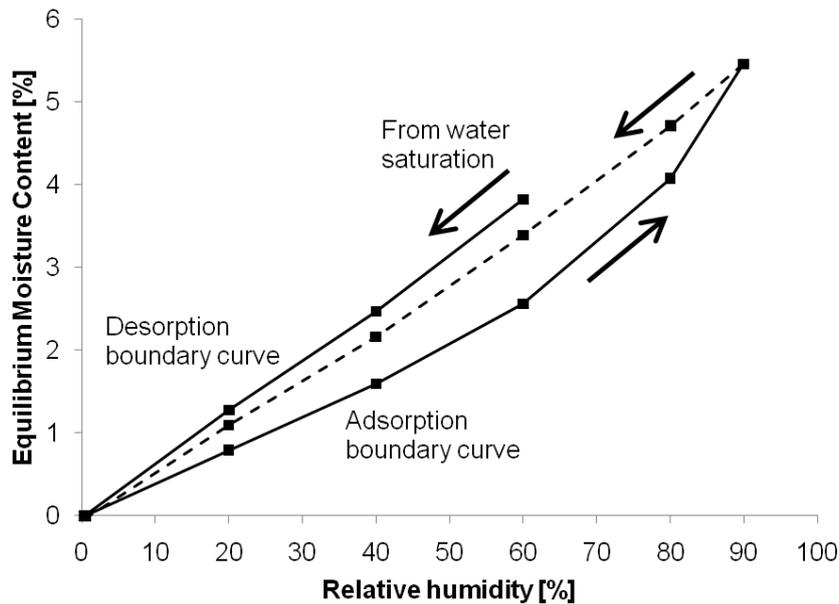


Figure 5: Adsorption and desorption boundary curves for acetylated Radiata pine (Accoya) along with a scanning curve from 90 % RH to 0 % RH.

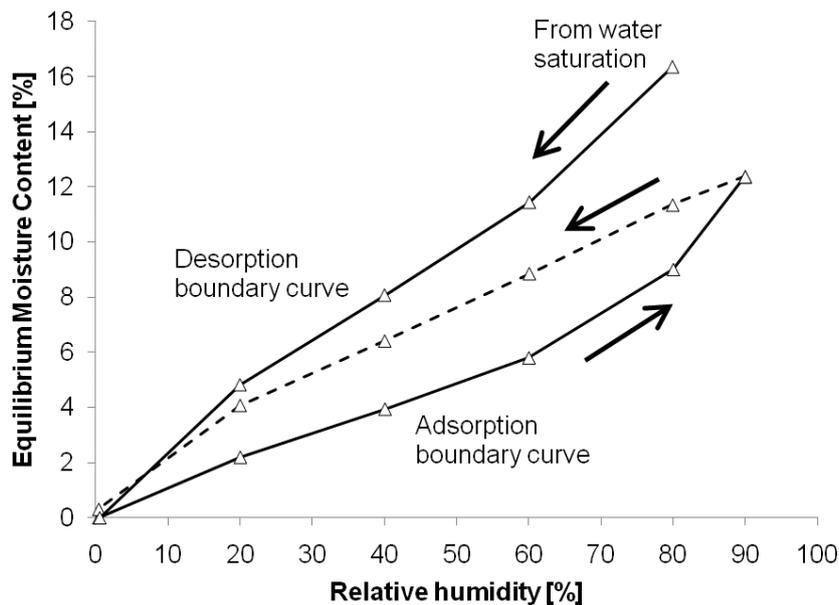


Figure 6: Adsorption and desorption boundary curves for heat treated Scots pine (Celloc) along with a scanning curve from 90 % RH to 0 % RH.

It is clear that the desorption curve obtained from equilibrium at 90 % RH is far from the desorption boundary curve obtained from water saturation. The first is thus only a scanning curve. It is

remarkable to see that the scanning curve from 90 % RH only converges with the desorption boundary curve below 20 % RH. Typically, scanning curves for samples conditioned over a liquid water surface converge with the desorption boundary curve around 60-70 %RH (Spalt 1958). Thus, the difference of just 10 % RH between conditioning over liquid water and at 90 % RH makes a huge difference on the derived sorption isotherms. This should be kept in mind when deriving sorption properties from sorption experiments such as the ones reported here.

The hysteresis effect can be quantified by the ratio between adsorption and desorption equilibrium moisture contents at similar climatic conditions (Seborg et al. 1938). This is illustrated in Fig. 7 where an increasing hysteresis ratio is observed for both heat treated Scots pine and acetylated Radiata pine. Thus, it seems the relative difference in hygroscopicity between the adsorption and desorption conditions is lower for higher RH, i.e. the amount of available sorption sites become increasingly similar between the two conditions.

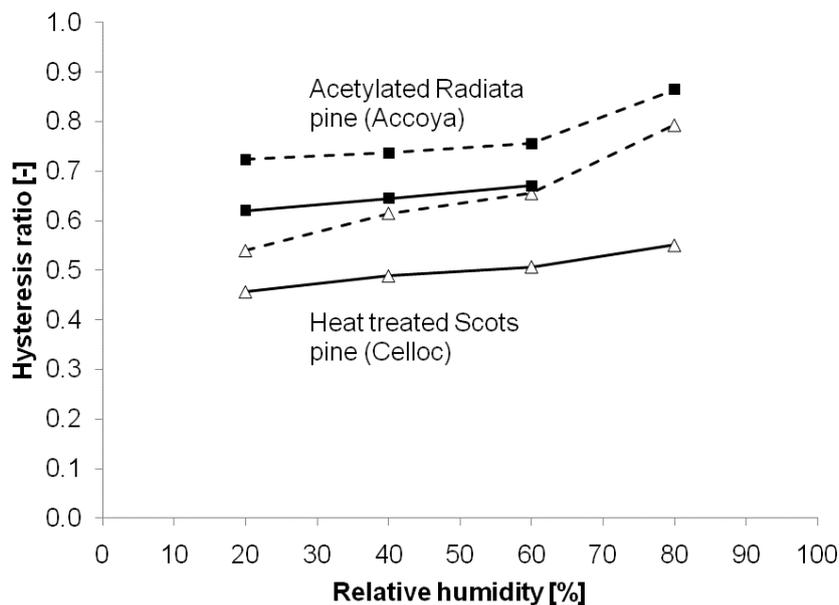


Figure 7: Ratio between adsorption and desorption equilibrium moisture content for heat treated Scots pine (triangles) and acetylated Radiata pine (squares). The solid lines represent desorption boundary moisture content, whereas the dashed lines represent moisture contents derived from the scanning curves.

However, the hysteresis effect for especially heat treated Scots pine is significantly higher than 0.7-0.8 which is commonly observed for hysteresis in untreated wood (Seborg et al. 1938). This indicates that the heat treatment is causing a greater locking of sorption sites (Urquhart 1929) than for untreated wood. This locking can only be reversed upon full saturation of the cell wall, i.e. by vacuum saturation with water. For desorption from 90 % RH the hysteresis ratio for both types of modified wood is higher due to the incomplete opening of the structure compared with a fully saturated condition.

3.2 Effectiveness of modification treatments

There are several ways of assessing the effectiveness of the different modification treatments. Since the primary objective of the modification is to lower the sorption isotherms to prevent attacks from fungi, examining the sorption isotherms shown in Fig. 4 is perhaps the most obvious way of assessing the effectiveness. In this figure it is clear that the moisture content of both types of modified wood is below the basic rule-of-thumb limit for fungal decay of 20 % moisture content (Carll and Highley 1999).

Another way to quantify the effectiveness of treatment and compare several modification treatments is by the moisture exclusion efficiency, MEE (Hill 2006). This can be calculated as the difference in moisture content between untreated and modified wood over the moisture content of the untreated wood (Hill 2006). However, in this study the acetylated and untreated wood are compared despite a difference in species. The uncertainty in doing this should be insignificant due to the small variation in the sorption isotherms between softwood species (Kollmann 1968). Therefore, the untreated Scots pine sapwood sample is used as reference to both types of modified wood presented in this study. The MEE is illustrated in Fig. 8 where it is seen that the effectiveness of treatment is fairly constant for both acetylated and heat treated wood of about 76 % and 39 %, respectively. This constancy indicates that the way moisture is taken up by the wood does not change upon modification. Instead, sorption sites in the cell wall are made inaccessible by either chemical modification or thermal degradation of the sites. However, whether the thermal degradation results in capillaries inside the cell wall can only be revealed at much higher levels of humidity where capillary condensation is significant. Thygesen et al. (2010) found that capillary condensation in untreated and acetylated wood does not occur below 99.5 % RH. However, the heat treatment might create internal voids in the cell wall in which capillary condensation can occur at a lower levels of RH.

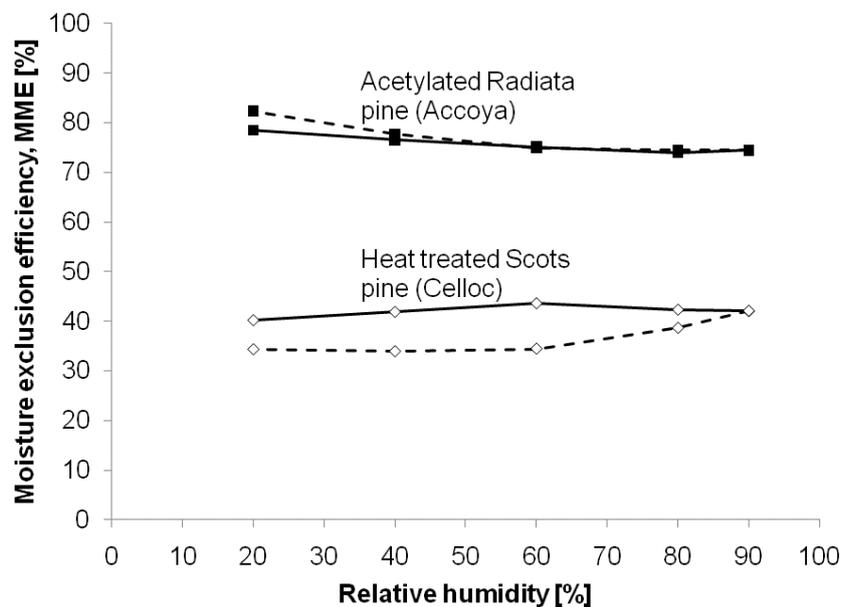


Figure 8: Moisture exclusion efficiency, MEE of the two modification treatments as function of relative humidity. The solid line is the MEE derived from the adsorption curves and the dashed line is the MEE derived from the scanning curves.

4. CONCLUSIONS

The sorption properties of both modified and untreated wood were investigated using dynamic vapour sorption (DVS) instrumentation. It was pointed out that care must be taken when interpreting the results such as the obtained sorption isotherms, e.g. if the desorption is not commencing from full water saturation, the desorption curve will not coincide with the true desorption boundary curve.

The fast data acquisition enabled a rapid assessment of the sorption properties of both acetylated and heat treated softwood. The hysteresis effect was seen to be greater for heat treated Scots pine than for acetylated Radiata pine. Also, the effectiveness of the modification treatments was quantified by determination of the reduction in equilibrium moisture content relative to untreated Scots pine sapwood. This may be used in future documentation of the resistance of modified wood to fungal decay.

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