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Fractionation of CMC-modified hardwood pulp

MINNA BLOMSTEDT* AND TAPANI VUORINEN**

SUMMARY

ECF-bleached hardwood pulp was treated with carboxymethyl cellulose (CMC) under specified conditions. The CMC-modified pulps were then fractionated in a hydrocyclone and DDJ (Dynamic Drainage Jar) apparatus and the different fibre dimensional properties of the reject and accept fibre fractions were determined with three commercial analysers. The reject fibre fractions in general had greater fibre length, width and coarseness than the accept fibre fractions. In addition, the cell wall thickness and curl value of the accept fractions were lower than those of the corresponding reject fractions. The internal strength of handsheets made from the reject fractions was about twice the strength of sheets made from the accept fractions, although the CMC contents of the accept fibre fractions were higher. One explanation for the differences in strength properties between the fractions could be that the reject fibres, in spite of their greater coarseness, are more flexible due to their higher fibre width to cell wall thickness ratio. Another important observation was that sodium and calcium salts should be added to pulp prior to the sorption of CMC to obtain the strongest possible handsheets.

Keywords
Hardwood pulp, carboxymethyl cellulose (CMC), fractionation, hydrocyclone, dynamic drainage jar (DDJ), sheet and fibre properties

Previous studies conducted in the Laboratory of Forest Products Chemistry have shown that carboxymethyl cellulose (CMC) can be attached to the external surfaces of cellulose fibres (*1-3*). CMC is an ideal polymer for tailoring the structure and properties of fibres, because its degree of substitution (DS) and degree of polymerisation (DP) are easy to control. When the aim is to modify fibre surfaces, the CMC to be used should have a sufficiently high DP to prevent penetration into the cell wall. Permanent sorption of CMC on cellulose fibres is possible only if the DS of CMC is low enough (< 0.5). The amount of CMC sorbed on pulps was found to be dependent on several factors, including DP, DS and charge of CMC, pH and ionic strength of the medium and beating level of the pulp. Addition of CMC on the pulp was also found to improve the bonding properties (bonding ability, tensile strength) of the handsheets made. Similar investigations have been conducted by Laine et al. (*4,5*).

Wood fibres vary considerably in terms of their morphology. The fibre morphology largely determines the final paper properties. Softwood fibres are in general classified into thin-walled earlywood and thick-walled latewood fibres. Paper properties can be controlled by adjusting the ratio between earlywood and latewood fibres in the pulp. This type of separation can be made by fractionation. The hydrocyclone is the best equipment available for fractionation (*6-13*). Surprisingly little is know about the separation mechanism of the hydrocyclone.

Paavilainen (*7*) compared the separation efficiencies of a hydrocyclone, a Johnston fractionator and a Jacquelin apparatus in fractionating sulphate pulps. The hydrocyclone gave the highest separation efficiency, concentrating the thick-walled summerwood fibres in the reject fraction and the thin-walled springwood fibres in the accept fraction (*7,9*). Other studies have shown that fibre length, fibre width, specific fibre surface, fibre wall thickness and coarseness significantly distinguish the accept from the reject fibre fractions. Thin-walled accept fibres in general also have lower coarseness than reject fibre fractions (*10*). According to earlier studies with softwood pulp and mechanical pulp, pulps with a higher proportion of earlywood (accept) fibres give a higher tensile index and density (*7,8,14,15*).

The fractionation of hardwood pulp fibres is exceptionally demanding due to the relatively small variation in their dimensions. Only a few attempts have been made to fractionate hardwood pulps with a hydrocyclone. Li et al. (*6,16*) have shown that the apparent density is a major factor controlling the separation of eucalyptus pulp fibres in a hydrocyclone. More information is needed to gain a better understanding of the separation mechanism of the hydrocyclone, especially when fractionating hardwood pulps.

The present study was designed to examine the combined actions of CMC modification and hydrocyclone fractionation of hardwood kraft pulps on their papermaking properties. The differences between the reject and accept fractions were studied by measuring the fibre properties with STFI FiberMaster, Kajaani FS-200 and KajaaniFiberLab analysers (*12,17*). The STFI FiberMaster is programmed to measure the fibre length, fibre width and fibre shape factor of about ten thousand fibres in a sample (*18,19*), whereas the Kajaani FS-200 characterises the coarseness and length of the fibres. A drawback of the latter analyser is that the coarseness number is an average for the whole pulp sample. The KajaaniFiberLab analyser also gives information on the cell wall thickness, fibre length, width and coarseness and curl value of the fractions (*20*). The responses of the CMC treatment and hydrocyclone separation mechanism were then evaluated by determining the properties of the handsheets.

MATERIALS AND METHODS

Pulp

The pulp used in the experiments was an industrial ECF-bleached birch (*Betula pendula*) kraft pulp from a mill in Finland. The pH of the undried pulp was adjusted to 7 with NaOH. Distilled water was used to wash excess Na^+ salts away from the pulp.

The pulp was refined 30 kWh/t with a Voith-Sulzer mill. The pulp was beaten with the 2/3-1.4-40D blade. The beating consistency was 4 % and the SEL (specific edge load) 0.5 Ws/m.

Carboxymethyl cellulose

A commercial CMC sample, Nymcel ZSB-16 (DS 0.32, DP_V 700), was obtained from Noviant. The degree of substitution (DS) of the Nymcel ZSB-16 grade was increased with the following treatment (3): CMC (200 g) was mixed

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Table 1
Hydrocyclone-fractionated unbeaten ECF-bleached hardwood pulp samples.

CMC dosage (% on pulp)	Na^+ addition (g/L)	Ca^{2+} addition (g/L)
-	0	0
-	0.2	0.5
0.5	0	0
0.5	0.2	0.5

with 2-propanol (5200 mL) in a beaker. After 15 minutes, 40 % sodium hydroxide (450 mL) was added. After mixing for 30 minutes, chloroacetic acid (65.3 g) was added over another 15 minute period. The beaker was covered and kept at 55ºC for 4h. After four hours the mixture was filtered in a Büchner funnel (Whatman No1) and 70 % methanol (700 mL) was added to the filter cake, mixed and filtered. After cooling the filter cake 90 % acetic acid (about 100 mL) was added. The mixture was filtered and washed with 70% methanol (700 mL) and 90 % methanol (8000 mL). The CMC sample was subsequently dried at room temperature.

A portion of the modified CMC (3 g) was mixed with 65 % nitric acid in methanol (73 mL). After 3 h of mixing the mixture was filtered and washed with 70 % methanol (~700 mL). The sample was dried at room temperature. A sample of the CMC (500 mg) was weighed in a beaker and mixed with 70 % methanol (4 mL). After a few minutes, deionised water (50 mL) and 0.5 M sodium hydroxide (12.5 mL) were added. This mixture was mixed for two hours. The residual hydroxide was titrated with 0.1 M hydrochloric acid using a phenolphthalein indicator. The consumption of sodium hydroxide corresponded to a DS of 0.51 of the CMC sample.

Sorption of CMC on pulps

The unbeaten pulp was mixed with water and a stock CMC solution (5.4 g/L) to obtain a final pulp consistency of 5 % (50 g/L), an initial concentration of CMC of 0.5 % (0.3 g/L) on pulp and a pH of 7 (*3*). The temperature was raised in 10 minutes to 60ºC. After 60 minutes, the pulp suspension was cooled, filtered and washed with deionised water. Sorption experiments were also carried out with addition of sodium and calcium ions (0.2 g/L Na^+ and 0.5 g/L Ca^{2+}), both added as chlorides.

Samples of the free liquid were withdrawn (50 mL) after sorption, filtered with 0.02 µm membranes and then analysed for dissolved carbohydrates by the phenol-sulphuric acid test and acid methanolysis combined with gas chromatography (GC) (*21,22*). The reference pulps were treated under similar conditions but without CMC. Thus, the results of the phenol-sulphuric acid test were corrected for polysaccharides other than CMC.

Hydrocyclone fractionation

The unbeaten ECF-bleached hardwood pulp was modified with CMC as described in Table 1 and then fractionated with an Alfa Laval hydrocyclone 10 mm in diameter (*6-13*). The added amount of pulp was approximately 145 g and the consistency 0.3 %. The experiments were performed under the following conditions: underflow pressure 1 bar, inlet pressure 5 to 6 bar and feed flow 240 L/h. After fractionation, the reject fractions were filtered in a Büchner funnel, using a 200 mesh wire. The accept fractions were sedimented for a few days to remove as much water as possible.

Fibre properties

After fractionation, the reject and accept fibre fractions were measured using three different commercial analysers: the STFI FiberMaster, Kajaani FS-200 and KajaaniFiberLab (*17,19,20*). The Kajaani FS-200 and KajaaniFiberLab analyses were carried out at Helsinki University of Technology in Finland according to TAPPI T271. The STFI FiberMaster analysis was carried out in M-real Corporation's Technology Centre at Örnsköldsvik, Sweden. Samples were prepared according to the equipment manufacturers' recommendations (KCL standard 225:89). The stock consistency used to calculate the coarseness values was determined by the standard method SCAN-C 17:64. More detailed information about the analysers can be found in the publication by Turunen et al. (*17*).

Some corrections are needed before the values determined by the analysers can be compared with each other. If the fractionated pulp sample contains a large amount of fines, the coarseness measurements are disturbed by a notable effect on the weight of the sample but not on the fibre length. Because the fibre analysers cannot detect such small particles, the coarseness values tend to be overestimated. According to Ämmälä (*23*), this error can be corrected by measuring the proportion of Bauer-McNett or Dynamic Drainage Jar P200 fractions in the pulp sample. The corrected coarseness values were calculated with the following Equation 1.

$$\text{Corrected coarseness} = (1 - W_{fines}) * \text{Measured coarseness} \quad [1]$$

where W_{fines} is the weight proportion of fines

The STFI FiberMaster shape value was converted into a curl value by using the following Equation 2 (*18*). The shape factor is defined as the diameter of the smallest circle that can contain the fibre divided by the true fibre length. In other words the higher the shape value is, the straighter the fibre is.

$$\text{Calculated 'curl value'} = ((100\ \% * (\text{Shape value})^{-1}) - 1) * 100\ \% \quad [2]$$

Sorption of CMC on reference pulp fractions

The untreated pulp fractions were further modified with CMC as described above (*3*). The additions of electrolytes were in this case 0.2 g/L sodium (Na^+) and 0.1 g/L calcium (Ca^{2+}), both added as chlorides.

A sample of the solution (50 mL) was withdrawn after sorption, filtered through a 0.2 µm membrane and then analysed for dissolved carbohydrates with a phenol-sulphuric acid test and GC after cleavage into monomeric units by acid methanolysis (*21,22*). The references were prepared under similar conditions but without CMC.

DDJ fractionation

The fines contents of the accept and reject were determined by using a Dynamic Drainage Jar-apparatus (DDJ) equipped with a 200-mesh wire (hole size 73 µm). 500 mL of the pulp suspension (0.5 % concentration) was transferred into the DDJ. Agitation (800 r/min) was started and duplicates (2 times 100 mL) of the fine filtrates were taken from the centre of the wire. The fines contents were then determined by filtration on filter paper, drying (105ºC) and weighing. The fractionation procedure is illustrated in Figure 1.

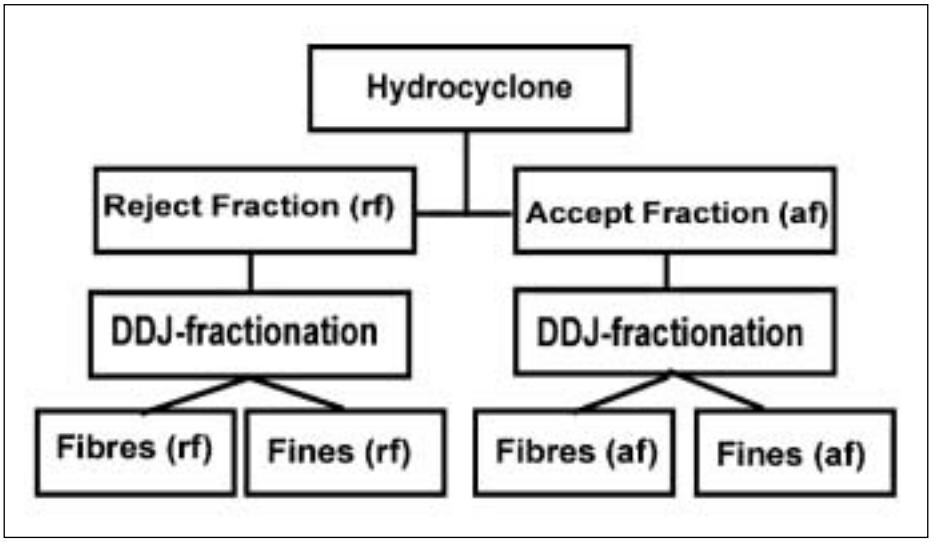

Fig. 1 Scheme of birch pulp fractionation procedure.

Papermaking properties

Laboratory handsheets were made by standard method SCAN- P 26:76, with the exception of wet pressing at 490 kPa and drying in a drum dryer at 60ºC for 2 h. The sheets were prepared from the unfractionated pulps, the reject and accept fractions of CMC-modified hardwood pulp and from the corresponding reference pulp fractions in deionised water (water < 10ºC).

The density of the handsheets was determined by standard method SCAN 7:75. The light scattering coefficient was measured with an Elrepho reflectometer by standard method SCAN- P 8:93. The bonding ability (internal strength) was measured according to TAPPI UM 403.

Determination of metal ions

Metal ions were determined for the reference pulp handsheets (*24,25*). The samples (about 500 mg dry weight) were mixed with 15 mL nitric acid (HNO_3) in a dissolving vessel made of Teflon. The vessel was closed and then kept for 1 h at 200ºC in a microwave oven (CEM, Mars-5). After cooling, the sample was diluted with water (Milli-Q, 100 mL). The metal analyses were then made by atomic absorption spectrometry (AAS). Na, K, Ca, Mg were determined with a Varian 600 spectrometer.

RESULTS AND DISCUSSION

Sorption of CMC on pulp

The degree of sorption of CMC on the pulp fractions was first evaluated by estimating the content of residual CMC in the sorption liquor with the phenol-sulphuric acid test. The reliability of the results was, however, weakened by interference from soluble xylan, whose content varied depending on the conditions during sorption. For this reason, the results were also confirmed by acid methanolysis combined with GC. Because the latter technique was based on quantification of carboxymethylated glucose units, the results obtained were considered more reliable. Thus, the degree of sorption of CMC varied between 80 and 100 %, depending on the treatment conditions.

Fractionation

The tests with handsheets made from CMC-treated pulps clearly showed that hardwood pulps do not behave in the same way as softwood pulps do (*3*). Generally, the strength properties of hardwood pulps were less affected by addition of CMC than those of softwood pulps. Therefore, the question was raised whether the differences in responses of the pulps were caused by the fines content or some other variable in the fibre morphology. Theoretically, because the fines contents of hardwood pulps are higher, less CMC could be located on hardwood pulp fibres. To cast light on these questions, fractionation experiments were carried out with hardwood pulps to separate long fibres from fines.

Fibre properties

The unbeaten hardwood pulps were fractionated with a yield of 23 to 33 % for the reject fibre fractions and 68 to 77 % for the accept fibre fractions (Table 2). The fibre lengths of the fractionated fibres were measured with Kajaani FS-200, STFI FiberMaster and KajaaniFiberLab analysers (*17*). Generally, the FiberMaster gave greater length-weighted fibre lengths than the Kajaani FS-200 and

Table 2
Yield, cell wall thickness, length-weighted fibre length, fibre width, fibre curl value and fibre coarseness of hydrocyclone-fractionated hardwood pulp (REF = no CMC added, CMC = 0.5% CMC added, electrolyte = 0.2 g/L Na^+ and 0.5 g/L Ca^{2+} added).

	REF Reject	REF Accept	REF electrolyte Reject	REF electrolyte Accept	CMC Reject	CMC Accept	CMC electrolyte Reject	CMC electrolyte Accept
Yield (%)	22.9	77.1	24.4	75.6	30.4	69.6	32.5	67.5
Kajaani FiberLab								
Cell wall thickness (µm)	5.1	4.7	5.1	4.5	4.9	4.6	5.0	4.4
Fibre length (mm)	1.09	0.91	1.08	0.91	1.11	0.89	1.05	0.87
Fibre width ((m)	23.9	20.6	23.5	20.5	23.4	20.4	23.0	20.2
Curl value (%)	19.5	14.8	20.7	15.5	20.4	14.8	20.0	15.1
Coarseness (mg/m)	0.098	0.084	0.098	0.089	0.096	0.081	0.098	0.086
STFI FiberMaster								
Fibre length (mm)	1.18	0.97	1.12	0.94	1.18	0.94	1.10	0.92
Fibre width (µm)	21.8	20.3	21.5	20.4	21.2	20.2	21.2	20.1
Curl value (%)	16.4	12.4	14.7	13.3	15.5	12.4	14.3	12.7
Kajaani FS-200								
Fibre length (mm)	1.02	0.86	0.99	0.84	1.01	0.86	0.97	0.83
Coarseness (mg/m)	0.111	0.956	0.112	0.097	0.114	0.092	0.113	0.095

KajaaniFiberLab analysers, although the trends were similar with all three. The average length-weighted fibre length of the original pulp or fibre was about 0.9 mm measured with the Kajaani FS-200. The differences in average length values between reject and accept fractions were surprisingly small (*6,19*). In addition, the fibre widths and curl values were substantially higher for the reject fibre fractions. Another important finding was that the cell wall thickness and coarseness were greater for the reject fibre fractions. Therefore, it seems probable that the hydrocyclone concentrates thick-walled and coarser latewood fibres in the reject fraction and thin-walled earlywood in the accept fraction (*7*).

Small amounts of the fractionated pulp samples were afterwards freeze-dried and analysed by acid methanolysis (GC). Table 3 clearly shows that the reject fibre fractions contained less CMC than the accept fibre fractions. Furthermore, the electrolyte addition did not increase the degree of sorption of CMC on the fibres. The reference samples with and without calcium and sodium addition gave no response for CMC.

Table 3
Content of sorbed CMC on fractionated pulp samples analysed by acid methanolysis (GC). The added CMC amount was 0.5 % on fibres.

Sample	Sorption filtrate ($(C_{CMC}/W_{sample})*100$ (% CMC on pulp)	Reject fraction ($(C_{CMC}/W_{sample})*100$ (% CMC on pulp)	Accept fraction ($(C_{CMC}/W_{sample})*100$ (% CMC on pulp)
CMC	-	0.38	0.48
CMC electrolyte	-	0.30	0.45

Table 4
Fines content of DDJ-fractionated pulp samples. Values are calculated as a weight percentage from absolutely dry pulp (REF = no CMC added, CMC = 0.5 % CMC added, electrolyte = salt added).

Sample	Reject fraction (%)	Accept fraction (%)
REF	2.0	0.5
REF electrolyte	3.0	4.6
CMC	0.7	3.6
CMC electrolyte	1.9	1.4

Table 5
CMC contents (% of dry solids) of fibre and fines fractions (DDJ) of reject and accept fibre fractions obtained from hydrocyclone fractionation of unbeaten birch pulp modified with CMC (0.5 % on fibres).

Sample	Reject fraction Fibres (%)	Reject fraction Fines (%)	Accept fraction Fibres (%)	Accept fraction Fines (%)
CMC	0.45	0.52	0.18	0.46
CMC electrolyte	0.69	0.96	0.56	0.81

Sorption of CMC on reference pulp fractions

The sorption of CMC on the untreated pulp fractions was evaluated by estimating the content of residual CMC in the sorption liquor by acid methanolysis combined with GC. The sorption was most extensive when the pulp had been treated with sodium and calcium chlorides before fractionation (Fig. 2). Significant amounts of xylan were solubilised during the CMC sorptions and reference treatments of the reject fractions (Fig. 3).

Distribution of CMC between fibres and fines

As noted in the foregoing, the CMC contents of accept fibre fractions were higher than those of the reject fibre fractions obtained from hydrocyclone fractionation. The reject and accept fibre fractions were further fractionated in a Dynamic Drainage Jar apparatus (Table 4). As could be expected, there were on average more fines in the accept fractions representing shorter fibres. The CMC contents of the fibre and fines fractions obtained were subsequently determined by acid methanolysis combined with GC. The CMC contents of the fines fractions were clearly higher than those of the fibre fractions (Table 5). These results also indicated that the CMC contents were higher when sodium and calcium salts

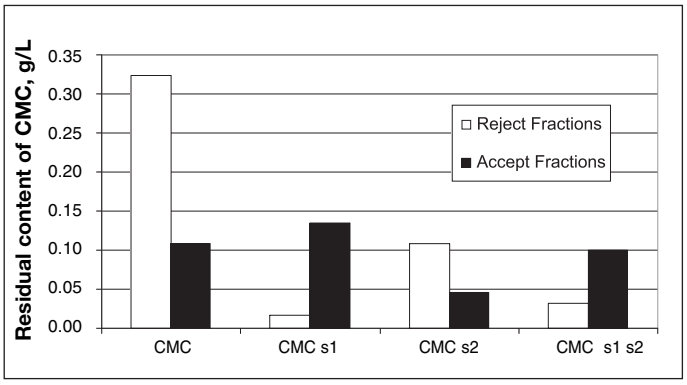

Fig. 2 Residual content of CMC (g/L) in sorption filtrates analysed by acid methanolysis combined with GC. Abbreviations: CMC = 0.5 % CMC added, s1=salt added before fractionation and s2=salt added in the sorption stage.

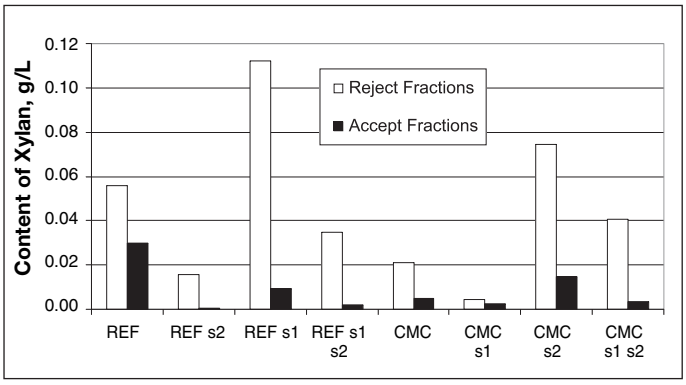

Fig. 3 Xylan content (g/L) in sorption filtrates analysed by acid methanolysis combined with GC. Abbreviations: CMC = 0.5 % CMC added, REF = no CMC added, s1= salt added before fractionation and s2 = salt added in the sorption stage.

Table 6
Metal ion content in birch pulp fractions.

Metal ions µg/g	Original pulp	REF (not fractionated)	REF Reject	REF electrolyte Reject	REF Accept	REF electrolyte Accept
Na	380	530	106	83	104	110
K	20	62	55	53	55	50
Ca	59	680	1080	1060	1070	1060
Mg	224	64	123	123	118	121

Table 7
Accessible xylan (mg/g) contents of fibre and fines fractions (DDJ) of reject and accept fibre fractions obtained from hydrocyclone fractionation of unbeaten birch pulp sorbed with CMC (0.5 % on fibres) or corresponding reference pulps (REF = no CMC added, electrolyte = salt added).

Sample	Reject fraction Fibres (mg/g)	Reject fraction Fines (mg/g)	Accept fraction Fibres (mg/g)	Accept fraction Fines (mg/g)
REF	116	210	140	303
REF electrolyte	109	196	217	170
CMC	211	164	267	210
CMC electrolyte	141	142	146	208
Average	139	176	186	217

were added in the sorption stage, although the opposite was shown in Table 3. Therefore, it is not completely clear at this stage how much sodium and calcium addition actually affects the attachment of CMC. It may also be noted that the metal profiles of cellulose pulps vary greatly. The original pulp used in this study contained, besides sodium, significant amounts of magnesium and calcium (Table 6). Calcium was the only compound that increased remarkably after fractionation.

The contents of CMC in the fractions were estimated from relative peak areas of carboxymethylated glucose units in the gas chromatograms. Because of the low CMC contents these peaks are tiny and therefore difficult to integrate. As a result, the values given are not very accurate, although they certainly show the main trends. From the same chromatograms it was possible to calculate the amount of accessible xylan in the fractions. While the variation between the samples was significant, the fines, as an average, contained more xylan than the fibres and the accept fraction more than the reject fractions (Table 7).

Handsheet properties of CMC-modified fractionated pulps

The internal strength of the handsheets made clearly correlated with the way how the sorption of CMC was performed (Figs. 4 to 6). The strongest sheets were obtained when the pulp was treated with sodium and calcium salts before fractionation.

Another observation was that the unfractionated pulps behaved more like the accept fractions. Removal of the accept fibres had a similar effect on strength as beating of unfractionated pulp (Fig. 4).

In addition, the internal strength of sheets made from the reject fibre fractions was about twice the strength of those made from accept fibre fractions (Figs. 4 and 5). The main contributor to these strength properties was the density of the handsheets. Although the reject fractions were coarser than the corresponding accept fibre fractions, the former gave denser sheets probably due to their higher fibre width to cell wall thickness ratio. Furthermore, the greater cell wall thickness could explain the lower light scattering values of the reject fibre fractions at zero internal strength or at a sheet density corresponding to the zero strength (Figs. 6 and 7).

CONCLUSIONS

The results obtained strongly suggest that hydrocyclone fractionation separates the hardwood pulp fibres according to their coarseness and cell wall thickness (earlywood versus latewood). Similar conclusions have been drawn by Paavilainen and Vomhoff (*7,8*). The internal strength (Scott Bond) of handsheets made from reject fibre fractions were twice the strength of sheets made from accept fibre fractions. Surprisingly, the accept or fine fibre fractions contained more CMC, although the reject fibre fractions gave

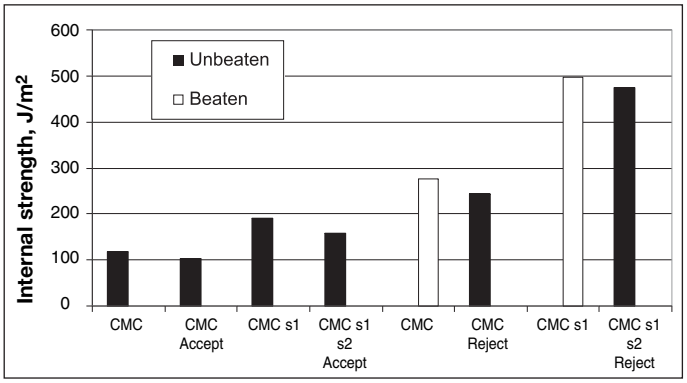

Fig. 4 Effects of fractionation and CMC and electrolyte addition on internal bond strength of handsheets made from unbeaten pulps. Results for beaten pulps (Voith-Sulzer mill, 30 kWh/t) are shown for comparison. Abbreviations: CMC = 0.5 % CMC added, s1 = salt added before fractionation and s2 = salt added in the sorption stage.

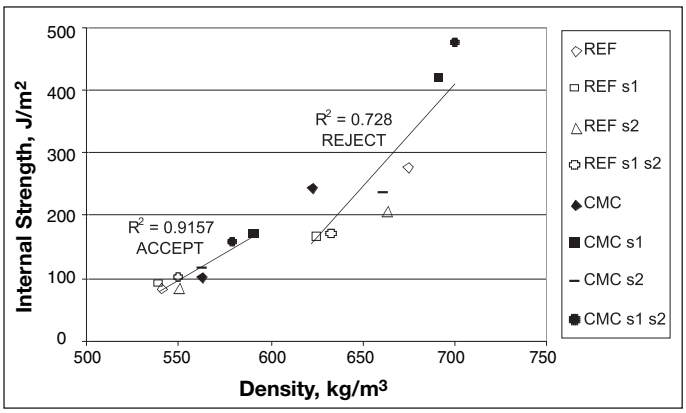

Fig. 5 Effect of CMC and electrolyte addition on density versus internal strength of handsheets made from CMC-modified reject and accept fibre fractions. Abbreviations: REF = no CMC added, CMC = 0.5 % CMC added, s1 = salt added before fractionation and s2 = salt added in the sorption stage.

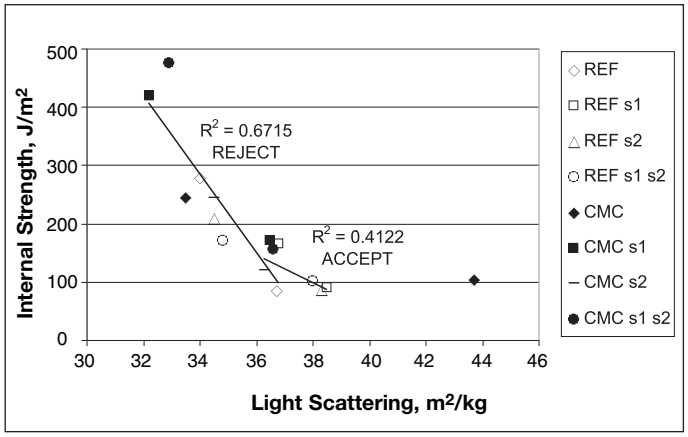

Fig. 6 Effect of CMC and electrolyte addition on light scattering versus internal bond strength of handsheets made from CMC-modified reject and accept fibre fractions. Abbreviations: REF = no CMC added, CMC = 0.5 % CMC added, s1 = salt added before fractionation and s2 = salt added in the sorption stage.

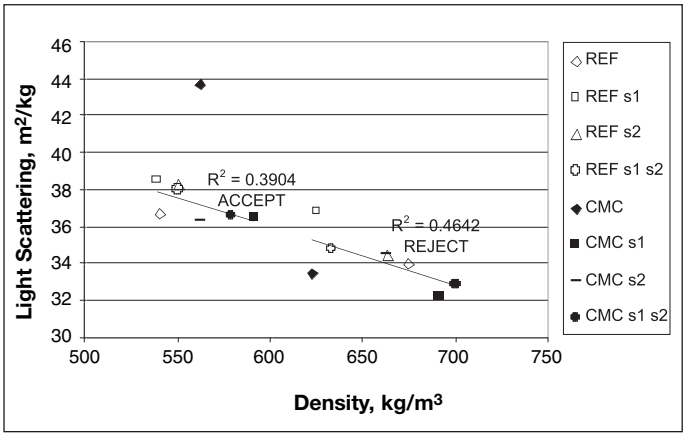

Fig. 7 Effect of CMC and electrolyte addition on density versus light scattering of handsheets made from CMC-modified reject and accept fibre fractions. Abbreviations: REF = no CMC added, CMC = 0.5 % CMC added, s1 = salt added before fractionation and s2 = salt added in the sorption stage.

higher strength properties. One explanation for the difference in strength properties between the fractions could be that the reject fibres, in spite of their higher coarseness, are more flexible due their higher fibre width to cell wall thickness ratio.

Another important finding is that to increase the internal strength as much as possible the pulp should be treated with a calcium salt prior to the sorption of CMC.

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