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THE HEAT OF SORPTION IN PAPER DRYING – AN INVESTIGATION OF MEASUREMENT METHODS AND INFLUENCE OF PULP PARAMETERS

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ABSTRACT

When the dry content during pulp drying reaches a level above 75% to 80% the free water, i.e. unbound water, has been evaporated. The remaining water is bonded to the surface due to physisorption, additional energy is necessary to overcome these bonding effects. This additional energy is called heat of sorption. At 80ºC and a dry content of 95% for unbleached softwood kraft pulp the evaporation energy increases up to 2800 kJ per kg water compared to the latent heat of water of about 2300 kJ/kg at the same temperature.

Different measuring methods to determine the heat of sorption H_S are described in the literature, the reported values for H_S of pulp show large differences. The first aim of this work is to compare the results of different measurement methods using the same sample pulp. We investigated calculation of H_S from sorption isotherms collected with a conventional climate chamber (ESC) and differential vapor sorption (DVS) analysis. Furthermore we applied direct measurement of the heat flux generated by sorption using differential scanning calorimetry (DSC), differential scanning calorimetry combined with thermogravimetric analysis (DSC/TGA) and reaction calorimetry (RC). All but one measurement method delivered consistent results in the range of H_S=40 kJ/kg to 70 kJ/kg additional energy due to surface sorption. The advantages and disadvantages of the different measurement techniques are discussed.

In the second part of this work the impact of pulping and pulp treatment on the heat of sorption has been investigated. Refining and bleaching seems to have no impact. Pre drying reduces the overall heat of sorption by 15 %. The addition of inorganic fillers to paper reduces its heat of sorption due to a negligible H_S of the filler.

In conclusion the total additional energy caused by sorption effects is less than 2% of the overall energy necessary to fully dry the pulp. Additionally the heat of sorption is nearly unaffected by pulping, bleaching, refining or pre-drying of the pulp. Therefor the heat of sorption H_S is playing only a minor role for industrial applications of paper drying.

1 INTRODUCTION

The drying process in paper can be divided into several different phases, see figure 1). The x-axis shows the moisture content X [kg/kg] and y-axis shows the drying rate [kg/s]. The energy consumed in the heat up phase (A-B) primarily increases the web temperature and is not used for evaporation of water. The first drying phase (B-C) is characterized by a constant drying rate and constant temperature. At the critical dry content C the water on the paper web surfaces has been evaporated and the remaining water has to diffuse through the fibers before evaporation. Diffusion is limiting the water transport which leads to a decrease in drying

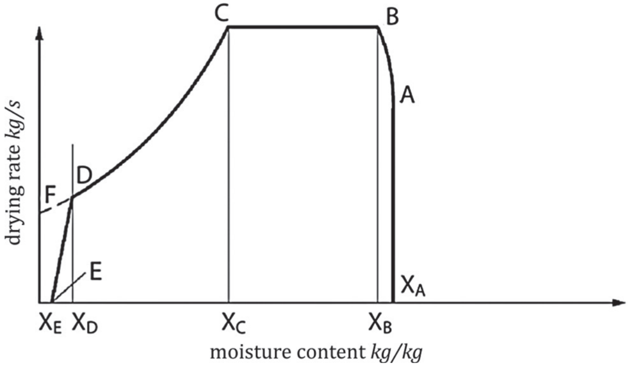

Figure 1. Drying rate as a function of moisture content during paper drying [1].

rate during the second drying phase (C-D). The last drying phase (D-E) starts at about 80% dry content. Capillary effects and intermolecular forces like hydrogen bonds and van der Waals forces are bonding the water to the fibre surface. Additional evaporation energy, apart from the latent heat of water, is necessary to overcome these effects which leads to an additional decrease in drying rate.

The increase of energy required to evaporate water at an increasing dry content is shown in figure 2. Below an equilibrium moisture content[1] (EMC) of 0.35 kg/kg the heat of vaporisation is increasing from about 2300 kJ/kg to more than 3000 kJ/kg at EMC = 0 kg/kg. The difference between vaporisation energy and the latent heat of water (2308.05 kJ/kg at 80 ºC) [2] is called the heat of sorption [3]. There are two different types the *differential heat of sorption* h_S and the *integral heat of sorption* H_S.

The **differential heat of sorption** h_S is the extra energy needed to vaporise water at a certain EMC. For example at an EMC of 0.1 kg/kg we have a latent heat of water of 2308 kJ/kg and a total vaporisation energy of 2700 kJ/kg, thus at EMC = 0.1 kg/kg the differential heat of sorption is h_S=392 kJ/kg. The integrated heat of sorption at EMC = 0.1 kg/kg is the integral of h_S between EMC = ∞ kg/kg and EMC = 0.1 kg/kg. The integrated heat of sorption is the extra energy consumed, compared to the latent heat of water, when you dry a paper sheet from EMC = ∞ kg/kg to a required EMC on a paper machine. The **overall integrated**

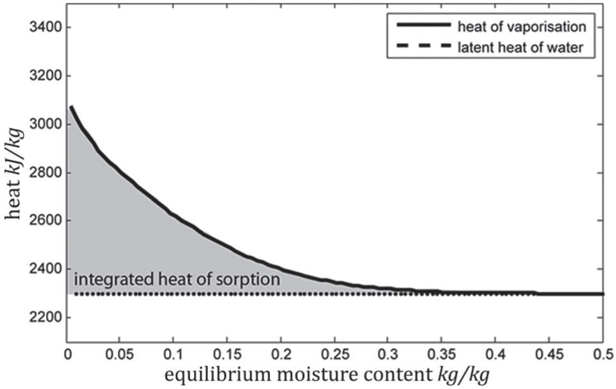

Figure 2. Heat of vaporisation of unbleached kraft pulp at 80ºC as a function of equilibrium moisture content. The heat of sorption is the difference between the latent heat of water (≈2308 kJ/kg) and the vaporization energy.

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[1] In the following EMC = 0 kg/kg is defined as the dry content after drying at T = 105 ºC for a minimum of 2 hours

heat of sorption H_S is defined as the additional heat required to dry from EMC = ∞ kg/kg to EMC = 0 kg/kg (grey area in figure 2).

The data for the heat of sorption reported in the literature are inconsistent. Values for the differential heat of sorption h_S at EMC=0.02 g/kg have been published by RHIM 400 kJ/kg [4], SOININEN 2.000 kJ/kg [5], HEIKKILÄ 1.000 kJ/kg [6] and OJALA 450 kJ/kg [6]. Values for the overall integrated heat of sorption H_S were e.g. published by VARGA 80–95 kJ/kg [7] or HEIKKILÄ 50 kJ/kg [8].

Finding reliable values for the heat of sorption of pulp is certainly interesting for basic research. It is, however, also relevant for applied research. Computer simulations of the paper drying process are undertaken, e.g. in order to optimize the drying process and reduce energy consumption [9]. In order to obtain a correct energy balance and realistic simulations, reliable values for the heat of sorption are required.

In this work we are describing different methods to determine the differential and integral heat of sorption of pulp. We are comparing the results from measurements with these methods in order to obtain reliable values for H_S and h_S and we are discussing the methods. Furthermore we are investigating to which extent different pulp grades and process parameters like beating, bleaching or pre-drying are affecting the heat of sorption and thus the drying energy in papermaking.

2 BACKGROUND

Before we are describing the methods to measure the heat of sorption we are discussing some basic concepts regarding sorption and sorption isotherms.

2.1 Adsorption

"Adsorption is the adhesion of atoms, ions, or molecules from a gas or liquid to a surface." ([10]). Desorption is the reverse process of adsorption, it is the detachment of the gas or liquid from the surface. One can distinguish two types of adsorption [11]: *Chemisorption* (or chemical adsorption) and *physisorption* (or physical adsorption).

Chemisorption is adsorption based on chemical reactions between adsorbate and the surface. The adsorbed molecules are linked to the adsorbent by valence bonds. Only one layer of adsorbed molecules can be formed, i.e. so called monolayer adsorption. The chemical nature of the surface can be altered during adsorption. More information can be obtained in [12].

In **physisorption** (or physical adsorption) intermolecular forces (e.g. van der Waals forces or hydrogen bonding) are responsible for adsorption, the surface is not altered chemically. Multi-layer adsorption is frequently observed. The adsorbate uptake increases usually with increased partial pressure of the fluid and decreasing temperature. The adsorption phenomena concerning fibres can in general be classified as physisorption, so in the following adsorption and desorption always means physisorption. Adsorption of water molecules onto the fibre surface is exothermic – so thermal energy is released due to decreasing surface energy of the adsorbent. During paper drying the reverse process is taking place, the energy released during water adsorption is now consumed to desorb the water molecules from the fibre surface.

Another important mechanism contributing to the heat of sorption are capillary forces. This is due to the fact that the capillary pressure in small pores of the substrate has to be overcome during desorption which is also consuming extra energy [3].

2.2 Sorption Isotherms

Due to the complex and inhomogeneous structure of papermaking fibres the adsorption of water can not be expressed by simple mathematical relations. The water uptake for different fibre types is usually determined experimentally, where, under equilibrium conditions, the relationship between the amount of water in paper and the relative humidity of the surrounding air is displayed [13, 14]. These curves are called sorption isotherms, compare figure 3. Isotherms are determined by measuring the EMC of the paper at varying relative humidity and constant temperature for adsorption and desorption. During adsorption one can initially observe a concave graph; first a monomolecular layer of water molecules is formed on the fibre surface. After the whole fibre surface is covered with water molecules multilayer adsorption leads to a more or less linear increase. In figure 3

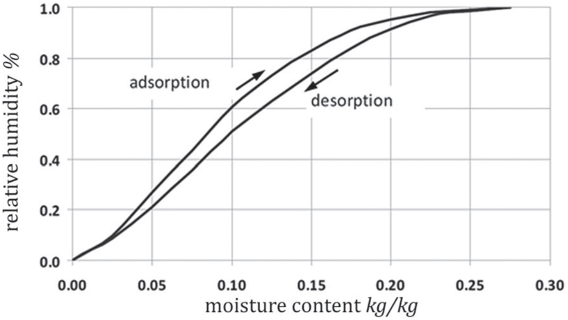

Figure 3. Sorption isotherms of water to pulp fibres at 70ºC [19]. Please note the hysteresis between adsorption and desorption.

one can see different water uptake during adsorption- and desorption isotherms of paper. This phenomenon is called hysteresis, the reasons for the hysteresis are discussed e.g. in [15, 16, 17, 18].

3 MATERIALS AND METHODS

There are two different measurement approaches to determine H_S and h_S, indirect measurements and direct measurements. Indirect methods are based on recording sorption isotherms at different temperatures and calculating H_S and h_S from physical relations. Direct methods are measuring the energy flux during desorption or adsorption of water and thus directly evaluate the heat of sorption.

3.1 Indirect Methods

Indirect methods are based on the recording of sorption isotherms with different measurement equipment. In this section we are discussing different devices to obtain isotherms and we are describing the physical relations to calculate the heat of sorption from the sorption isotherms.

3.1.1 Measurement of Isotherms

Environmental Simulation Chamber **(ESC)**. An ESC unit essentially is a box where humidity and temperature can be controlled. For our work we used the model Binder MKF 240. The ESC is additionally equipped with a precision balance. Paper sheets are placed in the ESC at varying temperature and at humidity. After reaching equilibrium the sample weight is determined and the EMC is calculated. The experiments in this paper were conducted at four temperatures, at each temperature eight different relative humidities were evaluated. Afterwards isotherm curves are fitted to the data points using different sorption isotherm models described in the literature, e.g. the Langmuir isotherm [20] or others [21, 22, 5, 6]. The choice of the fitting function has a strong influence on the resulting values for the heat of sorption. Especially the data points recorded at low and high relative humidity are severely affecting the result. LEUK has shown that H_S calculated from the same data points varied from H_S = 50 kJ/kg (using Heikkilä's function) up to H_S = 196 kJ/kg (using BET function) [8].

Dynamic vapour sorption **(DVS)** as described e.g. by [23]. A DVS unit can be understood as a fully automated ESC. A small is pulp sample is put into the DVS and the relative humidity is varied in very small steps within a predefined range. After reaching equilibrium at each humidity level the sample is weighed on an integrated balance and the EMC is calculated. There are enough data points (up to 50) to obtain a sufficiently smooth sorption isotherm curve by linear interpolation of the recorded data points. This is an advantage compared to the EMC because no curve fitting model has to be chosen to obtain the isotherm. Another benefit is that very low and very high humidity levels can be reached in the DVS, which is sometimes difficult to achieve for simple environmental simulation chambers.

3.1.2 Calculating the Heat of Sorption from Isotherms

The differential heat of sorption h_S can be derived, according to [3], by assuming equilibrium between the free enthalpy of water and vapour at a given constant temperature. By relating the adsorption energy to the EMC one can show that the differential heat of sorption h_S at a specific EMC z can be calculated [3] according to equation 1

$$h_S = -R_V \left[\frac{d \ln \phi}{d \frac{1}{T}} \right]_{z=const} . \tag{1}$$

ϕ relative humidity [-]
T temperature [K]
R_V gas constant of vapour [kJ/kgK]
z equilibrium moisture content [kg/kg]

The relative humidity ϕ in equation 1 is $\phi = \frac{p_V}{p_V^S}$ with p_V being the partial pressure of vapour [Pa] and $p^S{}_V$ being the saturated partial pressure of vapour [Pa].

The key term in equation 1 is the derivative $d \ln(\phi)/d(1/T)$, i.e. the derivative of $\ln(\phi)$ with respect to $1/T$. There are two possibilities to obtain results for the differential heat of sorption according to equation 1. One way is the graphical differentiation of $d \ln(\phi)/d(1/T)$. The other is using a fitting function for ϕ which is depending on the temperature T, then the term $d \ln(\phi)/d(1/T)$ can be calculated analytically. Both ways are described here.

Graphical differentiation is described e.g. by [3]. Isotherms are recorded at different temperatures in a DVS or ESC, in figure 4 for example the desorption isotherms at 30ºC and 50ºC are given. These isotherms are redrawn in a diagram with $1/T$ as x-axis and the relative humidity $\ln(\phi)$ as y-axis, see figure 5. Each of these lines – called isosteres – represent different relative humidities ϕ at a specific EMC. At e.g. EMC=0.07 in figure 4 we have a relative humidity ϕ=0.38 for 30ºC and ϕ=0.50 for 50ºC resulting in two points in figure 5 connected by a line – the isostere for EMC = 0.07. The derivative $d \ln(\phi)/d(1/T)$ at a specific EMC from figure 5 is found as the slope of the line with the according EMC and this value is used to calculate h_S from equation 1. As an example a value for $h_S \approx 600$ kJ/kg at

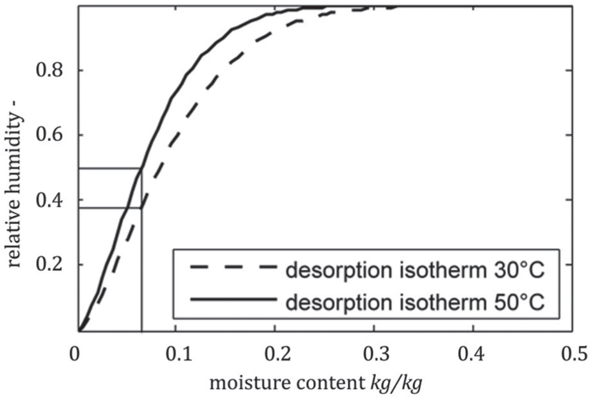

Figure 4. Desorption isotherms at two temperatures for unbleached SW kraft pulp. The EMC was measured with ESC and the curves were fitted using Heikkilä's function, equation 2.

EMC = 0.07 kg/kg (marked as a point in figure 6) can be found from the slope of the highlighted line in figure 5 multiplied by $-R_V$. By applying this calculation for each isosteric line a graph of the differential heat of sorption over EMC, see figure 6, is obtained point by point.

Analytical differentiation [19]: A closed form function for the isotherms $\phi(\vartheta, z)$ which is depending on the temperature T and the moisture content z has to

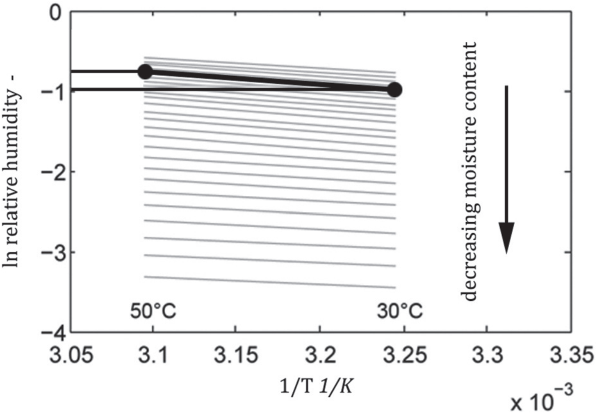

Figure 5. Ln(ϕ) over 1/T at EMC = constant for an unbleached SW kraft pulp. The lines were calculated from the isotherms in figure 4.

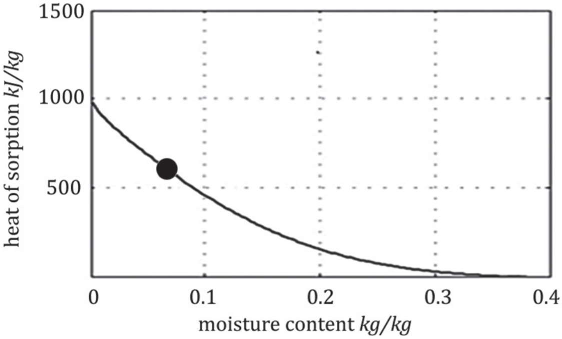

Figure 6. Differential heat of sorption over EMC, calculated from figure 5 and equation 1.

be employed for this method. An example is Heikkilä's function, equation 2 [6]. The function is fitted to the isotherms using the fitting parameters A, B, C and D.

$$\phi = 1 - e^{-(Az^B + C\vartheta z^D)} \tag{2}$$

$$h_s = -R_V \frac{1 - \phi(\vartheta, z)}{\phi(\vartheta, z)} C z^D T^2 \tag{3}$$

ϕ	relative humidity in equilibrium [–]
ϑ	temperature [ºC]
z	EMC value [kg/kg]
A,B,C,D	fitting parameter
R_V	gas constant of vapour [kJ/kgK]
T	temperature [ºK]

Please note that other widespread isotherm functions, like e.g. the BET function, do not include temperature. Relative humidity then is simply only a function of equilibrium moisture content, $\phi(z)$. Such a function delivers the same heat of sorption for all temperatures, which is not realistic. Thus the BET isotherm function, and other functions not including temperature, were not found to be suited for calculation of the heat of sorption.

The differential heat of sorption for Heikkilä's isotherm function can then be calculated according to Equation 3. It is the result from the analytical calculation of the differential $d \ln(\phi)/d(1/T)$ of the function for $\phi(\vartheta, z)$ given in equation 2. Using this method the h_S value is directly calculated by putting the EMC values z

measured in the ESC or DVS at the corresponding relative humidity ϕ and temperature T into equation 3.

The analytical differentiation method seems more practical than the somewhat cumbersome graphical differentiation method which involves redrawing of the isotherms. However, the accuracy of the results from analytical differentiation entirely depends on the quality of the isotherm fitting function, equation 2. Please note that the function must fit the measured isotherms at *all different temperatures T*. Considering that – in our case – four fitting parameters are required to fit 32 data points the result sometimes exhibit substantial instability in convergence. Graphical differentiation on the other hand can also be fully automated on a computer, but it does not have the disadvantage to rely on the performance of a fitting function. However a sufficient number of data points in the isotherms have to be measured, especially in the region of low EMC which is particularly relevant for the heat of sorption. This is usually only feasible using an automated recording of the isotherms using a DVS. If there are only a few data points available, like it is usually the case when working with an ESC, also an isotherm model function has to be fitted to obtain the isotherm curves. As discussed above the choice of this isotherm fitting function is heavily influencing the resulting values for the heat of sorption [8].

3.2 Direct Methods

The results of the indirect measurement methods for the heat of sorption are depending on the accuracy of the sorption isotherms and on the chosen fitting function. That makes it interesting to measure the heat of sorption directly by calorimetric methods. The following methods for such thermal analysis are available and discussed in the literature.

3.2.1 Reaction Calorimeter (RC)

The basic idea of the reaction calorimeter [7] is to measure the adsorption energy which is released during wetting of a completely dry sample. As physisorption is fully reversible the energy released during adsorption must be equivalent to desorption energy consumed during drying. This approach is particularly elegant because it avoids all problems from desorption measurements which involve large amounts of energy for the evaporation of water, discharge of the vapor and high precision weighing of the sample mass.

The heat flux emitted from rewetting a dry paper sample with water in an isothermal reaction chamber (in our case 80ºC) is detected by a heat flow sensor, figure 7. First the sample is flushed with pure nitrogen at 90ºC for about one hour to fully dry it. After that time, in our case 3200s, the sample is rewetted and the

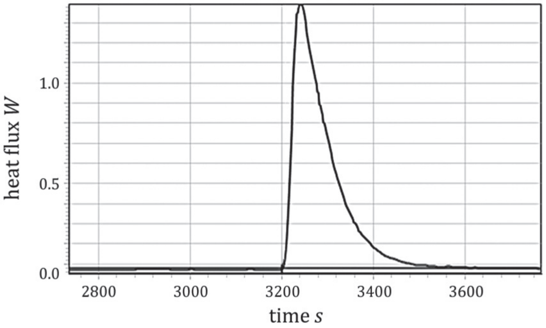

Figure 7. Heat flux (total power) over reaction time measured in a reaction calorimeter (RC) for unbleached SW kraft pulp at 60ºC.

heat flux is measured. In our measurement the total Power (W) increased to a maximum of 1.4 W at 3260 s and approached zero at 3570 seconds.

By knowing the oven dry sample mass the integrated heat of sorption H_S can be determined by integrating the heat flux over time. The main disadvantage of this method is that it is impossible to determine the differential heat of sorption h_S. The material is fully wetted, so the full sorption energy is released at once, making it impossible to relate sorption energy to different levels of moisture content.

3.2.2 Differential Scanning Calorimeter (DSC)

The determination of the heat of sorption using differential scanning calorimetry is described in [24]. For this method a sample with a specific moisture content is put in the DSC. The temperature is increased in small steps from – 15ºC up to 200ºC while all of the water in the sample is evaporated and the heat flux is measured. Knowing the original moisture content of the sample one can calculate the average energy to evaporate the water. Due to increasing temperature during the measurement the DSC can not determine a vaporization energy at a defined temperature. However, the heat of sorption is per definition, see equation 1, determined at a specific temperature. Thus the measurement result is not exactly the heat of sorption, it is called *cumulated average vaporization enthalpy* [25]. Nevertheless, measurement of fully wetted samples provides an estimation for the integrated heat of sorption H_S and series of measurements with decreasing moisture content at the beginning can provide an estimate for the differential heat of sorption h_S at different levels of EMC, compare [24].

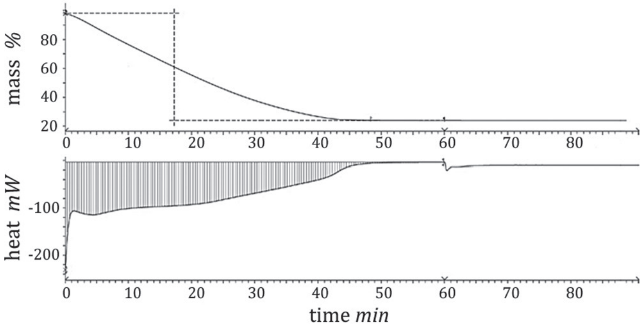

Figure 8. Signal of the DSC/TGA. Upper y-axis is the sample mass, lower y-axis is the heat flux, x-axis is the time.

3.2.3 Differential Scanning Calorimeter and Thermogravimetric Analysis (DSC/TGA)

For this measurement technique the heat flux is measured like in DSC while additionally the change in mass over time is recorded with an integrated balance, compare figure 8. A sample with a dry content of about 25% is placed in an aluminum pan with a volume of 110 μl. The paper sample is kept at a constant temperature of 80ºC and the vapor from the sample is flushed with N_2. After reaching mass constancy at 80ºC (in our example 60 min) the sample is heated up to 105 ºC to measure the oven dry mass. The measurement delivers the total heat of evaporation at different moisture contents as shown in figure 2. In order to obtain the heat of sorption h_S the latent heat of water at the measurement temperature has to be subtracted from the total heat of evaporation [26].

3.3 Discussion

Table 1 provides an overview on the differences between the measurement methods for differential heat of sorption h_S and integral heat of sorption H_S described in this section. Four of the investigated measuring methods are able to determine h_S and H_S, the reaction calorimeter (RC) can only determine H_S. Using an environmental simulation chamber (ESC) or the dynamic vapor sorption device (DVS) the differential heat of sorption h_S is calculated from isotherms and the integrated heat of sorption H_S is found by integrating h_S over the equilibrium moisture content range EMC=0 to EMC=∞.

Differential scanning calorimetry (DSC) is performed with continuously ascending measurement temperature, thus it does not deliver a true heat of sorption,

Table 1. Differences between the measurement methods described in this section. H_S is the integrated heat of sorption, h_S is the differential heat of sorption

	Determination of h_S	*Determination of H_S*	*Measurement Temperature*
ESC	calculated from isotherms	integral of h_S	constant
DVS	calculated from isotherms	integral of h_S	constant
RC	n. a.	heat flux measurement	constant
DSC	heat flux measurement	integral of h_S	continually increasing (ramp)
DSC/TGA	heat flux measurement	integral of h_S	constant

because h_S and H_S varies with the temperature of the material. Nevertheless the method provides estimates for h_S and H_S. Differential scanning calorimetry with thermogravimetric analysis (DSC/TGA) measures the heat to evaporate water at a defined temperature for different levels of equilibrium moisture content. After subtraction of the latent heat of water at the measurement temperature these values directly give the differential heat of sorption h_S for the material.

3.4 Experimental

3.4.1 Sample Material

There are two main goals for this work. First we want to **compare different measurement methods** to obtain reliable results and identify appropriate measurement methods. The sample material for these experiments were

- Never dried softwood kraft pulp (a mixture of pine and spruce) from an industrial pulp mill. The pulp was unbleached and unrefined (beating degree of 15° Schopper Riegler).

The second aim of our work is to quantify the influence of different pulp properties on the heat of sorption. We were studying three different data sets. First we wanted to **compare the heat of sorption between different raw materials**. We analyzed

- Never dried softwood kraft pulp (a mixture of pine and spruce) from an industrial pulp mill. The pulp was unbleached and unrefined (beating degree of 15° Schopper Riegler).
- Never dried hardwood sulphite pulp for viscose production from an industrial pulp mill. The pulp was bleached and unrefined (beating degree of 15° Schopper Riegler).

- Recycled pulp, grade W62 (old corrugated container board, OCC). The pulp was taken from the machine chest of a liner mill, it had a beating degree of 25º SR.
- $CaCO_3$ filler HC60, a ground calcium carbonate (GCC) from Omya. It has a particle size distribution with 60% of the particles smaller than 2μm.

Furthermore we investigated the **the impact of refining and the impact of drying**. Here we used the same pulp as for the comparison of the measurement methods, it was

- Never dried softwood kraft pulp (a mixture of pine and spruce) from an industrial pulp mill. The pulp was unbleached and unrefined (beating degree of 15º Schopper Riegler).

3.4.2 Sample Size

The results for ESC, DVS, RC and DSC/TGA are average values of three samples. The DSC results are taken from data in the literature [24], we calculated the h_S according to the formula given in [24].

3.4.3 Fitting Function for Sorption Isotherms

The chosen function in this work is the one from Heikkilä, equation 2. We chose it because it is including both, temperature and EMC, which is a requirement discussed in section 3.1.2.

4 RESULTS AND DISCUSSION

4.1 Comparison of Measurement Methods

Figure 9 gives the results for the integral heat of sorption H_S measured from an unbleached softwood Kraft pulp using ESC, DVS, RC and DSC/TGA. The results for the DSC is the cumulated overall evaporation enthalpy which is the estimate for H_S that can be obtained with DSC. This result is taken from data for an unbleached softwood Kraft pulp [24], it has been calculated according to equation 5 in the same publication [24].

The values for H_S are in a range of 41 kJ/kg to 70 kJ/kg, except DSC/TGA which is significantly higher. We think there are several reasons why this is the case. First of all the temperature at the beginning of the measurement was 63ºC, at the end it was 80ºC. The energy to increase the temperature of the sample was also included in the results. Assuming a specific heat of 4kJ/kg K this should

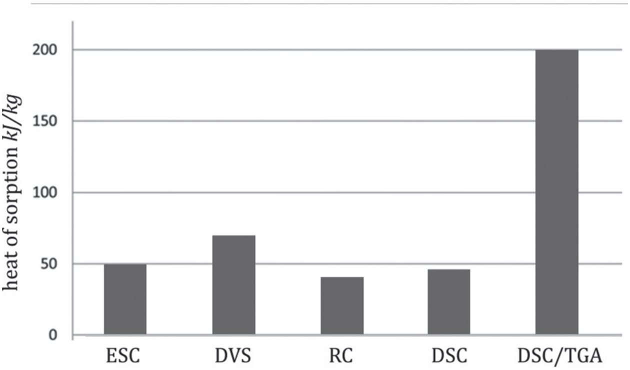

Figure 9. Integrated heat of sorption H_S (80ºC) of a SW kraft pulp measured with ESC, DVS, RC and DSC/TGA. The DSC estimates for H_S were calculated according to [24] from data given in [24].

amount to roughly 70kJ/kg. The remaining difference might be attributed to calibration problems. Calibration of DSC/TGA units is a delicate process, the calibration points are set for a specific temperature and a specific sample mass. The temperature of 80ºC is very low for DSC/TGA, calibration is difficult for temperatures below 100ºC. Also the large change of sample mass during the measurement might introduce some error.

The remaining four measurement results have differences of 70% between lowest and highest value with an overall average (excluding DSC/TGA) of H_S = 52 kJ/kg. The integrated heat of sorption at 80ºC, which is a typical temperature for drying on a paper machine, comprises the sorption energy over the whole EMC range, from fully wetted to totally dry. Thus a value of H_S = 52 kJ/kg means that for fully drying paper an extra energy of 52 kJ/kg is consumed due to adsorption of water on the fiber surface.

The result for the differential heat of sorption h_S of unbleached softwood Kraft pulp at 80ºC is shown in figure 10. We compared the measurement techniques DSC, DSC/TGA and ESC (with isotherms fitted using Heikkilä's function). The most prominent common feature of all three curves is a sharp increase of differential heat of sorption at an equilibrium moisture content around EMC = 0.1. At this point the differential heat of sorption h_S has a value around 200kJ/kg. This means that at a pulp dry content around 90% evaporating 1kg of water consumes an extra 200kJ/kg, an increase of 9% compared to the latent heat of water at 80ºC (2308.05 kJ/kg). At an EMC of 0.05 (dry content around 95%) the differential heat of sorption was found to be between 500kJ/kg and 1000kJ/kg. Evaporating water from pulp at such a high dry content is consuming considerably more energy

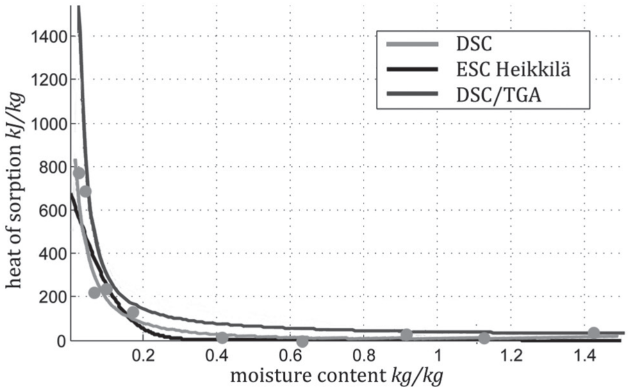

Figure 10. Differential heat of sorption h_S for three different measuring methods. Measured for unbleached SW kraft pulp at 80ºC.

than the latent heat of water. The curves of DSC/TGA and ESC (Heikkilä) are very similar, the curve for DSC/TGA is different in two aspects. First h_S is rising to rather high values as the EMC approaches zero, h_S in this case becomes larger than 1500kJ/kg. Second the DSC/TGA curve has a large tail with low but detectable h_S values up to an EMC=1 and above. This long tail is one of the reasons why the integrated heat of sorption H_S is much larger for DSC/TGA than for the other measurement techniques, figure 9. We are not sure if sorption is already playing a role at a dry content around 50%, thus this result seems less likely than the results from the other two methods.

The average integral heat of sorption at 80ºC is H_S = 52 kJ/kg. Drying paper from wet to fully dry thus has an increase in energy demand of 2% compared to the latent heat of water (2308.05 kJ/kg at 80ºC). Many paper grades are not dried higher than 96% dry content. Considering that the heat of sorption is increasing rapidly as the EMC approaches zero (see figure 10) this means that the true effect of sorption on drying energy on the paper machine is below 2%. Therefor the heat of sorption should only have a minor effect on the energy consumption during paper drying.

We would also like to point out that the relation between dry content and differential heat of sorption h_S is likely to be somewhat different for paper drying in a paper machine. The reason for this is that the moisture in the paper web during drying is not in equilibrium state. There are moisture gradients across the paper z-direction and also moisture gradients across the fiber cross sections. Beginning with the second drying phase, section C-D in figure 1, gradients must be high because they are driving the diffusion process carrying the water out of the web. We have to assume that there are regions with low EMC far before the end of the drying section. These localized regions with low EMC are expected to lead to an earlier increase in differential heat of sorption h_S in paper drying compared to the measurements in figure 10. In other words we are expecting that the curves for paper drying exhibit a less pronounced increase in h_S towards very low moisture content and longer tail than the ones in figure 10. The overall integral heat of sorption H_S however remains unchanged as the total amount of desorption energy between fully wetted and fully dried is unaffected by transient moisture disequilibrium in the material.

A summary on the pros and cons of the different measurement techniques is given in table 2. Based on our evaluation we think that the best results for the integrated heat of sorption H_S can be obtained with the reaction calorimeter (RC) or the dynamic vapor sorption (DVS) technique. The results of DSC/TGA are unlikely, calibration problems have affected the measurements. The result from ESC are instable due to missing data points in the low EMC region. DSC delivered results in the range of the other measurements even though its values can not be assigned to a specific temperature.

As a consequence from these considerations all measurements in the following sections were carried out using the reaction calorimeter RC.

Table 2. Advantages and disadvantages of the evaluated measurement methods for the heat of sorption.

	Advantages	*Disadvantages*
ESC	High accuracy in temperature and humidity, low cost, sample sizes up to 10 g possible.	Measurements at humidity below 20% and above 85% are not possible leading to instable results, no direct measurement of heat flux.
DVS	High accuracy in temperature and humidity, range of relative humidity 0 – 95 % up to 60 ºC, accurate values for isotherms, best cost/performance ratio.	Sample size below 100 mg, no direct measurement of heat flux.
RC	Direct measurement of sorption energy, sample size up to 2 g.	Only integrated heat of sorption H_S can be measured.
DSC	Direct measurement of heat flux.	No measurement at constant temperature possible, measures cumulated average vaporization enthalpy not h_S, sample size below 50 mg.
DSC/ TGA	Direct measurement of heat flux.	Temperature was not constant during measurement, sample size below 50 mg, calibration of DSC/TGA for temperatures below 100 ºC difficult, unrealistic results in our experiments.

4.2 Heat of Sorption for Different Raw Materials

In a series of experiments the integrated heat of sorption H_S for different papermaking raw materials was investigated using RC. Details on the sample material are found in section 3.4.1. The results for unbleached softwood kraft pulp, bleached hardwood sulphite pulp and recycled pulp (OCC, old corrugated containers) are shown in figure 11. The results for unbleached Kraft pulp and bleached sulphite pulp are very similar, 42kJ/kg, the value for recycled pulp is a little lower. The value for $CaCO_3$ filler is very low, nearly zero. Filler does not take up a relevant amount of water [27], so this result is plausible. It turned out, that the lower value of the recycled pulp can be attributed to its filler content. The heat of sorption value for OCC is about 15% lower than the one for the pulps, also the filler content for OCC was 15%. Correcting the OCC value for the filler content, the fibre material in the recycled pulp has similar values for H_S like the other two pulps, compare figure 11. Looking at the error bars comprising the 95% confidence limits no statistically significant difference between the pulp types can be found. So, somewhat surprising, no difference in integral heat of sorption could be found between unbleached SW kraft pulp, bleached hardwood sulphite pulp and a recycled softwood Kraft pulp. That leads to the unexpected conclusion that the heat of sorption, at least for the examined pulps, did not change due to pulping method or bleaching. It is well known that water uptake measured with water retention value is changing due to pulping and bleaching. Our results are indicating that these changes are not related to increased adsorption. Instead

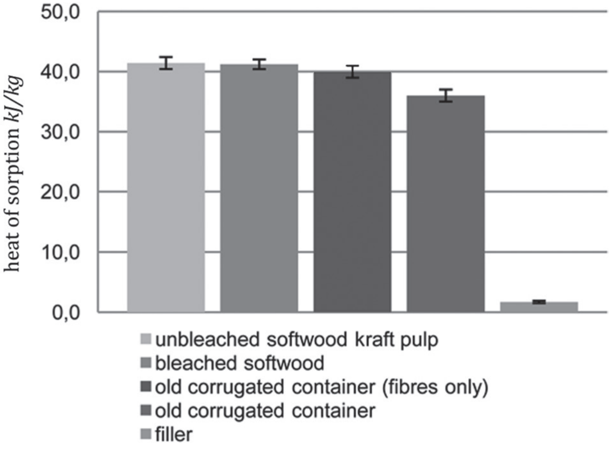

Figure 11. Integrated heat of sorption for different furnishes and $CaCO_3$ filler, measured with RC at 80ºC.

differences in the capillary structure between the pulps might be the reason for the differences in water uptake.

4.3 Effect of Drying

Many paper mills use once dried pulp. Depending on the paper grade also up to 30% broke is added during stock preparation. The usage of previously dried virgin pulp or recycled pulp is reported to permit an increase in paper machine speed and a decrease in the specific energy demand for drying. Pulp shows a reduced swelling tendency upon rewetting with an increasing amount of drying cycles. This irreversible decrease of water uptake caused by drying is assumed to be due to irreversible bonding within the cell wall. This phenomenon, called hornification, could therefore possibly lead to a decrease in H_S which was investigated in the following experiment. Never dried pulp was dried in an oven at 105 ºC and re-slushed. As expected the desorption isotherm after four drying-rewetting cycles are showing lower EMC at equivalent relative humidity than the never dried pulp, see figure 12. Calculating the overall integrated heat of sorption H_S from the isotherms using Heikkilä's function is leading to a small, statistically not significant difference (values are not displayed here) between never dried and once dried fibres. The results were rather unstable, thus we can not draw final conclusions on the development of H_S between never dried and once dried pulp. However after all we could see there seems not to be a large difference.

Further measurements were undertaken using a reaction calorimeter. We used the unbleached softwood Kraft pulp, for one measurement it was once dried and for the other measurement it was reslushed and dried five times. The influence of

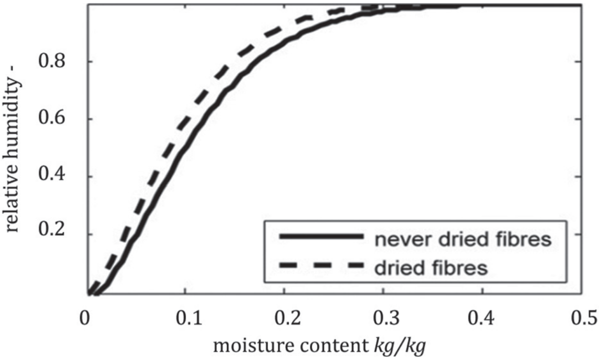

Figure 12. Desorption isotherms for SW kraft pulp, never dried and once dried fibres.

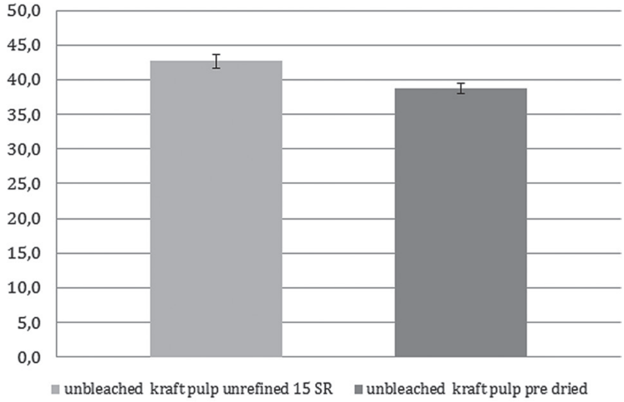

Figure 13. Integrated heat of sorption for once dried and five times dried SW kraft pulp, RC 80ºC.

the first drying cycle of a pulp cannot be determined with RC since for this method the samples have to be dried before the measurement. The decrease in the heat of sorption between once and five-times dried pulp was about 15 %, see figure 13. This leads to a total decrease in the evaporation energy in the paper drying process of only 0.3 %.

In our opinion the heat of sorption cannot provide an explanation for the advantages in terms of drying energy reported for the use of recycled- and once-dried fibers over never dried pulp. While we did see an increase in ESC measurements of H_S between once- and never dried pulp, it was not statistically significant due to measurement noise. Significant differences were found between once dried and five times dried pulp using RC measurements, however they were in the range of a few kJ/kg which is not enough to account for relevant differences. Possible other reasons for reduced drying energy consumption of pre-dried pulp could be a higher dry content after the press section and a higher permeability of the paper web from once-dried fibres, leading to faster drying and thus to lower drying temperature and lower energy consumption.

4.4 Effect of Refining

Refining of pulp is leading to structural changes in the fibre walls by fibrillation and delamination, furthermore fines are created. Refining also increases the water retention value. As a result of the beating the specific surface is increased which might increase the heat of sorption due to creation of new surfaces accessible for

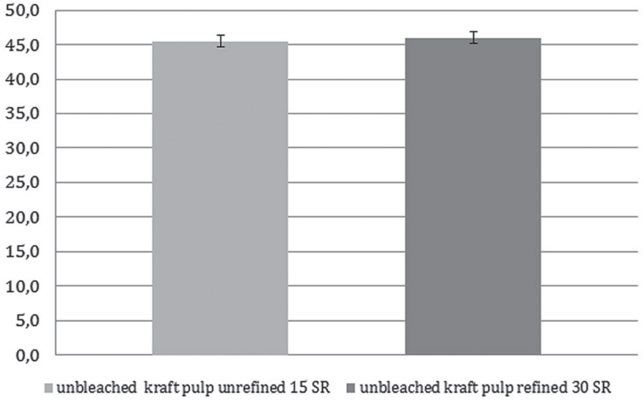

Figure 14. Integrated heat of sorption H_S for unrefined and refined SW kraft pulp, measured with RC at 80ºC.

adsorption. In order to investigate the effect of refining we measured the heat of sorption of an unbleached SW kraft pulp unrefined and refined 15.000 revolutions in a PFI-mill. Refining lead to an increase in beating degree from 15º Schopper Riegler (ºSR) for the unrefined pulp to 30ºSR for the refined pulp. ESC, DVS and RC were used to analyze these pulps. The results indicate that refining does not increase the heat of sorption. The isotherms obtained in ESC and DVS are virtually identical for the beaten and unbeaten pulp, as a result the heat of sorption calculated from the isotherms also remained unchanged. This was confirmed by the measurements of H_S with the RC which are given in figure 14. This leads to the conclusion that water adsorption is not increased by refining. The modification of the cell wall due to mechanical treatment does not seem to create new surface areas which have not been accessible to water before refining.

5 CONCLUSIONS

A broad study regarding the heat of sorption of pulp was carried out. The first focus was set on evaluation of different measurement methods. We have compared five different techniques to measure H_S and h_S. RC, ESC, DVS and DSC showed results for H_S in the same range (H_S = 40–70kJ/kg) whereas DSC/TGA was up to four times higher than the others. The average value of all methods excluding DSC/TGA for the overall integrated heat of sorption was H_S = 52 kJ/kg for an un-bleached, never dried softwood Kraft pulp. This means that the necessary energy for drying pulp is about 2% higher than the latent heat of pure water (2300kJ/kg).

The technological approach of the evaluated measurement methods is very different, still we found rather similar results for the integrated heat of sorption H_S. However, most of the measurements show substantial variation in the results for h_S. Nevertheless the measurement techniques showed similar trends regarding the impact of refining and pulp grade, filler addition and pre drying of pulp. DSC, DSC/TGA and DVS have an elaborate and delicate procedure for calibration and measurement. ESC exhibits some instability due to insufficient data. As a result we found it to be difficult to obtain stable and reproducible results for the differential heat of sorption h_S. The RC measurements were stable, however this method is only able to measure the integrated heat of sorption H_S.

The most important technological pulp parameters known to affect water take-up and drying energy consumption in papermaking were investigated to evaluate differences in the heat of sorption. No difference in heat of sorption was found for different pulps. Unbleached softwood kraft-, bleached hardwood sulphite- and recycled softwood kraft pulp had equivalent heat of sorption values H_S. Refining did not influence the heat of sorption. Pre drying had an impact on the measured heat of sorption which decreased by about 15% compared to a never dried pulp. Overall heat of sorption of $CaCO_3$ filler was found to be very low, negligible in comparison to pulp.

The most important conclusions from our work are, that the integrated heat of sorption for softwood pulp is between H_S=45 kJ/kg to H_S=55 kJ/kg. Pulping, bleaching and refining are not playing a role. A small difference is caused by drying of the pulp. As H_S is low compared to the vaporization energy of water and it is very little affected by pulp type or pulp treatment we are concluding that the heat of sorption has little practical impact on the overall energy consumption in papermaking.

6 ACKNOWLEDGEMENTS

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Transcription of Discussion

THE HEAT OF SORPTION IN PAPER DRYING – AN INVESTIGATION OF MEASUREMENT METHODS AND INFLUENCE OF PULP PARAMETERS

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Thad Maloney Aalto University

I read your paper just prior to seeing your presentation, and really enjoyed it. I found it to be a useful review of this important subject, so please do not be so pessimistic with your last statement that the heat of sorption has no practical relevance to the paper industry. It's true that you could figure that out before you did the study just reviewing the values that are in literature, but nonetheless that type of measurement is very useful for all kinds of ligno-cellulosic materials in a number of applications. If you look at a wider range of chemistry and surface areas, beyond just beating and hornification and things like that, then you do see big differences and you can get insights into structural and chemical issues, so I think your work was a worthwhile contribution.

Michael Schneeberger

Thank you very much for this statement.

Lars Wågberg KTH

I agree with the earlier comments that this was a very nice presentation. Regarding the beating measurements, I wonder how you prepared the pulps before you tested them in the reaction calorimeter (RC)? If I understand you correctly, you beat the fibres, then dried them and then you placed them in the RC? Isn't this is rather the opposite of what you would expect on the paper machine? Do you have any feeling for the contribution from drying?

Michael Schneeberger

Concerning drying, we also used DVS (Dynamic Vapour Sorption) analysis, so we had the possibility not to dry it in advance and the isotherms were the same. However, we saw a big difference in the kinetic effects: you reach the isotherms much earlier when it is not beaten than when it is beaten. So it also the observation on the paper machine, that beaten pulp needs more energy for drying than unbeaten pulp.

Bob Pelton McMaster University

It was a beautiful presentation! Years ago I had to teach thermodynamics, worst course ever, and I wish you were doing it for me, this was beautiful. What do you think the mechanism is? Did you mention the capillary effect as the primary one or is it just adsorption on surfaces? You have quantitative values now, what do you think the mechanism is?

Michael Schneeberger

That's a very difficult question. Of course, we have capillary effects, also bonding effects, water bridges . . . I am sorry, I cannot say that one of these items is the most important.

Ulrich Hirn Graz University of Technology (co-author)

As we have varied the treatment, bleached and unbleached, and we also had a recycled furnish, so I would suspect that the surface chemistry is very different between those. Therefore it is probably not adsorption and I would tend to think that it is a capillary effect.

Jean-Claude Roux Grenoble Institute of Technology-Pagora

I was a little surprised by the result you mentioned on beating. I was wondering if you have not reached the point where beating really has an effect on fibres, what we could call a critical value or inflection point; 30 °SR is perhaps too low. Can you comment on this? If we imagine that the mechanism is some capillary effect, so that we have a reduction of the pores, it must necessarily produce an effect. So if you do not see this effect, it probably means that you have not beaten the fibres to a high enough degree. It is an idea, I have no opinion.

Michael Schneeberger

Thank you for your comment, and I know what you mean. In our project, the paper mill involved used SW unbleached Kraft pulp, they beat up to 30 °SR, so we made this measurement at this level. Of course, we can do some further investigation with a higher beating degree.

Jean-Claude Roux

I have just a comment. I think that you are too pessimistic, because if you can obtain the heat of sorption, it is very important, from a paper-making point of view, because you get a critical humidity and you get also the influence of the evaporation rate. It can help you to dimension correctly the drying part of the paper machine.

Michael Schneeberger

You are right. Maybe I am pessimistic, but during this project, we found really a lot of potential at the paper mills. We saw energy savings between 3 and 10 per cent because they were very old paper machines and there was a lot of potential. But we also looked at the very new paper machine in Laakirchen and still found something. I come from industry, and I have learned a lot about investigating a research project since I have started my career at the university. In industry, it was usual to find a quick solution: let us find the first 90 per cent which you can gain in energy savings or similar. Here at the university, in our fundamental research, we are going to look sometimes at the last 10 per cent of potential gains. Maybe I am pessimistic although I know it is a good result, and that it is good research work, but I was hoping for more relevance in the paper industry, in terms of potential for energy savings.

Thad Maloney Aalto University

A comment about the beating. I think your results agree perfectly well with the literature. Beating does not increase the hydration water in pulp, certainly beating at moderate levels. It does many things: it swells the fibres and changes the structures, and it gives the physical impression that it might increase hydration water, but my own measurements and lots of other people's measurements over many decades have shown that moderate beating does not increase hydration water, so it should not increase the absorption energy. So I think your results are perfectly correct.