

Potential in paper drying – beyond heat and mass transfer

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The opportunity

All the mechanical properties that contribute to make paper such a useful material are developed during the drying phase of the production. At the same time, research on paper drying has focused on parameters like heat and mass transfer, as they control production rates. This has led to a situation where the link between the drying process and paper properties is poorly understood. In this paper, we argue that there is potential to improve the performance of paper in converting and end-use situations without significant capital investment by addressing this shortcoming. We also outline a roadmap for the work that is required to realize this untapped potential.

Drying is a necessity

Very few persons have failed to notice that paper interacts strongly with water. Even a paper that is perceived as perfectly dry will contain a certain amount of water that is absorbed from the humidity in the environment, and when the paper is put in liquid water, the water quickly enters the material, which swells and loses most of its strength (note that the term “paper” will be used in a loose sense, and we shall take it to include also paperboard and paper tissue). The affinity between the raw material particles (which in general terms can be referred to as lignocellulosic particles) and water is in many ways an advantage. It makes it easy to suspend the particles in water, and the entire pulp and paper production process is designed around operations involving such suspensions.

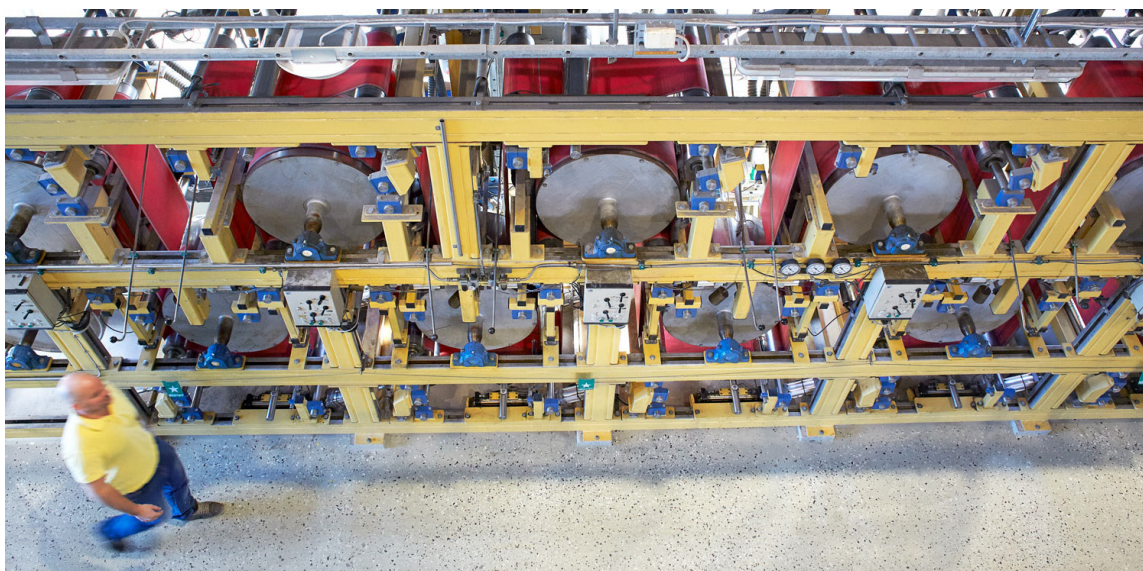


Figure 1. Drying section with electrically heated cylinders at RISE pilot paper plant FEX.

Filtering

However, there comes a point when the water needs to be removed to produce the final product. To the extent possible, this is done in a filtering-type process, in which the water passes through a permeable surface whereas the solid particles are retained as a dewatered layer. If gravity driven drainage is not enough, the filtering can be assisted by means such as vacuum. Nevertheless, due to the attraction between water and the lignocellulosic particles, the filter cake will still contain a lot of water. If we consider a paper machine, the layer of pulp material that will become the paper only has a particle content of around 20% (by weight) after the sheet forming process that corresponds to the filtering.

Mechanical pressure

The next step in paper production is to apply mechanical pressure directly to the pulp mat, to press water out. This normally allows the solids content to be raised to 40-50%. It has been estimated that the maximum dryness that can conceivably be achieved by wet pressing in paper and board production is around 60% – but such high numbers are not seen in practice. Beyond this point, one must resort to thermal drying to remove the remaining water, the mass of which is about the same as the mass of the actual product.

Drying processes are hence a necessity in papermaking and will be so also for other pulp-based materials that might reach the market in the future.

Drying provides opportunities

Removing water by heat is costly, and the capacity of the dryer section of a paper machine is often the bottleneck that sets the production limit. It is therefore natural that, over the years, a lot of attention has been given to developing energy efficient drying technologies, and to optimization of the drying efficiency. Early in the history of papermaking, contact drying with steam-heated cylinders was introduced, and remains the workhorse technology due to its energy efficiency and the fact that steam usage fits well with the process infrastructure of pulp and paper mills. Efforts to develop technologies providing higher drying rates have been made, for example by combined pressing and heating of the paper web. Some, such as the Condebelt drying process, which employs a different principle for transport of the evaporated water away from the paper sheet, have also resulted in a few commercial installations. Complementary drying techniques have also been introduced to address specific challenges, such as contact free infrared drying of paper coating layers.

Quality improvement can justify costs

Nevertheless, it has proven extremely difficult to dethrone steam-heated cylinders for paper products (market pulp is dried with different technologies but is not considered

here). It is telling that, apart from niche drying technologies that provide some advantage in a specific part of the production process, no fundamentally new drying technology for paper products has been introduced based on drying efficiency merits alone. Benefits in terms of superior product properties have proven a requirement for large-scale introduction of novel approaches. A prime example is “through-air drying” (TAD) of premium tissue products, which has seen widespread use due to its positive impact on sheet bulk (i.e. the volume per mass of product) and associated key quality parameters like softness and water absorption. In the case of TAD-drying, the quality improvements were sufficient to motivate employment of the technology *despite* a significant increase of the drying costs.

Poorly bonded fibres become a strong structure

Although there is still value in developing more efficient drying processes, both in terms of water removal rate and overall energy and cost efficiency, it is our opinion that the most interesting opportunities for research on drying of paper products currently lie in the connection to property development. To understand why, it suffices to note that when the paper web enters the drying section of a paper machine, it is a weak network of rather poorly bonded fibres. At the other end exits a well bonded, strong, light-weight structure. The detailed mechanisms controlling what happens in between, and which strongly contributes to make a paper what it is, remains poorly understood, partly due to the historic focus on heat transfer and water mass transport, and partly due to the difficulty to experimentally investigate many of the relevant phenomena.

Unexplored possibilities

Given the lack of understanding, it is not farfetched to assume that current drying processes perform sub-optimally in terms of property development, and that unexplored possibilities exist. Of course, new insights might lead to novel dryer technologies that expand the property window of paper products, as was the case with TAD-drying. Such developments would be welcome, but a few observations suggest that the lowest hanging fruits might be found elsewhere. First, as already noted, cylinder drying is an established technology for a good reason, as it provides a hard to beat combination of water removal rate and drying costs. Second, papermaking drying is done with production efficiency as the primary goal. A hypothetical drying technology that gave improved product properties, but which resulted in significantly reduced production rates, would almost certainly not be adopted. We argue that it is more fruitful to accept the general features of today’s drying technologies as boundary conditions to be respected, and instead seek to understand how “upstream parameters” like raw material selection, process and performance additives, and structural properties of the material to be dried, impact the mechanisms that lead to the development of bonds between fibres, structural changes such as shrinking and web consolidation, and residual stresses in the material. These all combine to determine the performance of the paper in further converting operations or end-use.

The degrees of freedom available by acting on upstream parameters are much larger than if we were to act primarily on the operational parameters of the drying process. We are confident that, by advancing our knowledge about the response of paper materials to drying, we will find opportunities to further develop the properties by engineering that response to a much larger degree than what is currently done. A key advantage of this approach is that it stays within the boundaries of existing drying technologies and leads to results that are more readily implementable than switching to new technological solutions.

The many scales of paper

Somewhat simplistic, we can consider the properties of paper to be determined by the arrangement of the constituent (mostly lignocellulosic) particles, their mechanical properties, and the nature of the bonds between them. The larger particles are slender pulp fibres, and usually one considers paper to be a networked material. Ultimately, our goal is to act on the mechanisms that give paper its properties during the drying process. To appreciate how this can be done, it is necessary to understand the structure of paper at different scales, from the ones observable with the naked eye down to the molecular level (see Figure 2), and how processes active at the different scales combine to affect the paper properties.

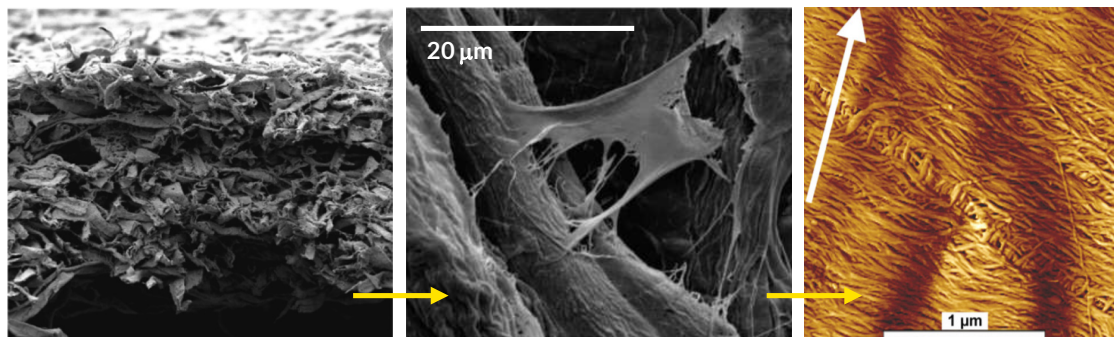


Figure 2. A few of the relevant scales in paper material. Left: Cross section of a paper showing the fibre network. Middle: Fibre-fibre contacts at the micro-level. Right: The surface of a kraft pulp fibre showing micro fibrils (the white arrow indicates the axial direction of the fibre). Not shown here are the nanometre and molecular scales. (Left and middle images: Jürgen Belle and Jürgen Odermatt, *Cellulose*, 2016. Right image: Fahlén, PhD Thesis, 2005).

Millimeter structure, flocs

The coarsest structures of relevance when we discuss how drying relates to properties are likely the inhomogeneities referred to as flocs, i.e. the lumps of particles that form from entanglement of the fibres and attractive forces between particle surfaces. The size of the flocs is usually in the millimetre range, but sometimes approaches centimetre

scale. Variability in the material distribution on larger length scales than this is very relevant but is best considered a process variability issue. Between the flocs, one finds volumes containing less material. Unevenness in the distribution of material of this kind will lead to differences in drying rate, differences in drying induced stresses, and locally different sheet properties with effects on paper quality tests and other performance measures. Scales that are larger than individual fibres are conveniently referred to as the macro level, and we should here include also structural features that describe the distribution of material across the thickness direction of the paper sheet.

Micrometer structure, fibres

The width of a typical pulp fibre is a few tens of micrometres, as is the lumen cavity that runs along the length of a non-collapsed fibre. Details of the fibre network structure, such as the apparent contact area at a fibre-fibre joint, will therefore be of micro-scale. The larger pores in the fibre wall are also of micro-scale. At this level, which is in principle (although not necessarily in practice) observable by optical microscopy, common engineering concepts such as water menisci and surface tension induced capillary forces are still valid. Historically, the macro and the micro levels have been the main focus of drying related research. To understand the effects of drying on bond development and induced stresses, we must however dig deeper.

Ultrastructure, fibrils and elementary fibrils

The fibre has a complex ultrastructure, and by that is meant the features that are below micrometre size, but still larger than what would be considered molecular scales. This is the realm where mechanics meets chemistry, and both scientific fields are required to explain phenomena. A paper is made out of fibres, but the fibres themselves are also composed of slender cellulosic particles with nanometre size width referred to as fibrils. These are organized in different layers in the fibre wall, each layer having a different thickness and a different degree of orientation of the fibrils with respect to the length direction of the fibre. A reasonably accurate description requires that we consider that these fibrils are themselves bundles of even thinner elementary fibrils, which in turn are formed from cellulose polymer chains. In some parts of the elementary fibrils, the cellulose chains are arranged in a highly ordered (crystalline) manner, in other parts there are disordered (amorphous) regions. Interspersed within this cellulose-based fibrillar structure, there are other components, such as hemicellulose and lignin.

The ultrastructure of fibres and their chemical characteristics are influenced by the origin of the wood raw material and the pulping process, as well as on further treatments such as mechanical refining of the pulp. A fraction of the pulp consists of particles smaller than the fibres. Some occur naturally in the wood and are referred to as primary fines particles (or “fines” for short), whereas secondary fines are fragments of fibre wall that are detached during pulp refining. The latter type of fines particles contributes a lot to the strength of a paper. In some cases, fibres are deliberately broken up to the point where the individual fibrils become available. These micro- or nanofibrils can then be

used as raw material for technical applications in their own right or added to papermaking pulp as a strength aid.

Fibres, fibrils, molecules and water

Due to the strong affinity between water and cellulose/hemicellulose, the lignocellulosic particles in a pulp suspension swells substantially as water enters the ultrastructure. Typically, a wet pulp holds more water than its dry mass after the water filling the voids between the particles has been removed. Due to the swelling of the fibres and fines particles, these are sometimes best described as hydrogels when in a suspension. When saturated with water, bonds within the fibre wall, and between particles, are weak. This makes the fibre compliant, and the fibres can deform as the wet paper sheet is compacted in the production process, thus giving rise to many contact points between the particles at which fibre-fibre joints can form. The swelling further allows molecules belonging to one particle surface to diffuse into the molecular structure of another surface, which is considered an important bond formation mechanism.

The formation of bonds

Compliance is important also at the micro- and nano-level to allow parts of the material to come close enough to form bonds at the molecular level. As long as there is abundant water, these bonds do not form to any large degree, since the water molecules interfere with the bonding interactions. When the water is removed through drying, attractive forces between different parts of the material start to be felt, and bonds form. The forces also induce stresses in the material, which leads to rearrangements in the ultrastructure. Fibrils change position relative to one another, and pores close. The structural changes may therefore have implications for the transport of water molecules through the material, and hence the drying rate. Perhaps more importantly, they have implications for the bond development, through its dependence on fibre conformability and the compliance of the fibril hydrogel. Some of the bonds that form during the drying are permanent in the sense that they do not break when the fibre material is rewetted. The result is a stiffening of the fibres that is referred to as “hornification”. Other types of bonds, such as hydrogen bonds, vanish at rewetting when water molecules are again available to interfere with the attractive forces.

Key concept – structure

We can now appreciate how mechanisms at different scales interact with each other during drying. The key concept is structure. Molecular and fibril configurations at different stages determine the strength of attractive forces, which in turn feedback to influence the ultrastructure. The combined effect of the bonding forces translates to stresses in the material that yield structural effects, for example micro-compressions of the fibre wall at fibre-fibre joint locations, again with potential implications for the bond formation at the molecular scales. The stresses that develop as the water leaves the pulp material results in shrinkage of the fibre wall, and the lumen cavity of thin walled fibres

collapses. The changes are propagated through the fibre network, resulting in structural changes at the macro-level, e.g. reduced thickness of the sheet with bulk loss and reduced bending stiffness as a result, and an overall shrinkage in the plane of the sheet. When the shrinkage is prevented by restraints, either external ones provided by the drying equipment, or related to the local structure of the fibre network, stresses are built into the material. Inhomogeneities in the material at the macro-scale, such as flocs, temporarily result in non-uniform distribution of water content, and non-uniform stress levels. These translate to residual stresses that influence the mechanical properties of the sheet, and its reaction to humidity and water in different situations.

A drying research roadmap

Past research on drying and bond development has not managed to clarify, in a coherent and unified way, how bonds form and how the interactions between different structural scales play out as water is evaporated from the material. We currently do not know in any great detail how the molecular forces during drying propagate to larger structural scales and create aggregated effects at the network level, with consequences for sheet thickness contraction, residual stresses in the material, and how this in turn changes the conditions for bond formation at the smallest scales through a two-way coupling between the structural levels.

Changing this state-of-affairs is an urgent task. New insights in this area would allow us to deliberately intervene with the active mechanisms in beneficial ways. Conceivable ideas include chemical additives that take a specific role at critical phases of the drying process, to give the material or other complementary additives improved conditions to establish bonds. Perhaps even the nature of the final bonds could be changed, in order to give more ductile paper materials capable of sustaining subsequent demanding product forming processes, or unwanted hornification prevented to improve the performance of the fibre material following recycling. Alternatively, the pulping process could be changed to influence the structure and the chemistry of the pulp for similar results. Fibre based functional additives, such as micro- or nano-fibrils, could potentially be made more efficient if their structure and chemistry was modified based on knowledge of how they interact with other parts of the pulp material during drying. The challenge is made more complicated by the fact that the relevant phenomena are dynamic in nature. In-situ studies of the drying process will therefore be necessary in many cases. Nevertheless, it is realistic to connect the different structural levels.

At the network level, it is comparatively easy to perform experimental measurements of how stresses and strains develop as the water content of a sample changes. One example of a device that is useful in this context is the bi-axial dryer instrument shown in Figure 3. Combined with other techniques, like digital image correlation (DIC), detailed time-resolved displacements of the material in the plane of the sheet could be determined and

coupled to geometrical features such as the floc structure in a sheet sample. Further developments of this type of setups should be encouraged and used to explore the effects of pulp composition and additives. It is important that the produced data is coupled to simultaneous measurements of the moisture content, for correlation to other data obtained from measurements at other structural levels. Near infrared spectroscopy (NIR) would be one way to make contact free determinations of the moisture level, potentially over the entire surface of the sample with quite high spatial resolution.



Figure 3. The bi-axial dryer instrument available at RISE. Stresses and strains are prescribed and/or recorded in the two directions of the sheet. The instrument was recently upgraded with continuous NIR-based measurement of the sheet dryness.

Various methods can be used to obtain information about the three-dimensional structure down to the fibre level as the material deswells, to determine changes in fibre network topology, and microscopic morphological changes of individual fibres, such as how their cross sections alter. Characterizations at this level are very valuable to understand the development of stresses and strains at the larger scale sheet level. When working with laboratory instruments, it will typically be necessary to stop the drying process at different stages, for example by abruptly freezing the sample followed by sublimation of the water without altering the micro-structure, after which the characterization can be done.

In-situ studies of the drying in realistic atmospheric environments is however a possibility by using synchrotron-based X-ray tomography, or neutron imaging. These opportunities for in-situ investigations have typically been used to relatively little extent for pulp-based materials. However, lately there has been a growing interest in the use of large-scale research facilities such as synchrotrons for development of advanced bio-based materials. The same tools should now be employed for more conventional paper products. In general, the sample setups can be designed to fit quite large-sized samples, which opens for simultaneous measurements of e.g. stresses and strains in the material using conventional load stages.

Also, the fibre ultrastructure and molecular scales can be probed during drying using various techniques. Microscopy methods can provide nanoscale resolution. Atomic force microscopy (AFM) has been used to probe pulp fibres at various levels of relative humidity (RH), and to determine the mechanical properties of swollen pulp hydrogels. Techniques like Fourier transform infrared spectroscopy (FTIR) can be used to detect changes in the bonds in the material, for example as the result of changed moisture conditions. However, also for the nano and molecular scales, X-ray and neutron scattering beamlines will provide powerful tools to obtain structural information in-situ during the transition of the material from wet to dry state. Again, it will sometimes be feasible to simultaneously perform measurements of stress and strain, as exemplified in Figure 4.

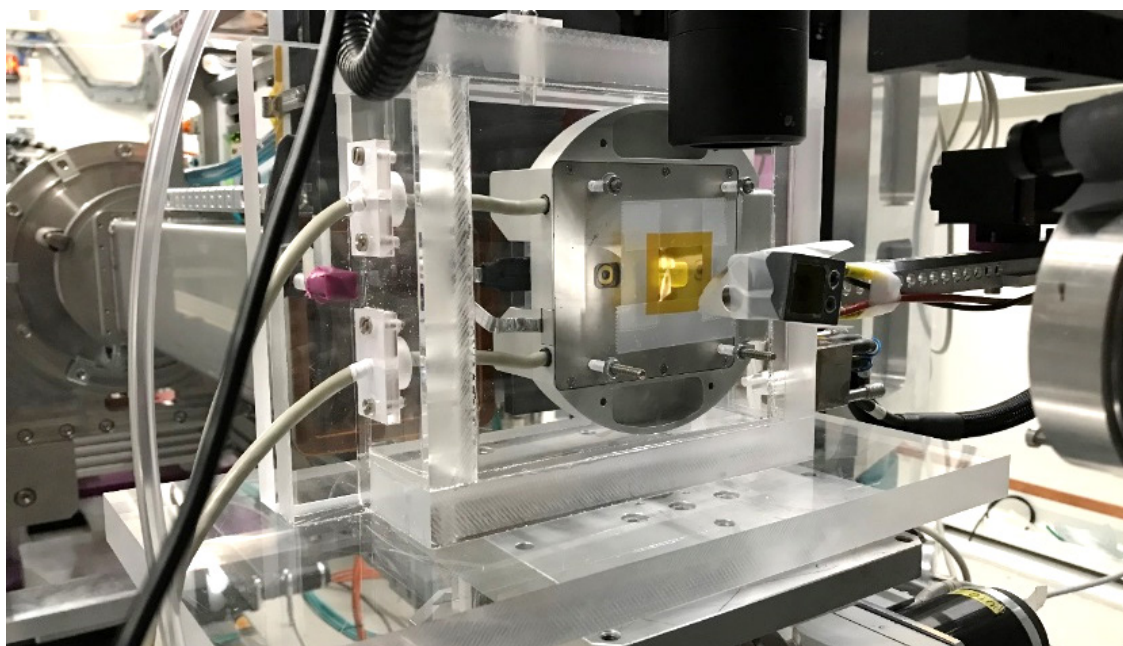


Figure 4. Climate controlled sample environment developed by RISE for structural characterization of paper samples with X-ray scattering. The sheet samples can simultaneously be subjected to tensile load testing. The device is shown mounted in the P03 beamline at the Petra III synchrotron in Hamburg, Germany.

Complementary to the experimental techniques, simulation tools should be employed to support interpretation of the results, and to help connect different structural levels. Computational models describing transport processes in paper during drying are already available. These often disregard the internal structure of the paper, and instead treat it as a continuous material. Nevertheless, such models have value and should be employed to understand the drying process at the largest scales. Models need however be developed that account for network structure and the microscopic perspective, coupled with the thermodynamics of the evaporation process. At the smallest scales, molecular dynamics modelling is needed. Modelling frameworks exist to deal with these challenges, such as Lattice Boltzmann methods and coarse-grained molecular modelling tools capable of dealing with many-particle systems. The work should be undertaken with the objective in mind to eventually develop a model that integrates all the structural scales that have been described in this paper. In recent years, the general interest in developing so called “multi-scale models” have been large in many scientific fields, and guidance is therefore available.

Conclusion

In this paper we have sought to demonstrate that there is much to be gained in terms of paper product performance by understanding the mechanisms at play during drying of pulp materials. We may then intervene with these mechanisms in a constructive way, to affect the paper properties, and increase the value added to paper products.

Why now?

- Untapped potential to improve properties of paper materials during drying.
- X-ray and neutron based experimental methods have made important inroads in pulp and paper research.
- Recently developed computational methods can leverage interpretation of results and guide experiments.

We also argue that now is a good time to take on the challenge, as pulp and paper researchers have started to embrace X-ray and neutron based experimental methods that hitherto were not widely employed by our community. In addition, computational

methods have been developed that could be used to leverage the experimental methods by aiding in the interpretation of the results, and by providing guidance in design of experiments.

It is important to realise that drying of paper material is a process that spans multiple length scales, from the world of molecules up to the structural features in a paper that we can see with the naked eye by looking at a sheet held up against a light source. The goal must be to understand the interplay between the different scales. This means that studies focussing on one structural level should be designed with the link to the other structural levels in mind for best effect. That way, the pieces of the puzzle will eventually fall into place. Given the size of the challenge, it is very amenable to be addressed by a larger research programme that can simultaneously and systematically address the different levels.

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