CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECTS OF REFINING TEMPERATURE AND PRESSURE ON CHEMICAL AND PHYSICAL STRUCTURE OF LOW-ENERGY THERMOMECHANICAL PULP (ASPLUND FIBERS) DETERMINED BY RAPID FTIR ANALYSIS

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Asplund fibers are manufactured using low-energy thermomechanical pulping. They have traditionally been used in fiberboard applications. Since Asplund fibers have a high specific surface area (SSA), they can find new uses as biorefinery feedstock. However, little is known about how the Asplund process parameters affect the chemical and physical structure of the fibers. This research examined the effect of refining temperature and pressure on softwood fiber properties at refining temperatures ranging from 170 °C to 200 °C. Spruce chips were subjected to a pilot-scale Asplund refining process. FTIR analyses revealed ordering of cellulose macromolecules at elevated temperatures up to 190 °C. Ordering of cellulose was confirmed by XRD analyses. FTIR analyses also suggested lignin condensation at elevated temperatures. SEM images showed improved fiber separation at higher temperatures when compared to the temperatures of 170 °C and 180 °C. These findings are useful when developing novel biorefinery concepts, where Asplund fibers are used as feedstock.

Keywords: Norway spruce, high-yield pulp, biomass fractionation, mass transfer

INTRODUCTION

Wood is an abundant renewable feedstock for future production of renewable fuels, chemicals, and materials. The available wood resources are enormous, because forests cover approximately 31 percent of the global land area.[1] However, wood is known to be recalcitrant towards fractionation and chemical conversion.[2,3] One of the most apparent challenges in the use of wood in biomass fractionation is related to the limitations in mass transfer, which is exacerbated by high viscosities of many of the novel green solvents, such as ionic liquids (IL)[4] or deep eutectic solvents (DES).[5] A successful delignification requires that chemicals are first transported to the reaction site. After the degradation reactions of lignin, its fragments need to be solubilized, so that they can diffuse out of the fiber wall to accomplish the delignification.[6] One effective way to overcome these constraints is to increase the specific surface area (SSA) of the feedstock. When the SSA increases, more surface area will be available for reactions and the overall rate of chemical reaction can be increased. In other words, the greater the SSA, the faster the overall conversion or fractionation.

By subjecting softwood chips to a low-energy mechanical refining, *i.e.*, the Asplund process, the process consumes only a fraction of the energy that is required for an industrial thermomechanical pulping (TMP) process. The wood fibers obtained from the Asplund process are called Asplund fibers. The Asplund process can successfully separate fibers with a specific energy consumption (SEC) lower than 200 kWh/t,[7] while the SEC of TMP is typically higher than 2000 kWh/t.[8] At the same time, fibers are not broken, which allows the recovery of whole fibers for further processing. The latter is a major advantage when compared to many other available size-reducing methods, such as the Wiley mill, rotary ball mills or hammer mills. However, the downside with the Asplund process is that the fibers are typically dark and covered with lignin, which effectively limits their use, for example, in papermaking.[9] It is generally understood that the fibers are separated at middle lamellae in the Asplund process – in a similar way as in the TMP process.[10] However, there appears to be little or no published literature specific to the Asplund process to substantiate this perception.

Moreover, too little published information is available about the effect of refining conditions on the lignin quality of Asplund fibers. While it is important to ensure sufficient lignin softening and therefore adequate fiber separation in the refining process, too high temperatures may have an adverse effect on lignin quality through increased lignin condensation, which in turn may slow down and complicate the subsequent delignifying reactions.

In our previous research with DESs, we have observed that using Asplund fibers enabled us to achieve a high degree of delignification under relatively mild conditions,[7] or to achieve rapid delignification under moderate conditions.[11] More recently, we observed that an IL is capable to completely solubilize Asplund fibers.[12] Moreover, high-yield pulp fibers, such as TMP and chemi-thermomechanical pulp (CTMP) are increasingly finding new uses as their versatility and potential is utilized in novel materials and products, such as composites[13] and films.[14] Due to the heterogeneous nature of high-yield pulp fiber materials, there is a growing need to gain a better understanding on their chemical properties, especially those related to lignin.

This paper presents research on carbohydrate and lignin quality and structure in Asplund fibers manufactured at varied levels of temperature and steam pressure. Four fiber samples representing refining temperatures of 170, 180, 190 and 200 °C were analyzed with Fourier Transform Infrared (FTIR) spectroscopy, and their spectra were compared to observe differences in lignin and carbohydrate quality. Previously, we introduced rapid methods using FTIR to analyze lignin condensation in kraft pulp[15] and acid sulfite pulp.[16] However, the condensation reactions that occur at the end of kraft cooking or during acid sulfite pulping are apparently not the same as those occurring during mechanical defibration. In this research, the fiber samples were also characterized for their chemical constituents to monitor whether the Asplund process had any significant impact on lignin or carbohydrate contents. In addition, images of the fiber surfaces were obtained using a high-resolution scanning electron microscope (HR-SEM), which allowed the observation of some physical differences in the Asplund fiber samples.

EXPERIMENTAL

Materials

Norway spruce (*Picea abies*) chips were obtained from an Austrian pulp and paper mill. Before chipping, spruce logs had been debarked. The chips were then shipped to Sweden in intermediate bulk containers (IBCs) to avoid excessive drying of the chips. A sample taken from the original wood chip batch was analyzed for its lignin and extractives content (Table 1).

Preparation of Asplund fibers

The Asplund fiber samples were manufactured at a pilot plant (Valmet AB, Sundsvall, Sweden). All Valmet's applicable protocols were followed in detail to ensure that our work can be replicated when needed.

Table 1
Lignin and acetone extractive contents of the spruce wood chip sample

Component	Spruce wood chips
Acetone extractives (%)	3.0
Lignin, Klason (%)	27.7
Lignin, acid soluble (%)	0.5

Figure 1 shows the schematic diagram of the refining process. First, the spruce chips were subjected to water soaking treatment at room temperature one night before the refining took place. The purpose of the soaking was to secure sufficient moisture content during the refining process to avoid "burning" of the chips, as well as to ensure a satisfactory fiber quality. Previous practical experience with the refiner has shown that steaming does not provide sufficient moisture if the chips have dried during transportation. The feed rate was around 60 kg/h. No chemicals were added to the chips before refining. The refining was carried out with a very low specific energy consumption (SEC), which was 80 kWh/ton. Based on previous experience, the authors assumed that even a very low specific energy input could produce fibers with sufficiently good separation, and the main objective with the Asplund process is to produce wood material with a large surface area. The refining temperature and steam pressure were varied to investigate how these conditions affect lignin quality in fibers. The heating to the desired temperature was achieved by steam, which also ensured sufficiently high pressure during the refining. It is important to note that temperature and steam pressure could not be varied as independent variables: the higher the desired temperature, the higher the required steam pressure. All Asplund fiber samples in this study were manufactured by preheating to a temperature well above the softening temperature. The fibers were not dried in the dryer. Table 2 summarizes the conditions during the Asplund fiber production. The dry matter content of the obtained Asplund fibers was determined according to the method ISO 638. The dry matter contents of the fiber samples varied from 39.5% to 47.5%, depending on the refining temperature (see Table 2).

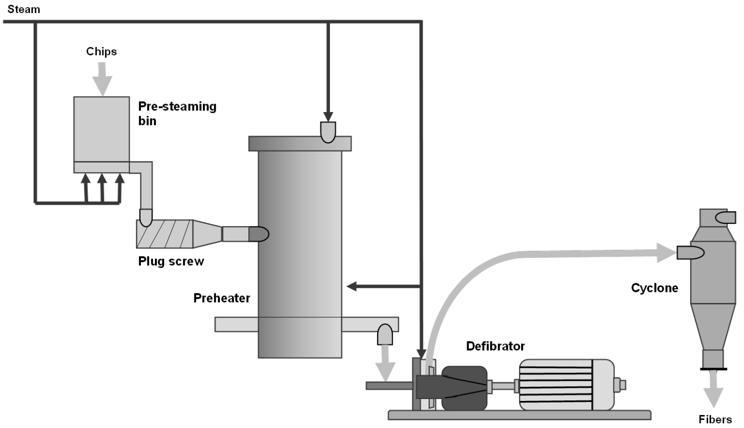

Figure 1: Schematic diagram of the refining process used in this research

Table 2
Asplund fiber test matrix in this research

Parameter/Sample code	111	211	311	411**
Temperature (°C)	170	180	190	200
Pressure (MPa)	0.69	0.97	1.18	1.45
SEC (kWh/BDt)	80	80	80	80
Dry matter content in pulp, (%)*	47.5	43.6	42.1	39.5

*Dry matter content values are expressed as a percentage mass fraction present in the fiber sample after the refining; **Asplund fiber samples are denoted with codes 111-411

Characterization methods

The analyses of the Asplund fiber samples were based on well-established methods in wood chemistry. MoRe Research (Örnsköldsvik, Sweden) analyzed Asplund fiber samples for their carbohydrates, lignin, and extractives. In addition, the original wood chip sample was analyzed for its lignin and extractives content (Table 1). Carbohydrates were analyzed according to SCAN-CM 71:09 and calculated as anhydrous sugars. The lignin contents of the samples were determined according to Tappi methods T222 (Klason lignin) and T-UM 250 (acid soluble lignin). Wood extractives were analyzed according to ISO 14453, which describes the determination of acetone-soluble matter, *i.e.*, acetone extractives.

FTIR analysis

An IRAffinity-1 Fourier spectrometer (Shimadzu) was used to register the IR absorption spectra of the samples in the mid IR spectral range, with the resolution of 2 cm^{-1} and the number of scans at 32. To record the spectra, 13 mm diameter disks were prepared by pressing a mixture of fibers with KBr powder. The experimental spectra were normalized on an integral of the absorbance band of stretching vibrations of CH bonds in the range of 2750-3010 cm^{-1}. The value of the integral was equal to 100 cm^{-1}.

The IR spectra were used to determine the characteristics of cellulose structure, lignin content, acetyl groups of hemicelluloses and the amount of water in fibers. Water is an important constituent in cell walls, known as bound water.[17,18] The data obtained were as follows: the intensities of the lignin bands at 1510, 1600 and 810 cm^{-1}; the intensity of the broad band of stretching vibration of hydroxyl groups at 3400 cm^{-1}; the intensity of the band of deformation vibration of water molecules in fibers at 1650 cm^{-1}; the intensity of the band of stretching vibration of C=O bonds of acetyl groups of xylans at 1740 cm^{-1}; the structure cellulose was described by parameter CIord., which evaluates the relative content of ordered ranges, formed by cellulose macromolecules of conformation CI.[15,16,19]

X-ray diffraction analysis

X-ray diffraction (XRD) was performed at room temperature using a Bruker D2 Phaser diffractometer, with Cu Kα radiation (wavelength 1.54 Å) at 30 kV and 10 mA in θ–2θ geometry. The increment was fixed at 0.05°. The samples were dried in an oven at 40 °C for 24 h. Thereafter, 50 mg of dried fibers from each sample were pressed to make identical coin-shaped specimens with a thickness of approximately 1.5 mm and a diameter of 2 cm. The specimens were placed on a silicon single crystal specially cut to provide a low background free from any interfering diffraction peaks. The XRD results on the replicate samples were almost identical, with <10% variation. The intensity values were only subtracted from the blank run intensity of the sample holder and presented.

SEM imaging

Samples of fibers were placed on a carbon conductive surface and left to air-dry. Thereafter, the samples were coated with an approximately 10 nm thick layer of iridium using a Q150 T ES sputter coater (Quorum Technologies Ltd., Laughton, UK) to obtain an electrically conductive surface. Digital images of the sample surface were acquired using a high-resolution scanning electron microscope (HR-SEM), Tescan MAIA3 model 2016. Secondary electron images (SEI) were generated using 5 kV accelerating voltage and a beam intensity index of 3.

RESULTS AND DISCUSSION

Chemical composition of wood

The Asplund fiber samples were characterized for their chemical constituents to study whether the refining conditions had any effect on the chemical constituent profile of wood. The analysis results are summarized in Table 3.

The refining temperature appeared to have a significant effect on acetone extractives content. The samples that were produced under two lowest refining temperatures, 170 °C and 180 °C, had similar acetone extractives contents, of 1.63% and 1.55%, respectively. The two samples produced with higher temperatures of 190 °C and 200 °C had seemingly elevated acetone extractive contents, of 1.85% and 2.35%, respectively. It seems that the removal of extractives was hampered, as the refining temperature and pressure increased. Kemppainen *et al.* have suggested[20] that under harsh steam pretreatment spruce extractives undergo condensation reactions, which turn water-soluble compounds into the water-insoluble fraction. Nevertheless, all four fiber samples exhibited acetone extractive contents lower than that of the wood chips. However, further research is necessary to validate these findings and gain a better understanding of interaction of different extractive compounds and lignin.

The total lignin content (Klason + acid-soluble lignin) showed little variation within our test series. All four samples had lignin contents between 28.7% and 29.1% of dry weight, which can be considered an insignificant variation and falls within the error of the measurement. Moreover, these values were in the vicinity of lignin contents of Norway spruce reported elsewhere.[21,22]

The contents of most carbohydrates, however, showed a consistent minor decrease with increased temperature. According to Alén *et al.*,[23] hemicelluloses generally show lower thermal stability than cellulose, which can be explained by the absence of crystallinity in hemicelluloses. Nuopponen *et al.*[24] observed an increased Klason lignin content in Scots pine (*Pinus sylvestris*) wood after a thermal treatment, which they explained to be due to the degradation of hemicelluloses.

Table 3
Chemical constituents of wood in Asplund fiber samples

Component/Sample	111	211	311	411
Glucose (g/kg)	434	404	386	400
Arabinose (g/kg)	9.4	8.7	8.5	8.2
Galactose (g/kg)	18.2	17.2	16.8	16.7
Xylose (g/kg)	51.2	48.1	46.0	47.1
Mannose (g/kg)	114	105	101	104
Acetone extractives (%)	1.63	1.55	1.85	2.35
Lignin, Klason (%)	28.3	28.7	28.6	28.3
Lignin, acid soluble (%)	0.4	0.4	0.4	0.5

FTIR and X-ray diffraction analyses

FTIR spectra of the four Asplund fiber samples were used to characterize the quantity and state of carbohydrates and lignin, as well as the water content in fibers. Due to the relatively mild mechanical treatment, the samples had chemical compositions resembling native wood. The IR spectra of these samples are sums of vibration spectra of all presented wood polymer components: cellulose, hemicelluloses, and lignin. Even a small amount of any component can give an input to IR spectra. Table 4 summarizes the values of the intensities of some selected absorbance bands. The intensities are presented in relative units: all data are normalized to an integral of the absorbance band of stretching vibrations of CH bonds in the range of 2750-3010 cm^{-1}. For additional illustration, the IR spectra of the fiber samples are shown in Figure 2.

Table 4
FTIR spectral data of the samples*

Band (cm^{-1})	Groups	111	211	311	411
I_1650	Water	7.6	8.0	6.3	4.8
I_3400	Water + pulp OH$^-$ groups	465	466	451	430
I_1740	Acetyl groups of hemicelluloses	11.3	13.7	13.5	12.6
I_1600	Lignin: conjugation of C=O and C=C	1.7	1.9	2.2	2.2
I_1510	Lignin	9.0	9.9	9.7	9.9
I_810	Lignin	1.50	1.75	1.80	1.85

*Relative to an integral of the absorbance band of stretching vibrations of CH bonds in the range of 2750-3010 cm^{-1}; the value of the integral was equal to 100 cm^{-1}

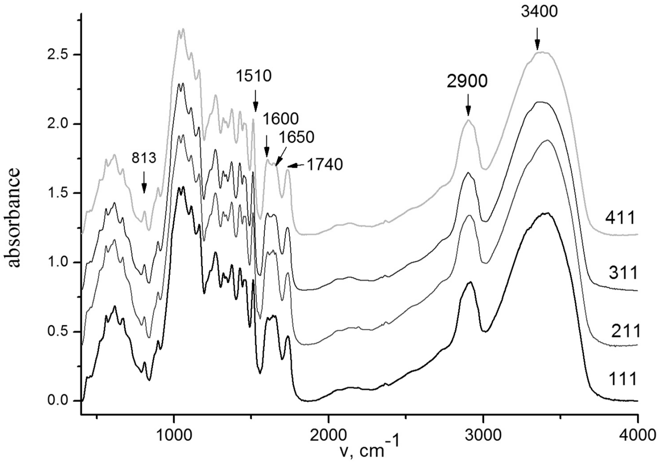

Figure 2: FTIR spectra of Asplund fiber samples: Sample 111 (170 °C), Sample 211 (180 °C), Sample 311 (190 °C) and Sample 411 (200 °C)

Table 5
FTIR spectral data of the samples – relative content of ordered regions in cellulose (CIord)

Cellulose structure parameter	111	211	311	411
CIord, %	28.0	29.2	34.6	34.0

Carbohydrates

Generally, the molecular spectroscopy method allows representing the physical structure of cellulose as a superposition of CI and CII celluloses with their ordered and disordered regions. In our previous studies, we have presented the physical structure of cellulose in natural fibers by a superposition of three of these components – parameters CIord, CIdis and CIIdis.[15,19] In this research, however, the Asplund fiber samples contained approximately the entirety of native lignin, and therefore only the structural parameter of cellulose – the CIord parameter – was calculated from the FTIR spectra using the cellulose structure model.[19] The calculation of the ratio of the integrals of the bands at 715 and 2900 cm^{-1} was applied to evaluate the relative content of ordered cellulose of native conformation CI according to Equation (1):

$$\text{CIord (\%)} = I\_715/I\_2900 \times 15.6 \qquad (1)$$

Before these calculations the IR spectra were deconvoluted. Values of the relative content of ordered regions CIord are summarized in Table 5.

Table 5 shows that the CIord parameter of the cellulose structure increased by 6 percentage points (ppt) when the refining temperature increased from 170 to 200 °C. This is apparently due to the destruction of amorphous carbohydrates, and possible ordering of cellulose macromolecules under the presence of water molecules at high temperatures. The increase in the CIord parameter was nonlinear with temperature and this parameter only increased slightly in the range of 170 to 180 °C. The refining treatment at temperatures of 190 °C or higher resulted in the value of this parameter at or above 34%. According to previous observations,[25,26] an increase in the quantity of ordered cellulose regions leads to better thermal stability, while the accessibility, reactivity and sorption ability of the fiber surfaces will be lower. In addition, this change will most likely affect the strength properties of the fibers, as well as their products. However, the latter is not addressed further in this paper, as it falls outside the scope of this research.

From 170 to 180 °C, we observed an increase in absorption at 1740 cm^{-1}, but at temperatures of 190 and 200 °C, there is no further increase. According to Kotilainen *et al*,[27] this increase is associated to the overall mass loss and degradation of hemicelluloses, although they could not give any straightforward explanation to this phenomenon. High temperatures and vapor pressure contribute to the ordering of cellulose macromolecules and, consequently, an increase in the CIord parameter. This is a result of the plasticity of cellulose and may be regarded as substantiation of the potential of adjusting the cellulose profile by varying temperature.

To validate CIord values of the four Asplund fiber samples, the crystallinity index (*CI*) values were calculated using analysis data from X-ray diffraction (XRD). To compare CIord and *CI* values, we carried out *CI* calculations based on background-corrected Segal peak-height method,[28] using XRD patterns of the samples. Figure 3 shows the XRD diffractograms of the four Asplund fiber samples.

As shown in Figure 3, the diffractogram peaks for all the samples are identical to the ones found for the cellulose I allomorph. These peaks are located at the diffraction angles (2θ) around 15°, 17°, and 23°, corresponding to the crystallographic plane reflections (1−10), (110), and (200), respectively.

The CI values were calculated based on the (200) peak intensity (I_{200}) using the Segal peak height method according to Equation (2), where the amorphous intensity (I_{am}) at approximately 19° 2Θ was considered:[29]

$$CI(\%) = \frac{I_{(200)} - I_{am}}{I_{(200)}} \times 100 \qquad (2)$$

The calculated *CI* values of the Asplund samples are given in Table 6.

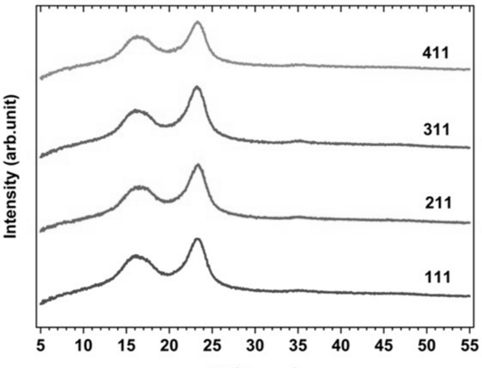

Figure 3: XRD patterns of Asplund fiber samples, with the corresponding Bragg peaks of the cellulose I allomorph[29]

Table 6
Calculated crystallinity index (CI) based on Equation (2) for all the samples

Cellulose structure parameter	111	211	311	411
CI (%)	65.1	66.3	69.8	65.8

The crystallinity of Samples 111 to 311 exhibited a slight increase, which is in good agreement with the results obtained from the FTIR analyses. No further increase in the crystallinity of

Sample 411 was observed. This can be interpreted that the cellulose crystallinity in the Asplund fibers increased due to the increasing temperature from 170 to 190 °C (as well as the simultaneous increase in steam pressure). Cellulose crystallization occurs under pressure and hot water vapor, and the cellulose macromolecules begin to order. However, no further increase in cellulose crystallinity was observed when the temperature increased to 200 °C.

Further, it is important to note that the CI calculation is a semi-quantitative approach, particularly when it comes to natural cellulose materials, such as Asplund fibers, which contain cellulose I allomorph. In fact, both FTIR and XRD are semi-quantitative methods. Asplund fibers contain large proportions of lignin and hemicelluloses, and these chemical constituents are not uniformly distributed on fiber surfaces, which can influence the results. This means that it is important to repeat measurements several times for each sample. We carried out three XRD measurements. Nevertheless, we managed to achieve a relatively good correlation between these two analysis methods. They revealed an increasing cellulose crystallinity (ordering) up to 190 °C. We also observed that the hemicellulose component contents did not decrease when the refining temperature increased from 190 to 200 °C (Table 3). In all, up to 190 °C, all three analysis methods, chemical analysis, XRD, and FTIR spectroscopy demonstrated chemical changes with increasing temperatures, and at about 200 °C, this action subsided.

Lignin

The band intensity at 1510 cm^{-1} corresponds to the lignin content in the pulp samples. Table 4 shows some increase in the absorption intensity of the lignin band at 1510 cm^{-1} at refining temperatures of 180 °C and higher. However, Klason lignin contents of all four samples were on the same level (Table 3). Moreover, two other absorbance bands of lignin at 1600 cm^{-1} and 810 cm^{-1} showed increasing intensity at temperatures from 170 to 200 °C. This was likely to be an indication of lignin condensation due to the increased occurrence of conjugated C=O and C=C groups.[15,24] Another explanation to the increasing intensity is the degradation of amorphous carbohydrates.

Bound water and OH-groups

The data presented in Table 4 also show that the content of bound water parameter I_1650 decreases with increasing temperature and pressure. Figure 4 presents a correlation between the bound water content and the content of substances analyzed as acetone extractives. It seems probable that the pores were occluded by extractives and lignin, which obstructed the exit channels for carbohydrates and decreased the hydrophilicity of the fibers. It is known that as water exits pores when the fibers are drying, the pores start to collapse, eventually resulting in pore closure by irreversible hydrogen bonding.[30,31] The latter is generally referred to as hornification. Borrega and Kärenlampi[32] observed substantial pore closure induced by irreversible hydrogen bonding in Norway spruce fibers at temperatures not exceeding 130 °C with extended drying time.

SEM imaging

The SEM technique was used to create images of the fiber surfaces.

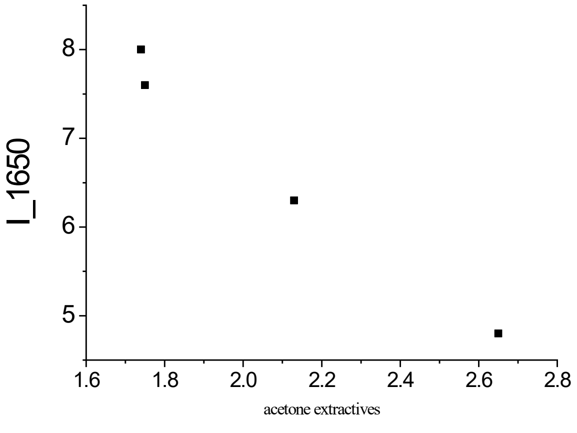

Figure 4: Content of bound water (intensity of band near 1650 cm^{-1}) and quantity of acetone extractives (%)

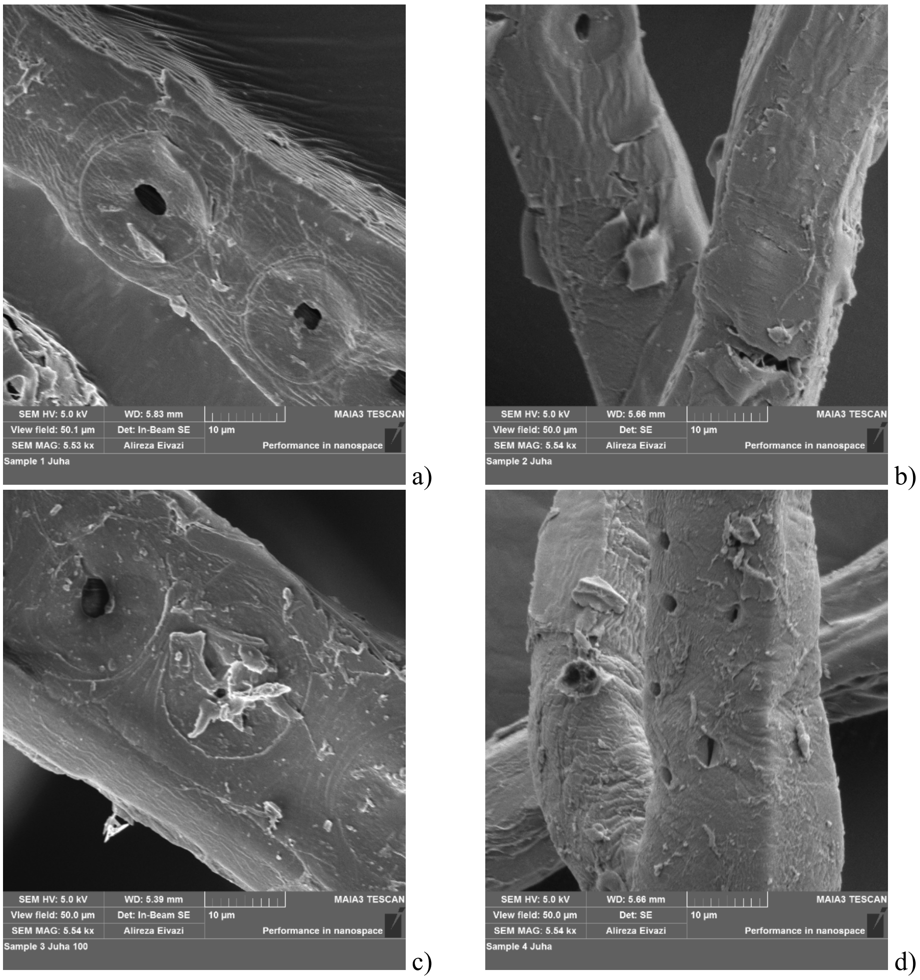

Figure 5: SEM images of Asplund fiber samples refined at: a) 170 °C, b) 180 °C, c) 190 °C and d) 200 °C

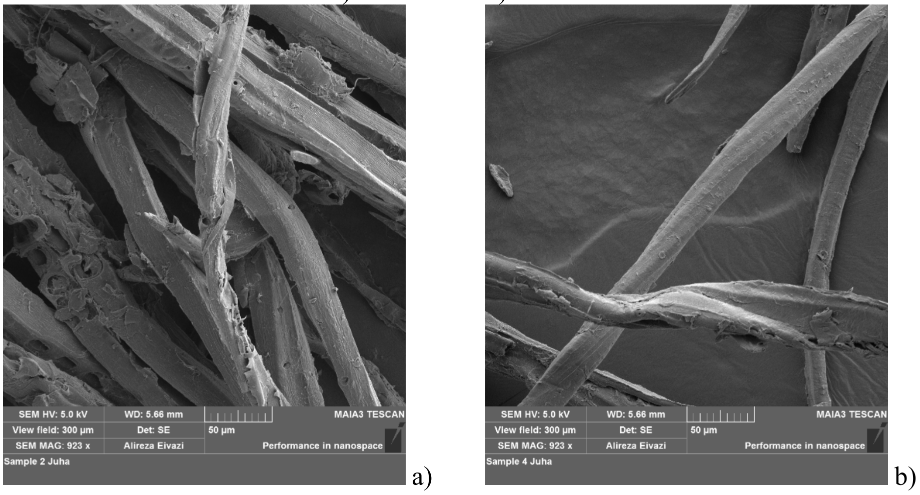

Figure 6: SEM images of Asplund fiber separated at (a) low (Sample 211 refined at 180 °C), and (b) high refining energy (Sample 411 refined at 200 °C)

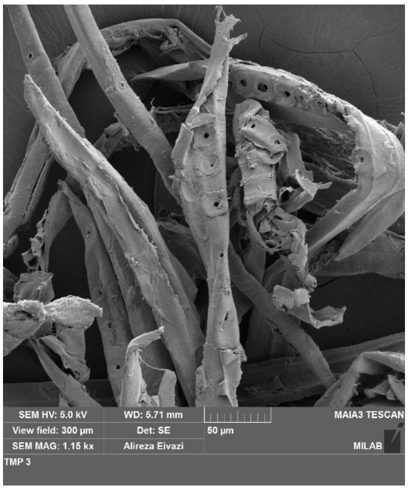

Figure 7: SEM image of industrial thermomechanical pulp (TMP) fibers of Norway spruce

The view field of 50.0 µm was used in comparison of individual fibers refined at different temperatures (Figs. 5 and 6). For comparison, the SEM image of an industrial TMP sample of Norway spruce was also included in this study (Fig. 7).

Characteristic details of spruce tracheid cells, such as pits, are easily visible in the SEM images. One apparent difference between individual fibers refined at different temperatures was their color; fibers refined at higher temperatures appear to be darker than those produced with lower temperatures. Another phenomenon that can be observed is the closure of the bordered pits at 200 °C (Fig. 5). SEM images also suggest improved fiber separation at temperatures of 190 °C and 200 °C, when compared to lower temperatures of 170 and 180 °C (Fig. 6). When Asplund fibers are compared to industrial thermomechanical pulp (TMP) fibers, it can be observed that TMP fibers are well separated, but also substantial fiber damage and more fiber curl can be observed, in comparison to the Asplund fibers. Increased fiber damage and substantial fiber curl in TMP pulp is due to the high amount of thermal stress occurring in the TMP process.[33,34] In any case, it can be observed that the Asplund process enabled a reasonably complete fiber separation at higher temperatures of 190 and 200 °C. The Asplund fiber separation was then comparable to the TMP process, but without noticeable fiber damage and fiber curl.

CONCLUSION

In this research, the FTIR spectra indicated some cellulose and lignin quality and structure changes on the surface of Asplund fibers, when the refining temperature increased to 190 °C. The contents of most carbohydrates exhibited a consistent minor decrease with increased temperature from 170 to 190 °C. However, for the most hemicelluloses, no further decrease with the temperature of 200 °C was observed. At the refining temperature of 190 °C, the value of the relative content of ordered regions in cellulose (CIord parameter of the cellulose structure) increased. The latter was confirmed by the analysis data from X-ray diffraction. The crystallinity index increased as the temperature increased to 190 °C, however, at 200 °C no further increase was observed. FTIR analyses also suggested increasing lignin condensation at elevated temperatures. In all, when increasing the temperature up to 190 °C, carbohydrate content analysis, XRD, and FTIR spectroscopy showed relatively consistent changes, and little or no further shift at 200 °C.

In contrast to the chemical properties, SEM images suggested improved fiber separation at higher temperatures of 190 and 200 °C, when compared to lower temperatures of 170 and 180 °C. These findings indicate that the optimal refining temperature of the Asplund process is most likely between 180 °C and 190 °C, when the goal is to produce lignocellulosic material for a biorefinery process. Fiber quality and allowing rapid reactions with the chemical constituents of wood are then important objectives. These findings are particularly useful for the development of the Asplund pretreatment concept on an industrial scale. However, further research is necessary to study the effect of altered lignin structure on reaction kinetics in biomass fractionation by green solvents, such as DESs and ILs.

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