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SWELLING PROPERTIES OF PULP TREATED WITH DEEP EUTECTIC SOLVENTS

The reaction of cellulose with water produces swelling and structural changes of the fibres, both effects being of crucial importance for the understanding of paper formation. It was investigated how the treatment of pulp with deep eutectic solvents affects the swelling kinetics of the fibres. Unbleached kraft pulp was treated with three deep eutectic solvents containing choline chloride (ChCl) – ChCl:lactic acid (1:9), ChCl:oxalic acid (1:1) and ChCl:malic acid (1:1) – and with the system alanine:lactic acid (1:9). The rate and maximum swelling of the pulp in water were determined using a modified monitoring unit for measuring swelling ability. Since paper swells extremely rapidly in water even at 23°C, this apparatus made it possible for the first time to obtain accurate rate data on the swelling of DES-delignified pulp in water.

Keywords: deep eutectic solvents, swelling, WRV, swelling kinetics, pulp

Introduction

The reaction of carbohydrates (cellulose and hemicelluloses) with water causes swelling and structural changes of the fibres. Water converts the ligno-hemicellulose to a microporous gel, where lignin acts as a crosslinking agent within the wall, and hemicellulose plays the role of a coupling agent between lignin and cellulose [Salmén and Berthold 1997]. Hemicelluloses promote fibre swelling, while lignin inhibits it [Niskanen 2000]. Swelling also yields more flexible fibres, and the increased fibre flexibility promotes conformability, thus allowing the formation of more fibre-fibre contacts and leading to improved web strength [Toven 2000]. Deep eutectic solvents (DESs) represent a new generation of compounds derived from renewable sources that have become a focus of interest in science and technology in recent years. These technologies are expected to be available by 2030, and according to forecasts they may come into full industrial use by 2050. There are several reports on the delignification

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of various types of biomass by DESs, and this research area is currently undergoing significant development [Jablonsky et al. 2015, 2018; Kumar et al. 2015; Skulcova et al. 2016a, 2016b, 2017; Majova et al. 2017]. Deep eutectic solvents are a breakthrough discovery and open the way to pulp production at low temperatures and at atmospheric pressure. Delignification with deep eutectic solvents has important advantages over oxygen delignification. The benefits of using DESs as a reaction medium include the fact that they are biodegradable, nontoxic and recyclable, and can be prepared easily using cheap raw materials. The advantages of DES application include the lower temperature (60°C) and the use of an unpressurized system, which reduces equipment costs. An apparent disadvantage may be the necessity to introduce a system for DES recycling; however, recycled DES can be repeatedly used for delignification. Another benefit is that the lignin obtained by DES delignification is relatively pure. Moreover, DES delignification is associated with a lower degree of cellulose degradation and thus higher selectivity. Given the fact that a similar degree of delignification is obtained with DES as with oxygen, reduced emissions from the bleach plant, reduced consumption of bleaching chemicals, and a higher brightness ceiling in a given bleaching sequence can be expected when using DES delignification. The aforementioned benefits may contribute to a broadening of research into the application of DESs in batch delignification, and later also its introduction into the process of bleached pulp production. It is important to remember that water penetration and swelling are processes with specific kinetics [Mantanis et al. 1995; Olejnik 2012; Botkova et al. 2013; Jablonsky et al. 2014]. Various methods are used to determine the swelling ability of pulp fibres in water. The most common of these are measurement of the centrifugal water retention value (WRV), microscopic measurement, and monitoring of the dimensional changes of pulp sheets immersed in water using sensors that convert the dimensions into electronic signals. These changes are reported in a number of studies [Bristow 1972; Stone and Scallan 1967, 1968; Racz and Borsa 1995, 1997; Botkova et al. 2013; Jablonsky et al. 2014; Geffert et al. 2017]. In the swollen state, the fibre wall is saturated until it is delaminated, the surfaces are fibrillated, and a high specific bonding strength in the papermaking process is achieved. The properties of pulp fibres depend on the representation of the major chemical components in the cell wall, and hence on the delignification method [Cao et al. 1998]. The hydroxyl groups are fully involved in hydrogen bonds [Stone et al. 1966]. From this standpoint, the cell wall is compact and relatively rigid. The entry of water into the cell wall leads to disruption of bonds, separation of the material, and change of structure [Scallan 1983]. The intrinsic cohesion of cellulosic fibres, containing inter- and intramolecular hydrogen bonds, influences the swelling properties and accessibility to reactive groups [Botkova et al. 2013; Jablonsky et al. 2014]. A critical factor affecting the resulting sheet strength is the chemical composition of pulp fibres, which affects interfacial and intra-fibrous bonding.

The influence of hemicellulose and lignin content is significant. The degree of swelling depends on the solvent used, temperature, ionic strength, chemical composition and internal fibrillation of the cellulose fibres [Salmén and Berthold 1997]. In our case, a modified glass monitoring unit was used to measure the swelling of pulp delignified by DESs, in addition to the standard measurement of water retention values. Our main goal was to investigate the change in the pulp's properties (swelling, WRV) resulting from the use of DES and to compare it with pulp that had undergone an oxygen delignification stage.

Materials and methods

Deep eutectic solvent delignification

All chemicals were purchased from Sigma Aldrich (Bratislava, Slovakia). The solutions were stirred in a water bath to form a homogeneous liquid. Pulp (50 g absolute dry weight) and 115 mL water were added to a specific DES at a ratio of 1:20 (wt/wt), with a pulp consistency of 4.8%. The DESs used were combinations of choline chloride with lactic acid (1:9), oxalic acid (1:1) and malic acid (1:1), and the system alanine:lactic acid (1:9). Delignification was carried out for 1 h in a drying oven with a preset temperature of 60°C. The delignified pulp was washed with water. The characteristics of the pulp and the effect on its properties resulting from DES delignification [Majova et al. 2017; Skulcova et al. 2017], expressed by kappa number and degree of polymerization, are listed in table 1.

Table 1. Characteristics of pulp and effect on its properties after DES delignification

	Kappa no.	Degree of polymerization
Kraft pulp*	21.7 ±0.6	1157 ±23
DES1: ChCl:oxalic acid	13.3 ±0.4	930 ±14
DES2: ChCl:malic acid	13.2 ±0.3	1130 ±13
DES3: alanine:lactic acid	12.3 ±0.6	1149 ±11
DES4: ChCl:lactic acid	13.5 ±0.4	1134 ±9
Oxygen-delignified pulp*	11.8 ±0.3	805 ±12

* – Mondi SCP, Ružomberok, Slovakia; ChCl – choline chloride.

Measurement of swelling kinetics

To monitor the swelling kinetics of pulp sheet, a modified monitoring unit for measuring the swelling ability of wood was used [Solar et al. 2006]. Swelling is determined as the difference of the current and initial dimensions of the sample expressed as a percentage (eq.1):

$$S_S = \frac{(F_{ti} - F_0)}{F_0} \times 100(\%) \tag{1}$$

where S_S is the swelling in a plane perpendicular to the paper, F_{ti} is the thickness of the paper during monitoring, t_i is any time from 0 to 6000 s, and F_0 is the initial thickness of the paper at the initial moisture content. The relative rate constant of the initial fast phase of swelling is computed as the gradient of a tangent drawn through the linear part on the kinetic plot [Solar et al. 2006]. The experiment used samples in the form of sheets with an initial diameter of 4 cm^2. All samples reached equilibrium moisture content; the initial moisture content of the paper samples ranged between 3.7% and 4.8%. The final reported values of swelling are averages of four measurements.

Water retention value (WRV) for pulp (fibres plus fines)

To calculate the WRV the following expression was used (eq. 2):

$$WRV = \frac{m_1 - m_2}{m_2} \times 100\,\% \tag{2}$$

where m_1 and m_2 are the masses of centrifuged wet pulp and dry pulp respectively. Determination of the WRV was performed according to ISO 23714. Centrifugation was carried out at 3000 min^{-1} for 30 min. After centrifugation, the samples were weighed and subsequently dried in an oven at 105 ±2°C to constant mass. Data points represent the average of four replicates, and the standard deviation is less than 4.6%.

Results and discussion

The spreading of liquids into paper is an intricate process. The kinetics of cellulose handsheet swelling are affected by several factors, such as the initial moisture of the sheets, temperature, pressure, type of swelling media used, and method of pulp treatment and bleaching. The diffusion of liquid into the paper can be described [Karppinen 2008] as a process of the movement of water within capillaries, pores and cavities [Gupta and Chatterjee 2003]. In our case water is transported to the sheet sample through the paper cross-section and from all directions at the beginning of the measurement. Here, the inhomogeneity of the sheet samples is due to the different arrangements of fibres in single sheets of paper.

Figure 1 shows swelling profiles of unbleached kraft pulp, oxygen-delignified pulp (fig. 1a) and pulp delignified with the DES systems (fig. 1b), in the form of plots of percentage swelling against time. The kinetic curves indicate two distinct phases: a short and fast initial phase, lasting for only a few seconds, with a high swelling gain, where the swelling rate reaches a maximum, followed by a long but slow phase with a low swelling increment, where the swelling rate approaches zero (final swelling). In this phase, the fibres become fully saturated and equilibrium is established. The maximum equilibrated swelling is reached after about 1 hour of swelling in water at 23 ±2°C. The swelling kinetics were evaluated by regression analysis (eq. 3):

$$y_1 = A \cdot \left(1 - e^{-kt}\right) \tag{3}$$

where y_1 is the swelling (%), A is the maximum swelling (%), k is the rate constant determining the rate of attainment of the limiting (maximal) value A (s^{-1}), and t is the swelling time (s).

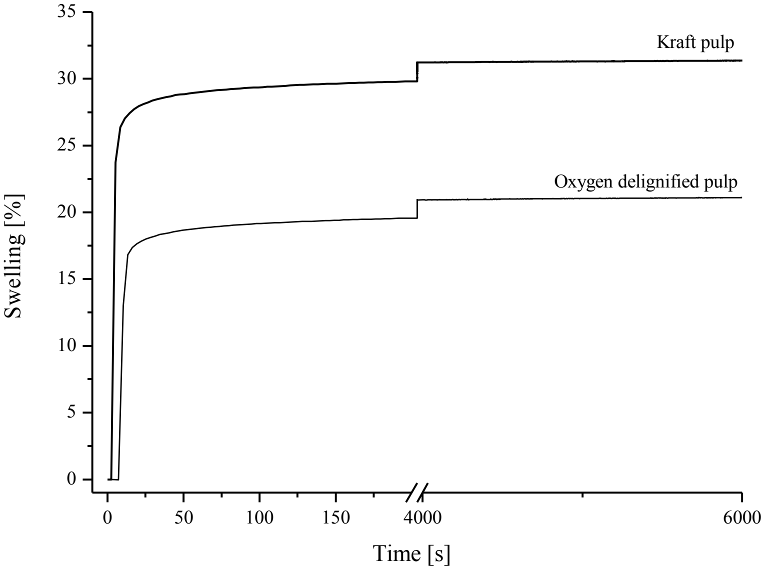

Fig. 1a. Swelling profiles of unbleached kraft pulp and oxygen-delignified pulp

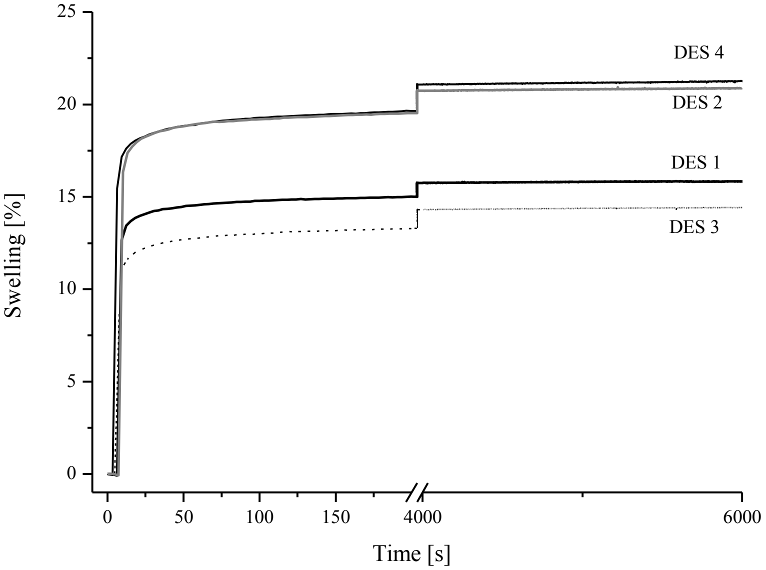

Fig. 1b. Swelling profiles of sheets of paper with different DES treatments. DES1: ChCl:oxalic acid; DES2: ChCl:malic acid; DES3: alanine:lactic acid; DES4: ChCl:lactic acid

The results in table 2 show the maximum swelling values and swelling rates of paper sheet. The rate constant of swelling for kraft pulp samples is 0.1549 s^{-1}, and the maximum swelling is 31.15%. This is the highest rate constant, and delignification leads to a very large decrease in its value. The rate constant of swelling for delignified pulp is 1.4-2.4 times smaller, and the maximum swelling is 1.5-2.2 times lower, than for the kraft pulp. For oxygen-delignified pulp 45.6% of the lignin content of the kraft pulp was removed. As a result, the pulp had a maximum swelling rate constant of 0.0648 s^{-1} and a maximum swelling of 21%. The data for the rate constant and saturation on swelling are given in table 2, and document the differences resulting from the use of particular DESs. Irrespective of the delignification method, both swelling rate constant and maximum swelling are lower for delignified pulp than for untreated kraft pulp. The pulp delignified using the choline chloride systems with lactic acid and malic acid had approximately the same maximum swelling (21.1% and 20.5%). A short and fast initial phase with a rate constant of 0.1152 s^{-1} was obtained for DES4 (ChCl:lactic acid); for DES2 (ChCl:malic acid) the value was 0.0746 s^{-1}. For pulp delignified with DES1 and DES3 the maximum swelling was 15.9% and 14.2% respectively.

Table 2. Maximum swelling values and swelling rates of samples

Sample	k (s^{-1})	Maximum swelling (%)	*WRV* (%)	Moisture (%)
Kraft pulp	0.1549	31.15 ±4.61	111 ±1.9	4.77
Oxygen-delignified pulp	0.0648	21.01 ±3.81	117 ±2.5	4.25
DES1: ChCl:oxalic acid	0.0853	15.88 ±3.16	95 ±1.6	3.71
DES2: ChCl:malic acid	0.0746	20.48 ±3.35	101 ±4.1	3.79
DES3: alanine:lactic acid	0.0854	14.18 ±2.39	95 ±3.2	4.65
DES4: ChCl:lactic acid	0.1152	21.08 ±1.10	99 ±2.4	4.08

ChCl – choline chloride

Fibres immersed in water are first wetted on the surface, and then the water penetration continues to the interfibre areas, lumens and capillary cell walls. The penetration rate for liquids is higher in larger capillaries, which actuate the liquid flow to a greater degree than narrow capillaries and have much greater suction power. The process of delignification can affect the properties of fibres. In previous reports [Sirviö et al. 2015; Li et al. 2017] the fibrillation effect of deep eutectic solvents on cellulose has been described. In these processes the fibrillation is facilitated by an increase in the anionic charges on the fibre surfaces with the introduction of charged groups. The fibre surface changes influenced the effect of swelling on the pulp. Inhibition of water penetration into the fibre leads to debonding and thus separation of the structural elements in the fibre wall, as well as softening of its structure. The swelling of the structure has a direct impact on the flexibility of the fibres. It was therefore decided to compare the swelling parameters discussed above with the water retention value (WRV) for pulp delignified by different DESs. The WRV values for pulp delignified with DES1, DES2, DES 3 and DES4 were respectively 95%, 101%, 95% and 99%. The original untreated kraft pulp has a WRV of 111%. On oxygen delignification the WRV of the pulp increased to 117%. It is clear that there is no correlation between the measured swelling parameters and WRV. This result, and the scattered attempts at rationalization of the pulp swelling process in the literature, have led us to the conclusion that the process deserves a more detailed discussion. Comparing the results of the swelling analyses obtained by these methods, it may be noted that in each of the methods the analysis is based on a different principle. For the continuous analysis of swelling kinetics using a modification of the monitoring unit, the method describes the real behaviour of the fibre on penetration of water into the paper structure and the cell walls. WRV measurement is a standardized method for determination of the quantity of water bound to the fibre after standardized centrifugation of the sample [Lindström 1980]. The fibre phase volume is referred to as the Donnan volume and is approximately equivalent to the water retention value (WRV) [Towers and Scallan 1996]. Donnan's theory probably describes the swelling of the gel phase (i.e. the fibre wall) [Grignon and Scallan 1980]. On the other hand, the WRV method explains different aspects of fibre behaviour and has been used for the calculation of the distribution of ions in pulp suspensions [Scallan 1989]. In a nutshell, one of the methods describes the behaviour of fibres on water penetration into a sheet of paper, while the other method relates to the behaviour of a fibre suspension from the standpoint of forces and properties of the paper that enable the retention of water in its structure; it therefore describes bound water in pulp and paper structures. The degree of swelling of the fibre is a result of a balance between swelling forces and the restraining network forces of the fibrillary fibre wall. As the yield of the pulping process decreases there will be less lignin in the fibre wall and hence also more empty space, giving rise to a less rigid fibre wall that may respond to the swelling forces induced by the charges in that wall [Fält 2003]. This effect was not unequivocally confirmed in our work. Despite the additional removal of lignin, the individual delignified pulps behave differently. This can be explained by the involvement of other factors that influence the swelling process, especially fibre fibrillation, hemicellulose degradation and the impact of interactions. The swelling of the fibre is affected mainly by the content of hydroxyl groups in the fibres and the content of ions in the swelling medium. The contribution to adsorption from a hydroxyl group in cellulose is assumed to be the same as the contribution to adsorption from a hydroxyl group in hemicellulose or in lignin [Berthold et al. 1996]. Additional swelling can take place if dissociable groups attached to the fibres are ionized. The observed swelling effect is determined, however, not only by the charge density but also by the degree of crosslinking of the fibre wall and the chemical environment around the fibres [Fält 2003]. Delignified wood or softwood kraft is more flexible and also more sensitive to different chemical conditions [Carlsson et al. 1983]. At higher degrees of delignification, there are few charges left in the pulp, due to the dissolution of hemicelluloses, and thus the swelling effect also decreases [Lindström 1980]. Depending on the conditions and degree of delignification, a broad range of differently charged fibres with different stiffness can hence be obtained. The balance between these two entities, i.e. the swelling forces induced by the charges in the fibre wall and the rigid fibrillary network, determine the swelling behaviour of the fibre wall. It should also be noted that a certain rigidity of the fibrillary network is necessary in order to restore the elasticity of the fibre wall [Fält 2003]. At higher temperatures, the water molecule penetrates into the fibre structure more easily because the strength of association of water molecules is lessened. The motion of molecular chain segments is activated at higher temperatures [Sumi and Kanai 1962]. On the other hand, it has been reported [Eriksson et al. 1991] that holocellulose, which is free from lignin, showed a high degree of swelling at 20°C, but as in the case of cellulose, the WRV was not affected by an increase in temperature. This effect was eliminated because deionized water at temperature 23°C was used in the swelling measurements. Eriksson et al. [1991] also identified the relation between swelling and the relative amount of cellulose and hemicellulose in delignified pulps. Authors such as Eriksson et al. [1991] and Carlsson et al. [1983] have confirmed the increase in swelling with increasing delignification. In the work of Kumar et al. [2011] it was confirmed that the accessibility of the cellulose, as indicated by the increase in the WRV value, increased with increasing lignin removal. Earlier works [Ahlgren and Goring 1971; Ahlgren et al. 1971] showed that chlorite delignification solubilized the high-molecular-weight lignin and consequently increased fibre swelling. When pulp is dried, the hysteresis phenomenon provides a substantial reduction in the WRV of the pulp [Foelkel 2007]. On the other hand, dried pulps, with lower WRV, have much better drainage in the wet end. However, excessive fibre swelling and hydration may be help to reduce hornification. Also, they facilitate refinement to some extent, and the desired strengths are attained more easily. The elasticity of the fibre wall and its ability to respond to swelling in different environments, as well as to create a rigid network, are extremely important in many paper products at industrial level.

Conclusions

The main outcome of this study was the continuous measurement of pulp fibre swelling in pulp that had been delignified using various deep eutectic solvents. The described method and apparatus made it possible to obtain accurate kinetic data on paper swelling. In addition, the WRV was used to describe the swelling. These two methods are based on different measurement principles. WRV testing provides an indication of the pulp's ability to take up water and swell, while the monitoring of swelling by continuous measurement describes the actual behaviour of the fibres and the paper structure due to the action of water. It was found that treatment and additional delignification (both DES and oxygen delignification) led to a rate constant that was 1.4-2.4 times smaller than for the original untreated kraft pulp, and a maximum swelling that was 1.5-2.2 times smaller. The WRV values following treatment with DES1 (ChCl:oxalic acid), DES2 (ChCl:malic acid), DES3 (alanine:lactic acid) and DES4 (ChCl:lactic acid) were respectively 95%, 101%, 95% and 99%, substantially smaller than the WRV of the original kraft pulp (111%) or oxygen-delignified pulp (117 %).

References

Ahlgren P.A., Goring D.A.I. [1971]: Removal of wood components during chlorite delignification of black spruce. Canadian Journal of Chemistry 49: 1272-1275

Ahlgren P.A., Yean W.Q., Goring D.A.I. [1971]: Chlorite delignification of spruce wood – comparison of molecular weight of lignin dissolved with size of pores in cell wall. Tappi Journal 54: 737-740

Berthold J., Rinaudo M., Salmeń L. [1996]: Association of water to polar groups; estimations by an adsorption model for ligno-cellulosic materials. Colloids Surfaces A – Physicochemical and Engineering Aspects 112 [2-3]: 117-129

Botkova M., Suty S., Jablonsky M., Kucerkova L., Vrska M. [2013]: Monitoring of kraft pulps swelling in water. Cellulose Chemistry and Technology 47 [1-2]: 95-102

Bristow J.A. [1972]: The swelling of fiber building boards on immersion in water. Sven Papperstidning 75 [25]: 844-852

Cao B., Tschirner U., Ramaswamy S. [1998]: Impact of pulp chemical composition on recycling. Tappi Jornal 81 [12]: 119-127

Carlsson G., Kolseth P., Lindström T. [1983]: Polyelectrolyte swelling behavior of chlorite delignified spruce wood fibers. Wood Science and Technology 17 [1]: 69-73

Eriksson I., Haglind I., Lidbrandt O., Sahnén L. [1991]: Fiber swelling favoured by lignin softening. Wood Science and Technology 25 [2]: 135-144

Fält S. [2003]: Model studies of cellulose fibers and films and their relation to paper strength. Licentiate thesis, MidSweden University, Stockholm, Sweden

Foelkel C. [2007]: The Eucalyptus fibers and the kraft pulp quality requirements for paper manufacturing. Eucalyptus online book and newsletter, ABTCP, 42

Geffert A., Vacek O., Jankech A., Geffertova J., Milichovsky M. [2017]: Swelling of cellulosic porous materials – mathematical description and verification. BioResources 12 [3]: 5017-5030

Grignon J., Scallan A.M. [1980]: Effect of pH and neutral salts upon the swelling of cellulose gels. Journal of Applied Polymer Science 25 [12]: 2829-2843

Gupta H., Chatterjee S.G. [2003]: Parallel diffusion of moisture in paper. Part 1: Steady--state conditions, Industrial and Engineering Chemistry Research, 42 [25]: 6582-6592

Jablonsky M., Botkova M., Suty S., Smatko L., Sima J. [2014]: Accelerated ageing of newsprint paper: Changes in swelling ability, WRV and electrokinetic properties of fibers. Fibers and Textiles in Eastern Europe 22 [2]: 108-113

Jablonsky M., Skulcova A., Kamenska L., Vrska M., Sima J. [2015]: Deep eutectic solvents: fractionation of wheat straw. BioResources 10: 8039-8047

Jablonsky M., Skulcova A., Malvis, A., Sima J. [2018]: Extraction of value-added components from food industry based and agro-forest biowastes by deep eutectic solvents. Journal of Biotechnology 282: 46-66

Karppinen T. [2008]: Characterizing physical properties of wetting paper by air coupled ultrasound and light. Ph.D. Thesis, University of Helsinki, Helsinki

Kumar A.K., Pharik B., Pravakar M. [2015]: Natural deep eutectic solvent mediated pretreatment of rice straw: Bioanalytical characterization of lignin extract and enzymatic hydrolysis of treated biomass residue. Environmental Science and Pollution Research 23 [10]: 9265-9275

Kumar L., Arantes V., Chandra R., Saddler J. [2011]: The lignin present in steam pretreated softwood binds enzymes and limits cellulose accessibility. Bioresource Technology 103 [1]: 201-208

Li P., Sirviö J.A., Haapala A., Liimatainen H. [2017]: Cellulose nanofibrils from nonderivatizing urea-based deep eutectic solvent pretreatments. ACS Applied Materials and Interfaces 9 [3]: 2846-2855

Lindström T. [1980]: Der Einfluss chemischer faktoren auf faserquellung und Papierfestigkeit. Das Papier 34 [12]: 561-568

Majova V., Horanova S., Skulcova A., Sima J., Jablonsky M. [2017]: Deep eutectic solvent delignification: Impact of initial lignin. BioResources 12 [4]: 7301-7310

Mantanis I.G., Young A.R., Rowell M.R. [1995]: Swelling of compressed cellulose fiber webs in organic liquids. Cellulose 2 [1]: 1-22

Niskanen K. [2000]: Paper physics, papermaking science and technology. Book 6A, Fapet Oy, Jyväskylä, 64-72

Olejnik K. [2012]: Effect of the free swelling of refined cellulose fibers on the mechanical properties of paper. Fibers and Textiles in Eastern Europe 20 [1]: 113-116

Racz I., Borsa J. [1995]: Carboxymethylcellulose of fibrous character, a survey. Cellulose Chemistry and Technology 29 [6]: 657-663

Racz I., Borsa J. [1997]: Swelling of Carboxymethylated Cellulose Fibers. Cellulose 4 [4]: 293-303

Salmén L., Berthold J. [1997]: The swelling ability of pulp fibers. Proceedings of 11th fundamental research symposium, 21-26 Sept 1997. Cambridge, UK, 683-701

Scallan A.M. [1989]: The electrical conductance of pulp suspensions. Tappi Journal 72 [11]: 157-162

Scallan A.M. [1983]: The effect of acidic groups on the swelling of pulps: a review. Tappi Journal 66 [1]: 73-75

Sirviö J.A., Visanko M., Liimatainen H. [2015]: Deep eutectic solvent system based on choline chloride-urea as a pre-treatment for nanofibrillation of wood cellulose. Green Chemistry 17 [6]: 3401-3406

Skulcova A., Jablonsky M., Haz A., Vrska M. [2016a]: Pretreatment of wheat straw using deep eutectic solvents and ultrasound. Przeglad Papierniczy 72 [4]: 243-247

Skulcova A., Kamenska L., Kalman F., Haz A., Jablonsky M., Cizova K., Surina I. [2016b]: Deep eutectic solvents as medium for pretreatment of biomass. Key Engineering Materials 688: 17-24

Skulcova A., Majova V., Sima J., Jablonsky M. [2017]: Mechanical properties of pulp delignified by deep eutectic solvents. BioResources 12 [4]: 7479-7486

Solar R., Mamon M., Kurjatko S., Lang R., Vacek V. [2006]: A simple method for determination of kinetics of radial, tangential and surface swelling of wood. Drvna Industrija 57 [2]: 75-82

Stone J.E., Scallan A.M. [1967]: The effect of component removal upon the porous structure of the cell wall of wood. II. Swelling in water and the fiber saturation point. Tappi Journal 50 [10]: 496-501

Stone J.E., Scallan A.M. [1968]: A structural model for the cell wall of water-swollen wood pulp fibers based on their accessibility to macromolecules. Cellulose Chemistry and Technology 2 [3]: 343-358

Stone J.E., Scallan A.M., Aberson G.M.A. [1966]: The wall density of native cellulose fibers. Pulp and Paper Magazine of Canada 67 [5]: T263-T268

Sumi Y., Kanai T. [1962]: Swelling of pulp fibers in hot alkaline solution. Sen'i Gakkaishi 18 [2]: 595-599.

Toven K. [2000]: Swelling and physical properties of ECF/ECF light bleached softwood kraft pulps. Proceedings of International Pulp Bleaching Conference, 27-30 June 2000. Halifax, Canada, 189-192

Towers M., Scallan A.M. [1996]: Predicting the ion-exchange of kraft pulps using donnan theory. Journal of Pulp and Paper Science 9 [9]: J332-J337

List of standards

ISO 23714:2014 Pulps – Determination of water retention value (WRV)

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