

FRACTIONATION AND CHEMICAL ANALYSIS OF FINES

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ABSTRACT

Thermomechanical pulp (TMP) has been fractionated into different fines fractions using a Britt Dynamic Drainage Jar (BDDJ). The different fractions have been measured using laser diffraction to estimate the fractionating efficiency and reproducibility. The fines fractions have also been analysed using FTIR and electroforetic mobility.

INTRODUCTION

Thermomechanical pulp (TMP) can be divided into two major fractions, namely fibres and fines. The fibres are more or less whole woodcells, while the fines are fragments of the same cells and/or the middle lamella. These fragments are produced during the extensive mechanical treatment in the refining process, and are peeled off mainly from the outer parts of the fibre. The fines consist of band- and thread-like particles from the secondary wall, flake-like pieces from the middle lamella, ray cells, pores, and very small "microfines" which can't be separated from dissolved and colloidal substances by ultra-centrifugation (as summarized in 12). The amount and intensity of the refining has a deep impact on the amount of fines produced, which again has an effect on the quality of the paper. The most important effects that are contributed to fines are the light scattering ability of the pulp (8) and the tensile index of the paper (9). Different TMP-paper qualities will therefore, among other properties, have different amount of fines.

The fines fraction is normally defined as the fraction of the pulp which passes a 200 mesh (76 μm) screen. The separation can be done using either a Bauer McNett or a Britt Dynamic Drainage Jar (BDDJ). The two fractionating methods work in different ways, and will give different answers to both the size distribution and the properties of the fines (12). As a result of the relative large amount of water used in the Bauer McNett fractionation, the fines will to a larger extent become washed compared to the BDDJ fractionation. One consequence is that the amount of colloidal extractives attached to the fines will be reduced (12). Extractives attached to fines or fibres have an impact on the binding ability of the pulp, and may therefore reduce the strength of the paper (1).

There have been many investigations on the different mechanical properties of the fines, but there has been very little attention paid to chemical variations between different fractions of the fines. The aim of the present work is to separate fines in different fractions as a function of their size and/or shape prior to measuring the chemical composition. The chemical composition was measured as the lignin/carbohydrate using FT-IR. In addition the zetapotential as a function of pH was measured.

MATERIAL AND METHODS

Thermomechanical pulp was taken directly from the grinder in a Norwegian integrated pulp and paper mill. The dry content of the sample was measured to 23,5%, before it was split up in batches of 213 g and stored in a freezer (-18 $^{\circ}\text{C}$).

213 g of pulp was mixed with 5 litres of distilled water, and agitated at 150 rpm for three hours at 60 $^{\circ}\text{C}$ in a thermostated bath, the procedure developed by Thornton (14). The pulp suspension then had a consistency of 1%.

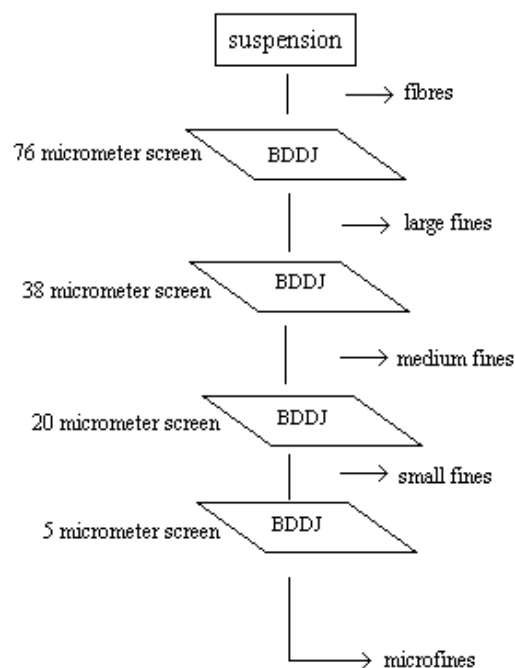


Figure 1: Procedure for fractionating fines by size and/or shape.

The fibres and fines in the suspension were fractionated using a Britt Dynamic Drainage Jar (BDDJ) with different screens. The pores in the different screens varied, the pore diameters used were 76 μm , 38 μm , 20 μm and 5 μm . One litre at a time of the pulp suspension was poured into the BDDJ. Each filtering operation defined two fractions; the fraction that passed and the fraction that did not. When 0.7-0.8 liters had passed each screen, the fractionation was

stopped, and the two fractions were collected. The procedure is schematically shown in Figure 1.

In order to wash remove any dissolved material (such as carbohydrates or dissolved lignin), the fractions were washed with pure water using an Amicon membrane (cut-off 100 kilodalton) equipped with a stirrer at constant speed rotating just above the membrane. There was an enhanced pressure (5 bar) across the membrane in order to speed up the filtering process. The fractions were washed 4 times by adding one litre of pure water, letting it agitate for 15 minutes at room temperature, and then removing the water. The filtrate (water) was collected and analysed for COD.

When the amount of COD in the filtrate had stabilized, the fines fraction was freeze dried for 48 hours in an Edwards Freeze Dryer Moduloyo (T= -48 °C and P =0,1-1 mbar). After freeze drying, the fractions were stored at T= -18 °C.

The particle size distributions of the fines were conducted using a Malvern Master-Sizer $\mu+$, which uses laser diffraction to measure the volume percent distribution of spherical particles in solution. The results from the measurements of the unspherical mechanical fines in solution were only used as a relative indication of the particle size distribution, as used by Rundlöf (12). Approximately 0.5 litres of distilled water was placed in the particle analyser and allowed to circulate. Each fines fraction was added to the circulating water until the resulting signal was strong enough, determined by the analyser.

For absorbance measurements of the fines in the infrared area a Perkin Elmer FTIR, model 1750 was applied. The freeze-dried fines were manually grounded, mixed with potassium bromide (KBr, stored at 105 °C) and pressed to tablets. The background absorbance was subtracted from the sample absorbance spectrum, prior to semi-quantitative determination of lignin and carbohydrates. The aromatic absorbance around 1510 cm^{-1} was used to quantify the relative amount of lignin (2, 11). To quantify the relative amount of carbohydrates, the C-O stretch at around 1060 cm^{-1} was used (4, 5, 6, 11).

A Malvern Zetasizer 2000 was used to measure the zeta-potential of the fines as a function of pH. The pH of the water-fines suspension was regulated by adding p.a. grade HCl or NaOH diluted with distilled water, and the pH was measured using a Radiometer Copenhagen PHM82 Standard pH meter. Prior to the pH regulations p.a. grade $\text{MgSO}_4(\text{s})$ was added to a concentration of 0.01 mole/L. The pH regulated water-fines suspension was injected into the Zetasizer where the electrophoretic mobility was measured and converted to the zeta-potential.

Extractions were carried out at both pH 9.0 and pH 3.5 using methyl *tert*-butyl ether (MTBE) in order to remove the colloids and lignans quantitatively (15, 16) from the water-fines suspension. The extractives were not weighed or analysed.

RESULTS

3.1 Fractionation and particle size distribution

The fractionation in the BDDJ and volume per cent distribution measurements was done several times. This was in order to make sure that there actually had been a fractionation, and that the particle distribution measurements were reproducible. The BDDJ was chosen instead of the Bauer McNett fractionation method since the latter easily changes the chemical and physical properties of the fines (12) as a result of the voluminous consumption of fresh water.

The relative standard deviation (RSD) of the modal size (the particle diameter which occupies the largest volume %) was 13.5 – 23.2% (table 1). This is considered to be quite high, but there is probably uncertainty associated with both the manual fractionation and the particle size distribution measurements.

Table 1: Statistics on the relative volume size distributions of the different fines fractions.

Fraction (*m)		<5	5-20	20-38	38-76
Replicate	1	5.87	15.45	21.33	28.42
	2	5.87	15.2	23.85	
	3	7.10	11.85	21.42	27.78
	4	6.08	15.6	23.79	31.71
	5	2.93	17.62	28.23	38.05
	6	6.68	18.14	31.96	44.41
	7	6.06	17.49	24.54	37.18
	average	5.80	15.91	25.02	34.59
	SD	1.35	2.15	3.83	6.45
	RSD	23.20	13.50	15.32	18.64

The data in Table 1 should be treated with care since the instrument assumes that the particles are spherical. This assumption is not valid when measuring mechanical fines. In this work, like in others (12), the size distribution curves were considered useful to measure a change in the particle distributions and the reproducibility of the fractionation.

Figure 2 gives an example from the size distribution measurements. It clearly shows how the modal sizes are reduced with the pores in the screens in the BDDJ. In the fraction with the smallest particles (<5 μm), the bimodal shape of the size distribution is interpreted to be a mix of small fines ("microfines") and colloides. This is in agreement with earlier work by Nylund (10). In his work the dissolved and colloidal material was separated from

the fibre by centrifugation (750 G in 30 min), and the size distribution was measured using dynamic light scattering. Nylund found the bimodal shape of the size distribution curve consisted both of colloidal extractives and colloidal fibre fragment ("microfines"). Since the colloidal extractives are spherical the measured size should be very close to the correct size. The sizes of the colloids in TMP white water have previously been measured to be in the range 0.1–2 μm (as referred in 13) which correlates well with the measurements in this work (Figure 2).

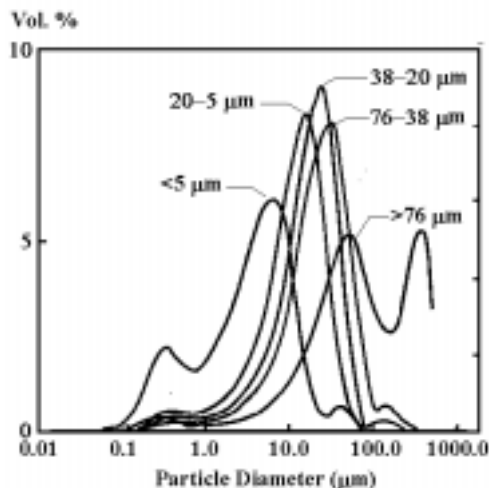


Figure 2: Relative volume distribution of the different fines fractions

3.2 Measuring the lignin/carbohydrate ratio using FTIR

Measuring the lignin/carbohydrate ratio using FTIR was done both before and after washing the fines with distilled water. After each washing, COD was measured in the water in order to quantify the amount of water-soluble material that was released into the washing water. After 2-3 washings the release of water-soluble material from the different fines fractions was stabilized (Figure 3).

The absorbance measurements of the different fines fractions before and after the washing procedure are given in Figures 4 and 5. The lignin/carbohydrate ratio given in both figures is measured as the absorbance in the infrared area at two different wavelengths (lignin 1510 cm^{-1} and carbohydrate 1060 cm^{-1}).

Since the measurements are done on freeze-dried fines before washing (Figure 4), there is no distinction between dissolved and particulate material. The trend may therefore be an effect of the amount of dissolved material. As a consequence the material was washed and the absorbance was measured again (Figure 5).

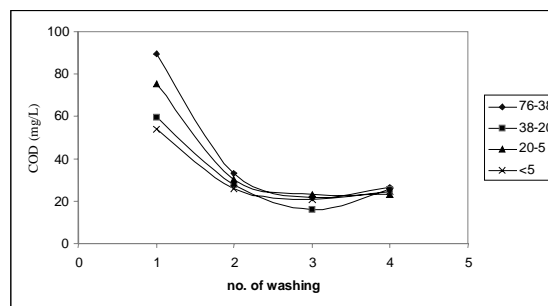


Figure 3: Development of COD in the washing water as a function of the number of washings. After 2-3 washings the release of water-soluble material from the fines was stabilized. Each measurement was done twice, and the pooled standard deviation of the COD measurements is 4.2.

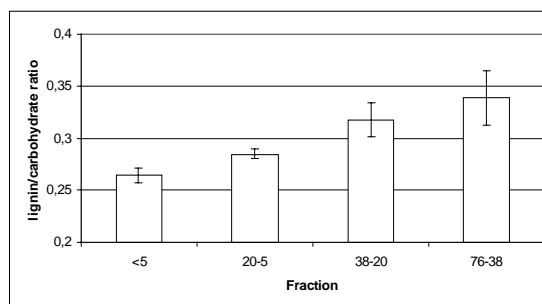


Figure 4: As the fines fractions become smaller the lignin/carbohydrate ratio is reduced. The error bars show the standard deviations ($N=3$, $RSD=1.7 - 7.7\%$).

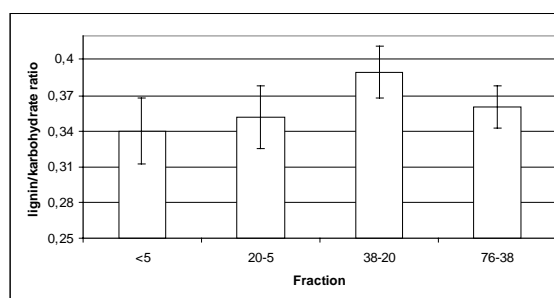


Figure 5: Measurements after washing the different fractions with distilled water. As the fines fractions become smaller the results indicate that the lignin/carbohydrate ratio is reduced. The error bars show the standard deviations ($N=4$, $RSD=4.9 - 8.1\%$).

The results shown in Figure 5 are more ambiguous than the one shown in Figure 4, but nevertheless both figures indicate the same trend. As the fines particles are reduced in size the lignin/carbohydrate ratio is reduced. This means that smaller fines particles have a higher relative amount of carbohydrates and a lower relative amount of lignin, than the larger ones.

3.3 Zeta-potential as a function of pH

The zeta-potential is determined by measuring the electrophoretic mobility:

$$\zeta = \eta U_e / \varepsilon$$

where ζ is the zeta-potential, ε is the permittivity, η is the viscosity and U_e the electroforetic mobility. The electroforetic mobility is dependent on the surface charge density.

The charges on the fines particles come from the hemicellulose. Uronic acids, containing carboxylic groups (-COOH) are parts of the hemicellulose (3). Native lignin contains little or no carboxylic groups, this is also the case for cellulose (a linear-polymer, glucan). If the pH in the fines water suspension is higher than the pK_a of the uronic acids, the acid will be ionized and thus create charges on to the fines. These charges will make the zeta potential more negative. If substances containing carboxylic groups are adsorbed on the surface of the fines they will be responsible for part of the net surface charge density, and therefore also for the zeta-potential.

In Figure 6 the zeta-potential measurements are shown for different fines fractions where the colloidal material is not removed. Between pH 3 and 4, the zeta-potential is reduced from slightly over -2 to between -3 and -4. This is interpreted as a result of that the ionization of the carboxylic acid groups creates a lower zeta-potential. The pK_a of one uronic acid (glucuronic acid) is reported to be 3.28 (as referred in 7) and is thus in agreement with the results in Figure 6.

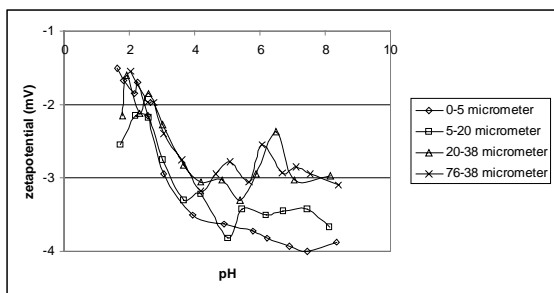


Figure 6: The zeta-potential of different fines fractions as a function of pH. The fines fractions are not extracted with methyl tert-butyl ether in order to remove colloidal substances.

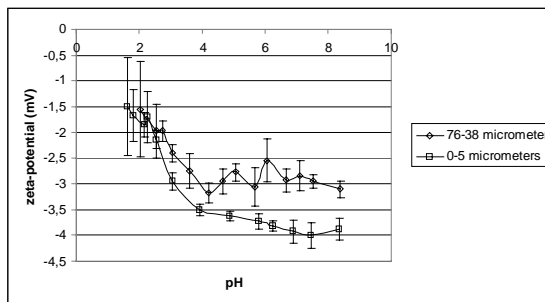


Figure 7: The figure shows the standard deviation of each point (N=4) of the largest and the smallest fines particles.

The absolute values of the zeta-potentials are low. This can be because the fines particles are not ideal, in the sense that they have no sharp surface. The theory behind the zeta potential describes how the absolute value of the potential drops from a sharp surface and goes towards zero in the surrounding liquid. The further out from the particle, the lower the absolute value of the potential. If it is more correct to view the fines as gel particles with a large relative volume of immobilized water, the immobilized water phase may force the shear plane out into the surrounding water solution. This may reduce the absolute value of the zeta-potential measurements.

CONCLUSION

It is possible to fractionate the fines using a BDDJ. When measuring the particle size distributions of the different fractions using light diffraction the results are reproducible (RSD = 13.5-23.2 %).

The dissolved material can be removed from different fines fractions by washing with distilled water and membrane filtration. 2-3 washings were needed.

FT-IR analysis of the fines fractions indicated that the relative amount of carbohydrate to lignin increases with reduced size.

The zeta-potential drops when the pH increases. This is interpreted as a result of an ionization process of the carboxylic acids in the hemicellulose.

The low values of the zeta-potential are interpreted as a result of the fines not being a particle, but more a water solvated gel with no sharp particle/water boundary. The zeta-potential is therefore measured relatively far out in the water solution.

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