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DEVELOPMENT OF IMPROVED CTMP WITH EVEN SULPHONATE DISTRIBUTION AT FIBRE LEVEL USING XRF ANALYSIS

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ABSTRACT

Optimizing the fibre property distribution could increase the pulp properties as well as the process efficiency of chemimechanical pulps (CMP/CTMP). This can only be achieved with a better understanding of how evenly distributed sulphonate concentrations are between the individual CTMP fibres. Given that the quality of wood chips varies with the chipping methods used in pulpwood processing and sawmill processing, as well as with the chip screening system, it is a challenge to develop an impregnation process that ensures even distribution of sodium sulphite (Na_2SO_3) in the liquid used to impregnate the chemi-mechanical pulp (CMP/CTMP). Therefore, the distribution of sulphonate groups within wood chips and individual fibres must be

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measured at the microscale level. On a micro level, the degree of unevenness, i.e., the amount of fibre sulphonation and softening before defibration, cannot be determined due to the use of excessively robust or complex processing methods. By having it, we could better understand how sulphonation occurs before defibration, so we could improve impregnation. Developing a laboratory scale miniaturized energy dispersive X-ray fluorescence (ED-XRF) method that measures sulphur distribution at the fibre level can enable us to study the influence of impregnation improving processes.

1 BACKGROUND

The packaging industry is seeing a rapid increase in the use of chemimechanical pulp (CTMP) a renewable resource that is becoming increasingly prevalent as fossil-based materials are replaced with bio-based ones. The hygiene sector also makes extensive use of CTMP and high temperature chemimechanical pulp (HTCTMP). To understand the CTMP process from a systems perspective, it is critical to evaluate the entire value chain. It begins with pulpwood chips obtained from sawmills and pulpwood chipping, goes through the washing, steaming, impregnation, and preheating and finally refining that control the fibre properties and lower the cost to a product with certain properties. The method of producing CTMP involves impregnation of woodchips with sodium sulphite (Na_2SO_3) or different combinations of $NaHSO_3$, Na_2SO_3 and NaOH depending on type of CTMP. The impregnation is followed by preheating at 140 – 180°C, 2–5 minutes and pressurized chip refining [1, 2]. The sulphonation of lignin in the fibre walls improves fibre separation of the wood chips so that it is possible to achieve a shives free bulky pulp at very low energy consumption [3]. In addition, it is possible to soften fibres by treating them with steam at high temperatures, followed by explosive decompression [4]. The purpose of wood softening before defibration in the chip refiner is to obtain well-separated fibres with the least amount of shives possible. But a key challenge in CTMP processes is to obtain even distribution of sodium sulphite (Na_2SO_3) and sodium hydroxide (NaOH) through the wood chips, this is extra challenging when it comes to high-density hardwoods as eucalyptus and birch. As a result, the chips' inner parts receive much lower degree of sulphonation than the outer parts leading to large differences in the degree of sulphonation between the produced pulp fibres. As CTMP capacity is now rapidly growing for packaging materials, uneven sulphonation at impregnation is generally acknowledged to be a major concern. A difficult challenge has always been evaluating the degree of efficiency of the earlier suggested

improvements to impregnation [5-11]. Our hypothesis is that the efficiency and evenness of fibre separation in the chip refiner is highly dependent on how evenly the preheated chips have been sulphonated. By minimizing the differences in sulphonate content between fibres, we can minimize the requirement for sulphite dosage to a certain degree of fibre separation, thereby reducing the total amount of electricity used in chip refining. It has been studied the feasibility of softening chips in order to produce CTMP that has well-preserved fibres with yields above 95%, shives content less than 1% before the screening, and energy consumption less than 200 kWh/h [12].

It is therefore important to have a reliable measurement technique of the degree of sulphonation at the fibre level to optimize the process. For this reason, ED-XRF methods primarily were used on thin CTMP paper sheet (20gsm) at the laboratory scale to conduct sulphonation degree measurement tests on individual fibre level and later validated by synchrotron beams.

2 MATERIALS AND METHODS

To investigate sulphur distribution, Valmet's CTMP-712 reference pulp was selected. SCA reference kraft K44 of bleached softwood kraft pulp (BSWK) was used to dilute CTMP. As the pulps were thoroughly washed, it was assumed that unbleached kraft pulps (UBK) with lignin would contain no rest sulphur, which would result in BSWK for which there was no rest sulphur. With this setup, we measured an unbeatable low grammage handsheet of 20gsm. Using a conventional sheet former with a surface area of 0.021m^2, a low grammage handsheet of 20gsm was made by mixing CTMP and BSWK as 100% CTMP and 50% CTMP/ kraft respectively, in accordance with ISO 5269-2:2004 at SCA R&D Centre, Sundsvall, Sweden [13].

X-ray fluorescence (XRF) imaging measurements were performed at STC (Sensible Things that Communicate) of Mid Sweden University, Sweden on a laboratory scale with a 50μm pinhole, made from tungsten carbide (WC, *Alfa Aesar* 99.95% pure metal) at XRF in a helium and air environment. A typical focal spot size of Moxtek X-ray sources (5 kV to 60 kV, 12W) is 400μm. The focus spot size of the beamline should be less than 20μm in order to obtain a high-resolution image for fibre; therefore, the beamline must be collimated by a pinhole to reduce the focus spot size.

A collaboration was also established with the Swiss Light Source PHOENIX I beamline of the PSI (Paul Scherrer Institute), Switzerland. Additionally, the APS (Advance Photon Source) USA, 2-ID-D beamline examined the sulphonation level of a single fibre of CTMP paper sheet.

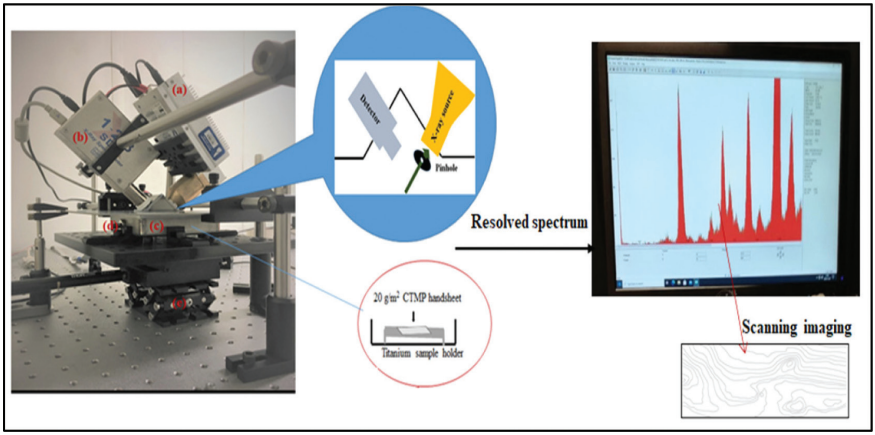

Figure 1. Image of ED-XRF measurement setup at Helium gas atmosphere in titanium box [Redrawn from 15].
The image shows: (a) a typical X-ray source (Moxtek), (b) a detector used to analyse the spectrum of element, (c) titanium shield box (10 x 10 x 2.5 cm) at helium atmosphere, (d) helium gas connection, and (e) a two-dimensional stepper motor (reaching in X and Y directions).

Figure 1 illustrates the process of placing the impregnated wood or paper samples in titanium boxes in air or helium gas environments. A simple scan with some steps of the sample surface (impregnated wood chips or paper sample) produces an elemental distribution image of the substances as photon counts, which is sufficient to illustrate the primary spectrum of sulphonation. The problem with this imaging technique is that low-energy fluorescence photons from sodium (Na) and sulphur (S) are easily absorbed by air, requiring the use of another atmosphere. The Monte Carlo N- Particle Radiation Transport Code (MCNP) was used to simulate the measurement setup and validate the setup and atmosphere [14]. Simulated spectra at helium, air, and vacuum environments showed that a 2cm thick layer of air completely absorbs the Na signal and 50% of the S signal, leading to a low signal on the XRF spectrum [15]. Even though a vacuum atmosphere is completely airless, the difficulties associated with maintaining moving parts in a vacuum greatly affect the design of the instrument. In this application, a helium gas chamber was sufficient for measuring sulphonate levels. Due to this, titanium (Ti) boxes filled with helium were used to reduce fluorescence photon absorption and minimize scattered photons.

3 RESULTS AND DISCUSSION

3.1 Study of Sulphonation at Laboratory

A CTMP/Kraft 20gsm paper sheet (50/50) was examined with a 50μm pinhole at 8keV in helium gas and air environments for 7 hours at XRF lab setup [15]. As shown in Figure 2, sulphur (S) exhibited an enhanced peak at 2.31 keV when compared to air. Based on MCNP (Monte Carlo N- Particle radiation transport code) simulation modelling [14], the helium gas environment is better than the air environment for detecting light elements like Na and S since the air environment has higher background noise and possible to get lower sulphur photon counts. We could not see the sodium (Na) peak at Kα 1.04 keV here clearly. This may also be due to sodium's lower energy below the noise width. To measure the extremely low concentrations of light elements like Na, high-resolution detectors are needed.

3.2 Study of Sulphonation at PSI Synchrotron Laboratory

The XRF spectra of two 20gsm paper samples of CTMP (100%) and CTMP/ Kraft (50/50) were obtained at the PHOENIX I beamline using incident beam energy of 2.4 keV, 4 seconds per pixel, and beam size of 0.1 x 0.2 mm for maps, as shown in Figure 3. The beam was monochromatized and focused on a vacuum chamber by mounting four crystal pairs inside the monochromator. CTMP shows

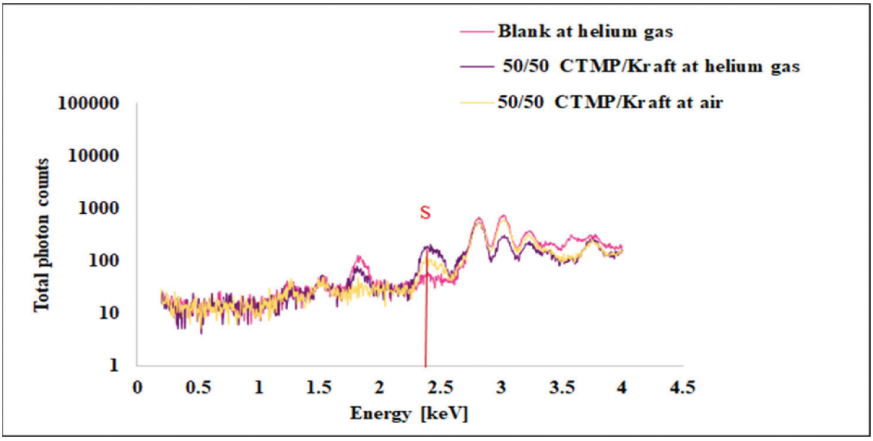

Figure 2. CTMP/Kraft (50/50) 20gsm paper sheet XRF analysis in helium and air environment.

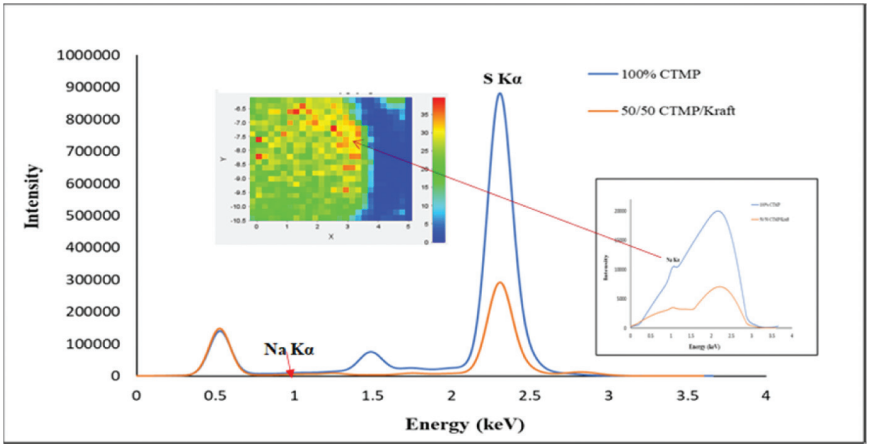

Figure 3. Comparison of the XRF intensities for S and Na of two different CTMP samples.
The figure shows the sodium (Na) Kα 1.04 keV peak is prominent in the 100 % CTMP sheet and visible when compared to the 50% CTMP sheet.

the strongest peak in the sulphur Kα spectrum, represented by the blue curve in XRF spectra. As the pulp consistency of CTMP was decreased by 50%, the peak for sulphur Kα was also decreased since kraft pulp is free of sulphur due to washing.

3.3 Study of Sulphonation at Single Fibre at APS Beamline

Furthermore, in our recent investigation, the synchrotron radiation beam intensity at APS, USA allowed a trade-off between better spatial resolution and shorter measurement times to generate enough signals to detect the characteristics lines of light elements at 1μm steps. We observed here significant differences in fibre sulphonate content using the 2-ID-D beamline at APS. It showed that sulphonated lignin surfaces can be distinguished down to the sub-fibre level. In Figure 4, sulphonated lignin is unevenly distributed within each fibre as well as on each fibre surface.

However, X-ray fluorescence (XRF) technology is used in our lab for measuring sulphonate content on fibre level as well as measuring the distribution of sulphonate on individual fibre surfaces. Further, it was possible to distinguish the level of sulphonation at the fibre level from two different paper sheets using lab-XRF. As far as we know, no synchrotron studies have been done yet of this type.

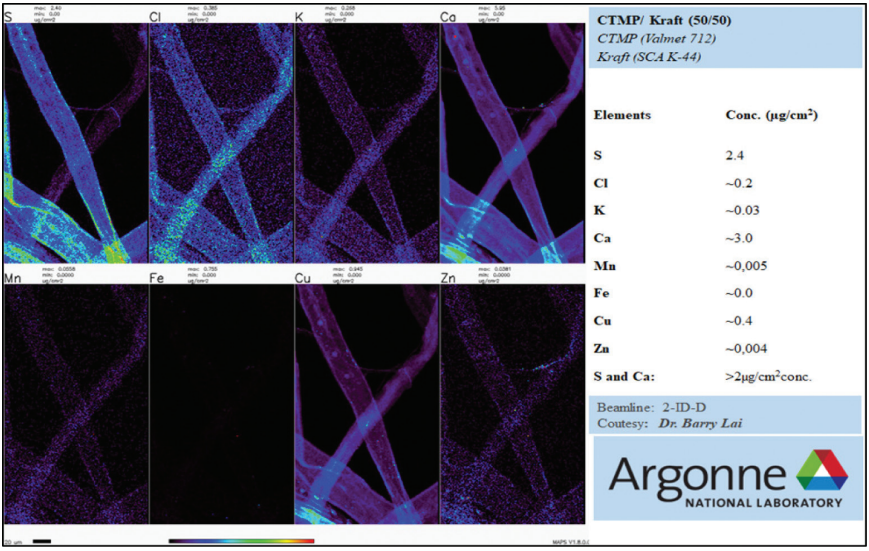

Figure 4. Measurement of sulphonation in single fibres of the CTMP paper sheet at APS, USA.
The figure shows S, Cl, Ca, Fe, Cu and Zn on thin CTMP/ kraft paper sheets. Throughout the preliminary figures, the colour scales represent the concentration range from zero to the highest concentration measured for each element. The colour map is "jet", where "red" represents the maximum concentration in the actual photo where the resolution of the image is 1µm.

4 CONCLUSION

Our results show that the degree of sulphonation of the individual fibres is also quite uneven based on the distribution of sulphonation in the wood chips after impregnation. With the help of x-ray fluorescence (XRF) built in our lab, we have demonstrated that it is feasible to measure sulphonate content at the fibre level, and our results have been validated using the beamlines of APS and PSI that have allowed us to also measure sulphonate distribution over individual fibre surfaces. In general, the distribution of lignin sulphonation on individual fibre surfaces is uneven, as expected; this may be traced back to the distribution on fibres as well. Upon development, this procedure will be able to be used in industrial labs to measure the distribution of sulphonic groups on fibre level. Polycapillary X-ray optics, on the other hand, may prove more effective in preparing the next laboratory stage than XRF pinholes since their X-ray flux is 150 times more powerful.

This will enable process optimization for impregnation, mixing, and reactors in full-scale systems and allows XRF measurements to be performed to evaluate the effectiveness.

ACKNOWLEDGEMENT

The Knowledge Foundation, the European Union Regional Fund, the Kempe Foundation and Mid Sweden University, as well as the companies Billerudkorsnäs, and Valmet supported this project. This article also acknowledges funding from Vinnova for the project "*Renewable packaging materials – Impregnation depth measurements for pulping industry using a synchrotron"* . Synchrotron measurements are conducted in collaboration with PSI, Switzerland and Advance Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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Steve Keller Miami University

I had basically one question that has two layers. First of all, can you speak to the depth of penetration that the beam has for characterising the sulphur content, because in one of your images, I noticed that crossed fibres seemed to have a higher intensity. This suggests that you have depth penetration greater than the thickness of the fibre and on top of that, are we looking at residual sulphur that has deposited over the surface, or are we looking at bound sulphur that has unequally bonded with the lignin compounds?

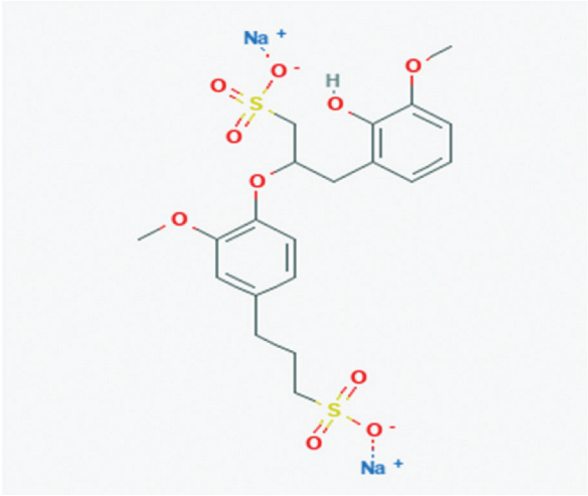
Hafizur Rahman

That is an excellent question. No, you cannot speak of depth for X-ray imaging of such thin samples. The sulphur content of cross fibres should be the sum of both fibres' sulphur contents.

Discussion

In APS, we used CTMP paper samples with a grammage of 8–10 g/m^2 and a spatial resolution of 10 μm, 30 μm and 100 μm for our sulphur distribution maps. It is true that crossed fibres appear to have a greater intensity since determining individual fibres of approximately 20–40 μm in width is difficult due to their small size. In order to prevent crossed fibres, APS requested a light-grammage paper sheet with fewer fibres. That's impossible.

The majority of our interest is in the analysis of fibre level sulphur (micro-scale). It means the sulphur bound to CTMP fibres is bound as sulphonate, $-SO_{3^-}$. Sulphonate groups are bound to lignin in fibres. The proportions of wood polymers in CTMP fibres, which is similar to native spruce wood, are 40% cellulose, 30% hemicellulose, and 28% lignin, 2% of the extractives in the wood are removed during pulping and manufacturing laboratory sheets. Wood chips are impregnated with sodium sulphite solution with a charge of 20–30 g Na_2SO_3 per kg in the Chemithermomechanical Pulp (CTMP). By reacting with lignin, sulphite ions (SO_{3^-}) make it less crosslinked and softer, resulting in a more efficient defibring process. The dominant structure is centred around the sulphur. What we're looking for looks like this:



Steve Keller

The reason that I ask this is because you did show spectral results and then you showed a photograph of the paper itself. Just a suggestion for the future, the relationship between that X-ray and either the topography or the formation will be an important aspect for you to characterise. It looks like the sulphur distribution from spectral

results was apparently related to the photograph, but I think if you try to relate it to the actual mass distribution, it might be something that would be helpful for your studies.

Hafizur Rahman

I appreciate the positive feedback you provided. Yes, that is also one of our investigation targets. As a first step, we wanted to validate the lab method using a Synchrotron setup.

Gil Garnier Monash University

You mentioned about non-uniform sulphonate. So I was just curious, did you correlate with the uneven distribution to the impact of properties, because you talked about processes and what role of improvement is there to make it lighter, better and stronger by improving your efficiency?

Hafizur Rahman

Unfortunately, we have not yet correlated it with the uneven distribution. By using XRF, we would like to investigate uniform sulphonate at fibre level to improve the process and product properties. In the impregnation process, we know that the inner parts of the wood chips absorb a much lower degree of sulphonation than the outer parts. Less sulphonated or unsulphonated wood chips tend to fracture in the outer secondary cell wall, leaving a carbohydrate-rich fibre surface with different bonding properties. The sulphonation of the secondary wall increases the sheet density and strength as well as the flexibility and conformability of fibre walls. Pulp properties with higher shives contents are adversely affected by this uneven sulphonation. Sulphonation of each wall layer can be controlled in order to meet specific end-use requirements. Using the XRF technique, we can at least minimise the differences in sulphonate content between fibres. It is possible to minimise fibre separation requirements by reducing sulphite dosage. Therefore, chip refining consumes less electricity overall.

Bill Sampson University of Manchester

Could you please put up your slide showing the concentrations of elements from the data obtained at Argonne? If we look at the images for sulphur, chlorine and calcium ions, which give strongest signals detected, overwhelmingly you detecting these ions at fibre crossings. If I look at the sulphur there is a large fibre running top left to bottom right, where you have also got some hotspots around the edge of the fibre. How confident are you that these are not artefacts?

Discussion

Hafizur Rahman

Thank you, that's a very good observation. It is due to crossed fibres where the sulphur signal combines that hotspots form.

At Argonne, we also saw significant differences in fibre sulphonate content using the 2-ID-D beamline. There is some evidence that we can distinguish sulphonated lignin surfaces down to a sub-fibre level. As shown in Figure, sulphonated lignin is unevenly distributed within the fibres and on the surfaces of the fibres. Sulphur content varies greatly not only between fibres, but also within one fibre based on these images. Since sulphur exists as a negatively charged sulphonate, it is interesting to observe that positively charged metal ions, such as Ca and Cu, are situated on surfaces with high levels of sulphonate. When CTMP fibres are separated in a refiner, middle lamella with significant lignin sits on one fibre surface, while secondary fibre wall material is predominant on the adjacent fibre surface, which may explain the uneven distribution of sulphonates. The distribution of elemental sulphur and its counterions, such as sodium and calcium, in CTMP must be analysed in order to improve impregnation technologies. As a result, we will be able to determine its level of sulphonation.

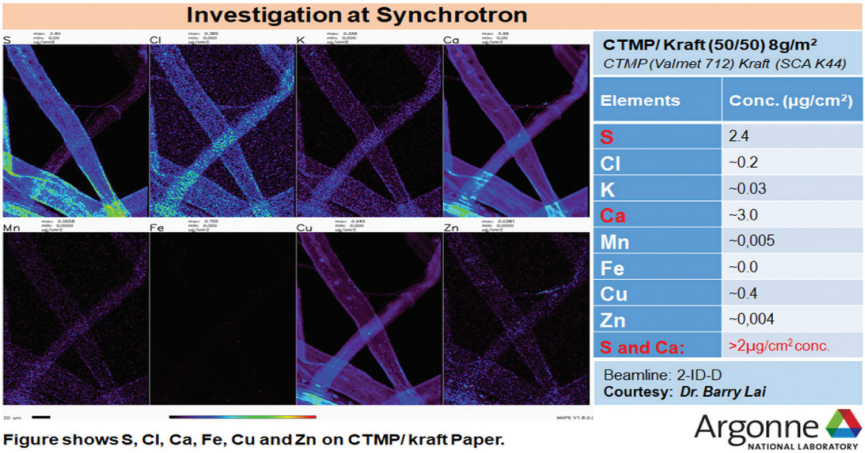


Figure shows S, Cl, Ca, Fe, Cu and Zn on CTMP/ kraft Paper.

The color map is "jet", where "red" represents the maximum concentration where the resolution of the image is 1µm.

Bill Sampson

If I understand the problem you are seeking to probe, it is about the uniformity of the sulphur ion concentration on the fibre. I would expect that to be stochastic along the length of a fibre. Then in your image – and I understand the challenge in getting single fibres to image – overwhelmingly you are detecting these elements

at fibre crossings, so that is very much not stochastic. Fibre crossings are stochastic in another very interesting way but you have not shown a stochastic incidence of these elements, and I think that is a real concern about the configuration of this non-uniformity.

Hafizur Rahman

According to our results from the APS beamline in the USA, CTMP fibres differ greatly in sulphonate content, and it appears that sulphonated lignin surfaces can be tracked at the sub fibre level. I find it interesting.

Elias Retulainen Fiber and Fibril

First a more philosophical question: Is it really a homogeneous distribution of the sulphonation that we want? I assume that we want first of all to affect the lignin. However, on a microscopic scale the lignin distribution is not even. We have more lignin on the surface layers and the corners of fibres. And if you have a thick-wall fibre, you have more lignin than a thin-wall fibre. Another thing is that in the figures you showed you have only fibres, even though you produce a lot of fines when you make CTMP, and I do not see any fines in these figures. Additionally, there is also the question: What are the objectives? Do you want mainly to reduce the amount of refining energy used? You probably also want to improve the bonding between fibres in paper and that means that you are affecting the swelling and conformability of the fibre wall. There are several complicated issues. If you want to optimise all these it takes lots of research.

Hafizur Rahman

Although it is your philosophical question, you have reached the depth of my research. Although it is hard to say that how much homogeneity we can achieve, at least we can minimise the sulphate dose and reduce the shive content, while saving a large amount of energy. As an example, you might notice I mention one slide in detail. In the Valmet pilot trials at Sundsvall, Sweden, we have evaluated the feasibility of softening chips in order to produce CTMP with well-preserved fibres with yields exceeding 95%, shives content below 1% before screening, and energy consumption less than 200 kWh/h. There is a greater chance of less shives when the homogeneity is increased.

In fact, we are looking for a CTMP development process for a packaging board application. A goal of developing CTMP for the middle layer of paperboard is to produce a fibre material with a higher bulk and lower grammage while maintaining stiffness. In the chip-refiner prior to defibration, getting well-separated

fibres at a minimum quantity of shives is essential in order to increase wood softening. It takes lots of research to optimise all of these, and we would love to do it right now. It is imperative for us to collaborate more effectively in order to achieve our goals.

Ulrich Hirn

If you go to the graph with the image from the synchrotron where you see the distribution of Sulphur, then what we see is quite strong edge artefacts and it seems that topography is playing a large role in the intensity. If you want to evaluate the unevenness of the sulphur, that is probably quite a big problem. I think this may also be related to the geometry of the instrument where you have kind of a 45° geometry (45° illumination and 0° imaging, i.e. illumination from the sides), which gives you shading from surface topography. I think that this contributes to an irregular distribution of Sulphur in the images, even if it were completely regular on the fibres. Probably that needs to be addressed somehow when progressing towards a quantitative evaluation?

Hafizur Rahman

There is a difference in angular geometry between the laboratory setup and the synchrotron setup. When thin samples are examined at the X-ray wavelength, shading due to geometry should not be a concern.