

THE INFLUENCE OF THE COUNTER-IONS TO THE CHARGED GROUPS ON THE REFINABILITY OF NEVER-DRIED BLEACHED PULPS

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Refining of bleached hardwood pulps and bleached softwood pulps having different counter-ions to the charged groups within the fibres was studied. The results show that an energy reduction of 50% for the hardwood pulps and 20% for the softwood pulp can be achieved if the fibres are converted into the Na⁺-form prior to refining. The results also show that the amount of charged groups in the fibres is important for the refinability, which explains why the refining efficiency is much lower for bleached softwood fibres, which have a much smaller amount of charged groups than the bleached hardwood pulp.

Keywords: Beating; Refining; Refinability; Swelling; Kraft Pulps; Charged Groups; Mechanical Properties

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INTRODUCTION

Refining is intimately connected to the swelling of fibres, although swelling in itself is not always desirable, since swollen fibres result in a paper web with a slower dewatering capacity. Besides a higher degree of swelling, refining of the pulp increases the strength properties of the produced paper. It is known that the counter-ions to the charged groups in the fibres play an important role in their swelling ability and that fibres in their Na⁺-form have the highest degree of swelling (Lindström and Carlsson 1978; Scallan and Grignon 1979; Scallan 1983; Lindström and Carlsson 1982; Lindström 1992). The cause of swelling according to the theory of charged electrolytic gels is electrostatic repulsion of negatively charged groups (Flory 1953). In order to swell, the fibres must have sufficient amounts of charged groups in the cell wall, and the cell wall must also have a sufficient elasticity to respond to charge interactions. Different pulps have different responses to pH and electrolytes, depending on their cell wall stiffness due to the lignin present in the cell wall, as was elegantly demonstrated by Lindström and Carlsson (1982).

It has been shown that handsheets made from fibres with carboxylic acid groups in different ionic forms have different tensile indexes, where fibres in the Na⁺-form have the highest tensile index and swelling ability, while hydrogen and aluminium counter-ions give less swelling and poorer strength (Scallan and Grignon 1979).

Torgnysdotter (2006) characterized the fibre/fibre joints and their influence on paper strength properties and concluded that the paper strength is determined by the joint strength between the fibres and the number of active fibre/fibre joints per unit volume of

the sheet and that a higher fibre flexibility leads to a larger number of possible fibre/fibre contacts in the sheet. However, the formation of fibre/fibre joints was also affected by the molecular interaction between the fibres when fibre/fibre contacts were developed. The change of counter-ion from Na^+ to Ca^{2+} or H^+ drastically reduced (by more than 50%) the joint strength, and this was ascribed to a loss in surface swelling with decreasing degree of dissociation of the carboxyl groups on the fibres; the observed smaller influence on the tensile index (between 15-20%) was suggested to be due to more efficient fibre/fibre contacts being formed due to a decreased electrostatic interaction between the fibres during the consolidation of the sheet (Torgnysdotter and Wågberg 2004; Forsström et al. 2005). In these studies, unrefined fines-free pulps at different pulp yields were used and no refining was considered.

The counter-ion to the charged groups in the fibre has also been reported to have a significant effect on the refinability of fibres in laboratory studies (Lindström and Kolman 1982, Hammar et al. 2000). Hammar et al. (2000) separated the effects of counter-ions on refining and on sheet moulding by converting all the pulp samples after laboratory Escher-Wyss refining into the Ca^{2+} form prior to handsheet-making. Their results showed that the energy required to reach a given WRV value or a given tensile index could be reduced by 50% by ion-exchange of the fibre charges into the Na^+ -form. This energy reduction was confirmed in a large-scale pilot trial with industrial refining followed by papermaking on the pilot papermachine FEX (Bäckström et al. 2009).

The amount of charged groups in the fibres is normally fewer in bleached than in unbleached softwood. Bleached hardwood has more charged groups than bleached softwood due to the higher hemicellulose content.

The objective of the present investigation was to study the effect of different counter-ions to the charged groups in the fibres on the refining efficiency and on the consolidation of bleached hardwood and softwood pulps. The study will also provide information on the importance of charged group for the refinability of chemical pulps.

MATERIALS AND METHODS

Materials

Never-dried bleached ECF softwood (a mixture of spruce and pine) and hardwood (mainly birch) commercial kraft pulps from Billerud's Skärblacka Mill were used in the trials. The pulps were produced in batch digesters and were taken from the wash filter in the pulp mill. The content of acid groups was determined to be 95 mmol/kg for the hardwood pulp and 49 mmol/kg for the softwood pulp.

Ion-exchange

After being washed with deionized water, the whole pulp was ion-exchanged to the H^+ -form by the addition of H_2SO_4 , for 24 h. This was done to ensure a complete ion exchange in the subsequent step. The excess of H_2SO_4 was removed by washing with deionized water. Portions of these pulps were ion-exchanged into the Ca^{2+} - and Na^{2+} -forms. A schematic drawing of the experimental setup is shown in Fig. 1.

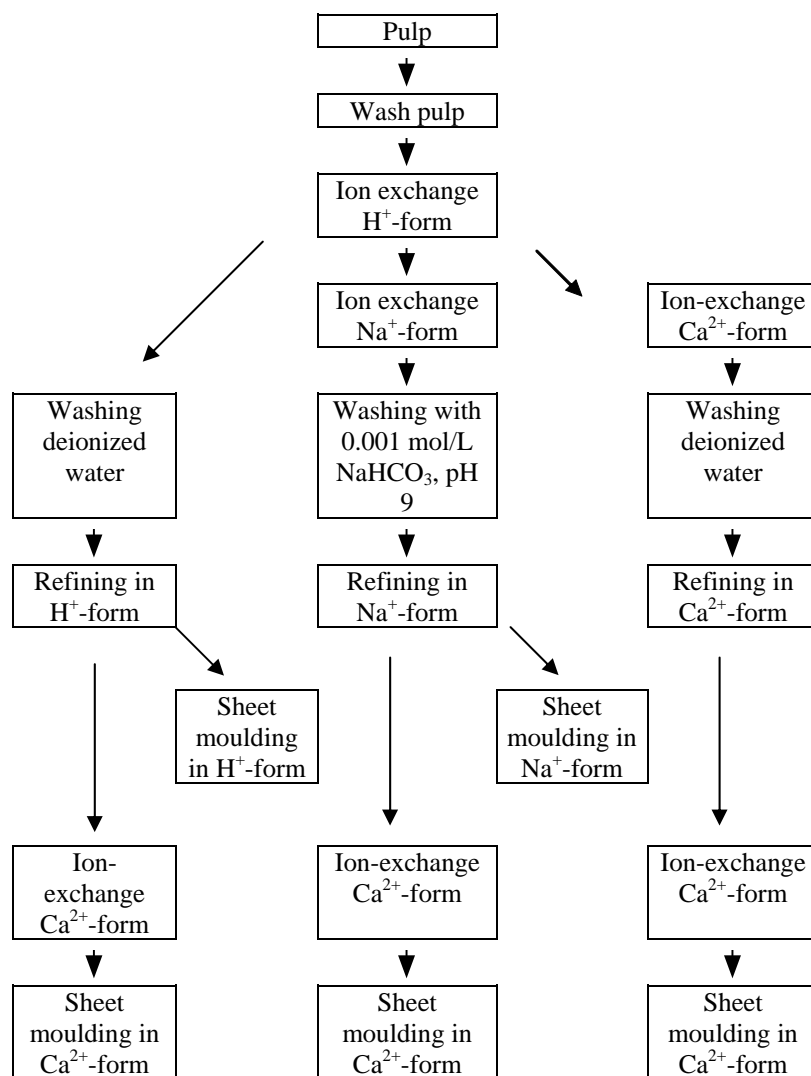


Fig. 1. Experimental design for ion exchange, refining, and sheet moulding

The pulps were ion-exchanged into the Na^+ - and Ca^{2+} -forms by treating for 24 h with NaOH at a pH of 10.5 and 0.1 mol/L CaCl_2 respectively (Table 1). Excess NaOH was removed by washing with NaHCO_3 (0.001 mol/L, pH 9). Excess of CaCl_2 was removed by washing with deionized water.

Table 1. Chemicals Used in the Ion-Exchange Experiments

Ionic form	Chemical used for ion-exchange	pH (20°C) during ion-exchange	Washing liquor	pH (20°C) after refining
Na	NaOH	10.5	0.001 mol/L NaHCO_3 , pH 9	7,5
H	H_2SO_4	2.5	deionized water	4.5-5
Ca	CaCl_2	8	deionized water	7

The metal ion content in the fibres was determined prior to and after the ion-exchanges (Table 2). Apart from the metals shown in the table, the untreated pulps contained some alumina and iron. The untreated and treated pulps also contained low amounts of barium, zinc, potassium, phosphorus, manganese, and nickel.

Table 2. Metal Content of the Fibres in Different Ionic Forms

Metal content, meq/kg			Total, meq/kg
Pulp	Na	Ca	
Hardwood			
Reference	48	31	91
Na ⁺ -pulp	82	4	88
H ⁺ -pulp	-	-	-
Ca ²⁺ -pulp	1	88	89
Softwood			
Reference	10	20	40
Na ⁺ -pulp	35	1	37
Ca ²⁺ -pulp	-	38	38
H ⁺ -pulp	-	1	1

* no metal analysis performed

The change in swelling, measured as WRV, as a result of the ion-exchange is shown for both hardwood and softwood pulps in Table 3. The highest swelling level was obtained for the hardwood pulp fibres, and the pulp in the Na⁺-form had the highest degree of swelling, while there was no difference in swelling between the other two ionic forms. In the case of the softwood pulp, there were no differences in WRV between the different ionic forms.

Table 3. WRV for the Unrefined Pulps in Different Ionic Forms

Ionic form	WRV, g/g	
	Hardwood	Softwood
Na	1.75	1.54
Ca	1.62	1.49
H	1.64	1.52

Refining

The refining was performed in an Escher-Wyss laboratory conical refiner R1L. Pulp consistency was 3.5%. The consistency of the pulp was adjusted using 0.001 mol/L NaHCO₃ (pH 9) in the case of the Na⁺-form and deionized water in the case of the H⁺- and Ca²⁺- forms (Table 1). The initial temperature of the pulp suspension was 20°C. The specific edge load during refining was 2.0 Ws/m. The effect of different net specific refining energy input levels was investigated.

Analysis

Kappa number was determined according to ISO 302:2004 and the Water Retention Value (WRV) according to SCAN-C 62, except that deionised water was used. At each refining level, WRV measurements were made both in the ionic form under which the refining was carried out, and in the Ca^{2+} -form. The metal content was determined by plasma-emission spectrometry, ICP-AES. Fibre dimensions and curl were determined using the STFI Fiber Master (Karlsson et al. 1999).

The handsheets were prepared according to EN ISO 5269-1, except that deionized water was used. The structural density was determined according to SCAN P-88:01 and the tensile properties according to ISO 1924-3. The primary data from the physical testing of the handsheets were treated as recommended in SCAN-G 2:63, within a 95% confidence interval.

The total charge of the different fractions was determined by conductometric titration (Katz et al. 1984; Lloyd and Horne 1993; Pu and Sarkanen 1989). Prior to the measurement, the sample was washed with HCl at a pH of 2. Thereafter, the sample was washed with deionized water until the filtrate had a conductivity less than 5 $\mu\text{S}/\text{cm}$ and a pH higher than 4.5.

RESULTS

Bleached Hardwood Pulp

The hardwood pulps in the Na^+ -, Ca^{2+} -, and H^+ - forms were refined, and their response to refining in terms of WRV is illustrated in Fig. 2. Portions of the refined pulps were converted to the Ca^{2+} -form before the WRV was determined.

Refining in the Na^+ -form followed by the WRV measurement in the Na^+ -form gave at a given energy input a pulp with the highest swelling. As expected, the WRV of the unrefined pulp was higher for the pulp in the Na^+ form than for the other pulps. When the pulp was subsequently converted to the Ca^{2+} -form, the WRV of the unrefined pulp was dropped to the same level as that of the other unrefined pulps.

After refining in the Na^+ -form, conversion into the Ca^{2+} -form decreased the WRV. The pulp refined in the Na^+ -form and then converted to Ca^{2+} -form (filled diamonds in Fig. 2) had a higher WRV than the other investigated ionic forms, which shows that refining of bleached hardwood pulps in the Na^+ -form is more energy efficient in terms of WRV-increase per unit input energy. The pulps in Ca^{2+} - and H^+ -forms had a weaker WRV development, and no difference between them was evident.

The energy required to reach a given WRV-value was thus lower for the pulp refined in the Na^+ -form than for the other ionic forms. For instance, for a WRV of 1.8, the energy demand for the pulp in Ca^{2+} -form was 40 kWh/t, while the pulp refined in the Na^+ -form required only 10 kWh/t. When the comparison was made with the pulp in the same ionic form, the Ca^{2+} -form, the energy requirement for the pulp refined in the Na^+ -form and WRV determined in the Ca^{2+} -form was 20 kWh/t. This corresponded to a 50% energy reduction.

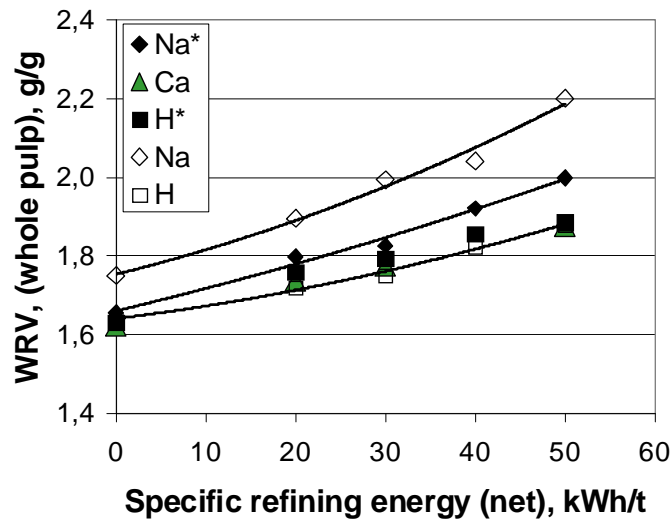


Fig. 2. WRV vs. the refining energy input for a bleached hardwood pulp refined in Ca^{2+} -, Na^+ -, or H^+ - form. After refining, part of the pulp was ion-exchanged into the Ca^{2+} -form (denoted *).

The type of counter-ion did not affect the degree of fibre shortening or the shape factor during refining at a given energy input, as shown in Fig. 3. The Fiber Master uses tap water, which contains a lot of calcium ions, which instantly convert the fibres into the Ca^{2+} -form, so therefore only one set of fibres (those converted to Ca^{2+} -form) was used for the determination.

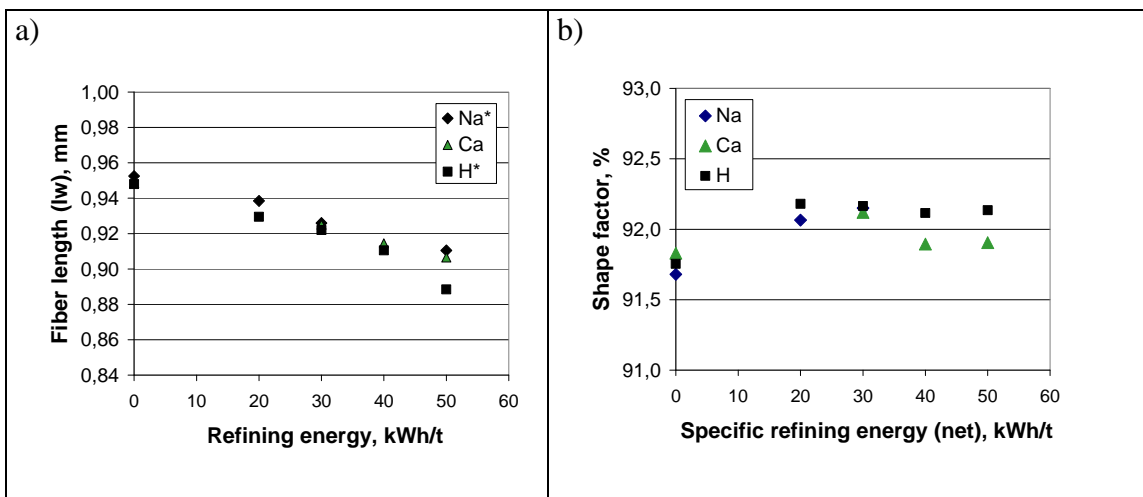


Fig. 3. The fibre length (length weight average) and shape factor (length weight average) versus the refining energy input for a bleached hardwood pulp refined in the Ca^{2+} -, Na^+ -, or H^+ - form.

The mechanical properties of handsheets are shown in Fig. 4. The energy demand to reach a given tensile index was lowest for the pulp refined in the Na^+ -form (Fig. 4a). For the pulp that was refined in Na^+ -form and sheet moulded in the Na^+ -form the energy saving was large. To reach a tensile index of 80 Nm/g, the energy demand for the pulp in

the Ca^{2+} -form was 40 kWh/t, whereas the pulp refined in the Na^+ -form required only 15 kWh/h.

If the comparison is made when the sheet moulding was done in the same ionic form, i.e the Ca^{2+} -form, then the effect was less. In this case, the energy demand for the pulp in the Ca^{2+} -form to reach a tensile index of 80 Nm/g was 40 kWh/t, while the pulp refined in the Na^+ -form required only 25 kWh/h. The pulps in the Na^+ -form also showed a higher tensile stiffness index for a given energy input than the other ionic forms (Fig. 4b).

If the comparison is made at a given WRV, the pulp refined and sheet moulded in the Na^+ -form had the lowest tensile index (Fig. 4c). A significantly higher tensile index at a given density was obtained for the pulps refined in the Na^+ -form (Fig. 4d). However, there were no differences in the relationship if the sheet moulding was done in the Ca^{2+} -form or in the Na^+ -form, indicating that the improved tensile-density relation originates in the refining.

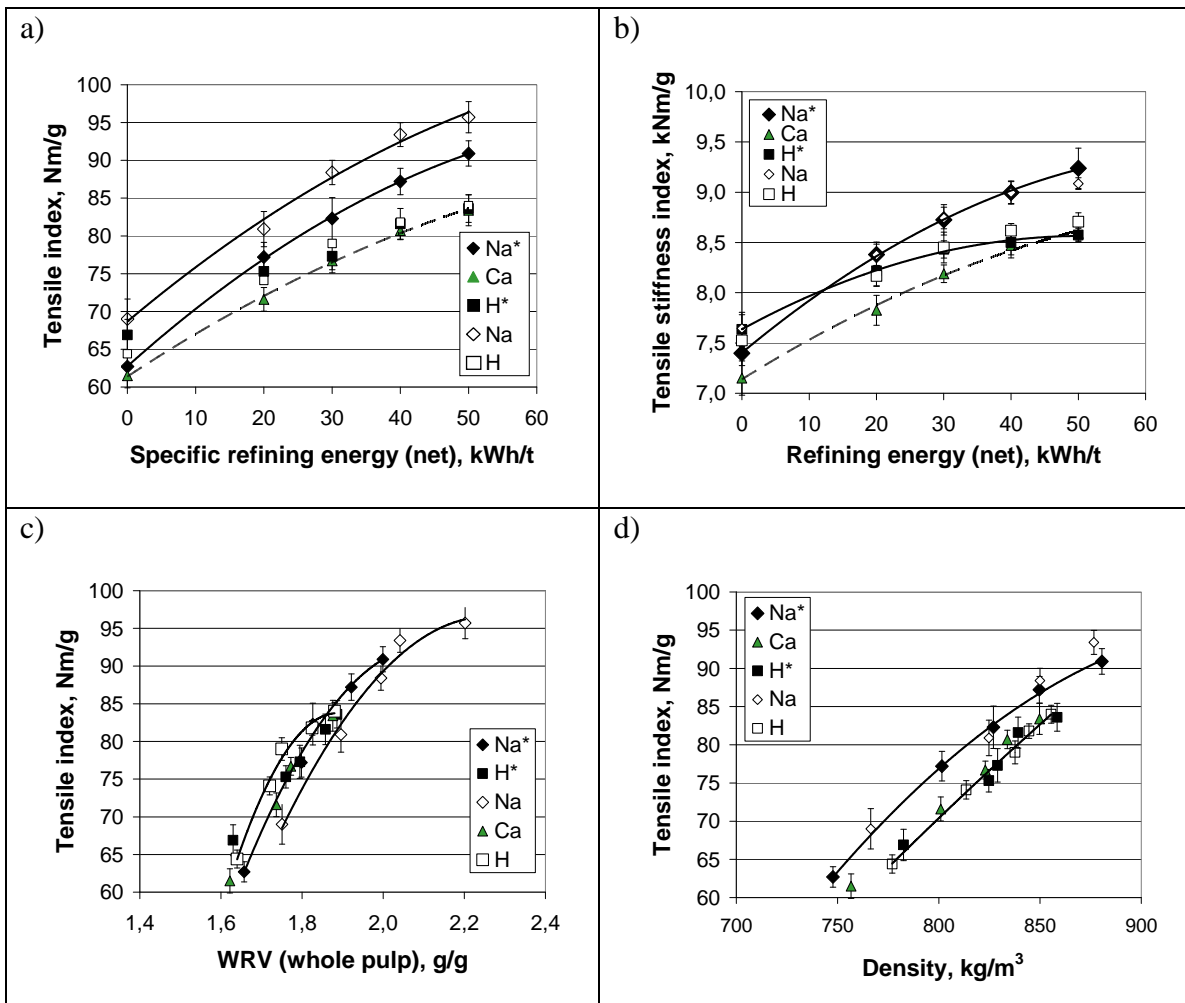


Fig. 4. The strength properties for a bleached hardwood pulp refined in the Ca^{2+} -, Na^+ - or H^+ -form. After refining, part of the pulp was ion-exchanged into the Ca^{2+} -form and sheet moulded in the Ca^{2+} -form (denoted *).

Bleached Softwood Pulp

The WRV values for the unrefined bleached softwood pulps in their different ionic forms were similar, as shown in Table 3. Nevertheless, the WRV development during refining was different, depending on the ionic form of the pulp fibres (Fig. 5). The lowest WRV was obtained for refining in the H^+ -form, and the value was only slightly increased when this pulp was converted to the Ca^{2+} -form prior to the WRV determination. As expected, the pulp refined in the Na^+ -form and measured in the Na^+ -form had the highest WRV, and when this pulp was ion-exchanged into the Ca^{2+} -form prior to the WRV determination, the WRV was still higher than for the other ionic forms.

The energy demand to reach a WRV value of 1.7 was 60 kWh/t for the pulp in the Ca^{2+} -form, whereas the pulps refined in the Na^+ -form required only 30 kWh/t, or 48 kWh/t if the measurement was made in the same ionic form, the Ca^{2+} -form. This energy reduction of 12 kWh/t corresponds to a 20% energy reduction.

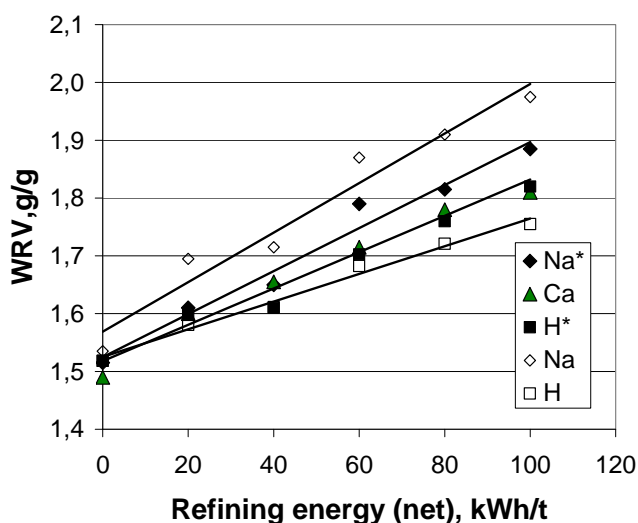


Fig. 5. The WRV versus the refining energy input for a bleached softwood pulp refined in the Ca^{2+} -, Na^+ -, or H^+ -form. After refining, part of the pulp was ion-exchanged into the Ca^{2+} -form (denoted *).

As in the case of the bleached hardwood fibres, no differences in fibre length as a result of the refining in different ionic forms were observed. However, there was a small influence on the shape factor, where the fibres refined in the Na^+ -form tended to be slightly straighter, and the fibres refined in the H^+ -form tended to have a slightly lower shape factor, as shown in Fig. 6.

The strength properties are shown in Fig. 7. The energy to reach a certain tensile index was less when the refining was performed in the Na^+ -form (Fig. 7a). The tensile index of the unrefined pulp in the H^+ -form was almost 10 Nm/g lower than that of the pulp in the Ca^{2+} - or Na^+ -form. This lower value was maintained during refining. In the tensile–WRV relation there was a tendency for the fibres refined in the Na^+ -form and sheet moulded in the Na^+ -form to have a slightly lower tensile index than the other investigated pulps (Fig. 7c). No differences between the pulps in the different ionic forms were found in the tensile-density relationship (Fig. 7d).

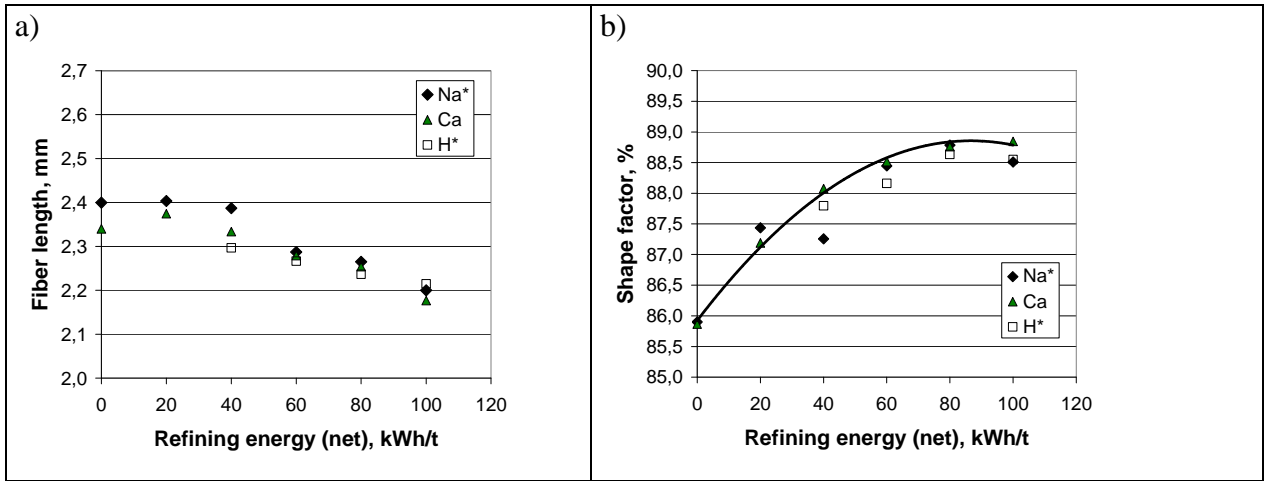


Fig. 6. The fibre length (length weight average) and shape factor (length weight average) versus the refining energy input for a bleached softwood pulp refined in the Ca²⁺-, Na⁺-, or H⁺- form.

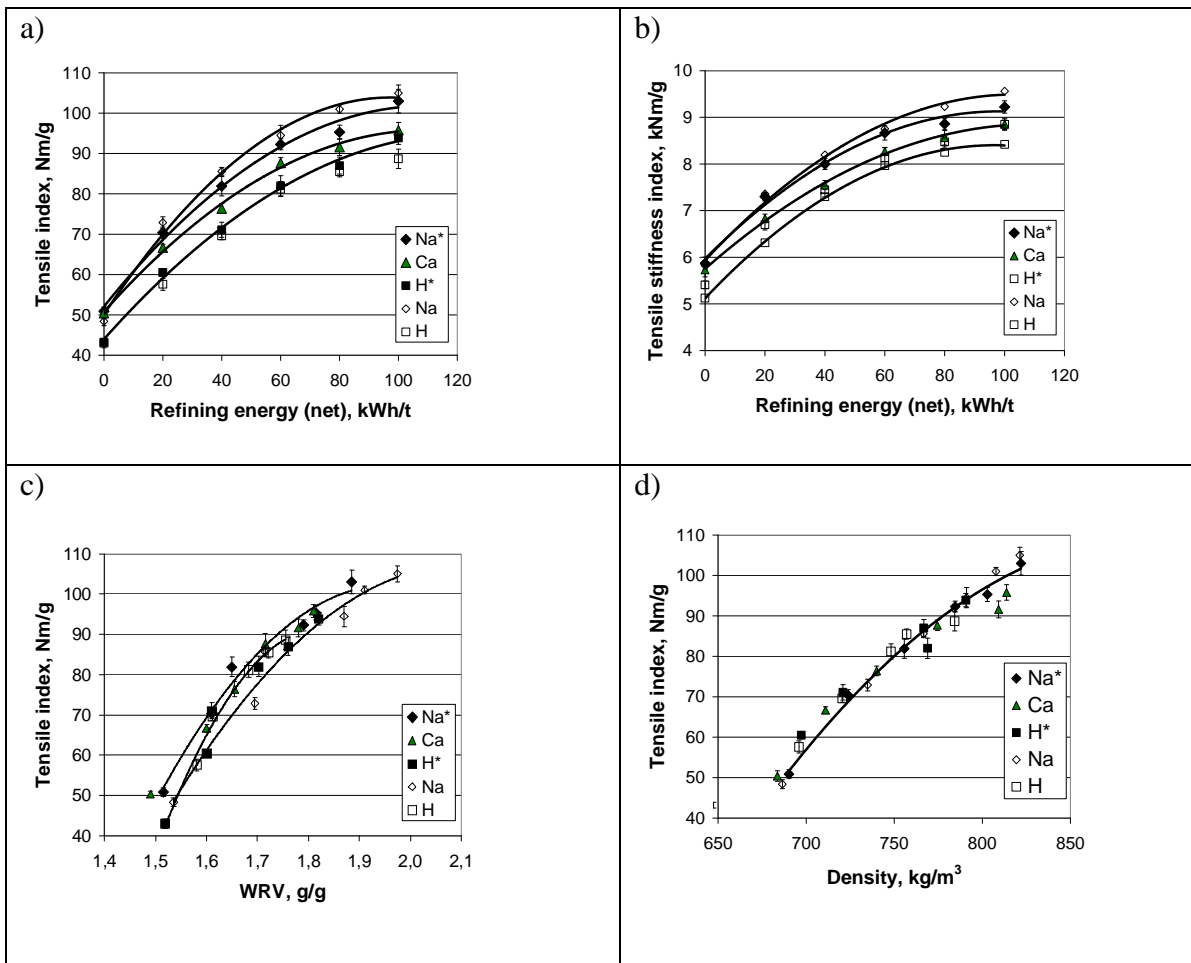


Fig. 7. The strength properties for a bleached softwood pulp refined in the Ca²⁺-, Na⁺-, or H⁺- form. After refining, part of the pulp was ion-exchanged into Ca²⁺-form and sheet moulded in Ca²⁺-form (denoted *).

DISCUSSION

The objective was to study the influence of different counter-ions to the charged groups on bleached pulps. Bleached pulps, and in particular bleached softwood pulps, have relatively few charged groups and a lower swelling ability than pulps with more charged groups such as unbleached pulps. Prior to refining, the counter-ions to the charged groups within the pulps were converted to the Na⁺, Ca²⁺, and H⁺-forms.

Although the swelling measured as WRV for the unrefined pulps in their different ionic forms was small, the pulps with different counter-ions responded differently to the mechanical energy input during the refining process. The refinability was evidently greater if the fibres were in the Na⁺-form, where a higher WRV or tensile index per unit energy input was observed for both bleached hardwood and bleached softwood pulps.

There were no major differences in shape factor for the pulps in different ionic forms at a given refining energy input (Figs. 3 and 6), which indicates that changes in the fibre form is not responsible for the observed differences between the pulps.

The refinability may be expressed in terms of the slope of the relationship between WRV and specific energy input, where the slope for the hardwood pulp refined in the Na⁺-form was 0.9 (WRV-units (g/g)/ 100 (kWh/t)), while the slope for the pulp refined in the Ca²⁺-form was 0.52 (WRV-units (g/g)/ 100 (kWh/t)). In the case of the softwood fibres, the slope of the pulp refined in the Na⁺-form was 0.44 (WRV-units (g/g)/ 100 (kWh/t)), whereas the slope of the pulp refined in the Ca²⁺-form was 0.32 (WRV-units (g/g)/ 100 (kWh/t)). The value of the slope for the softwood pulp refined in the Ca²⁺-form agrees well with the value reported by Mohlin (2005) for industrial market pulps. Commercial pulps can normally be considered as being in the Ca²⁺-form.

The results showed a potential to reduce the energy requirements by conversion to the Na⁺-form before refining. For a bleached hardwood pulp, the energy savings potential was approximately 50%, and for a bleached softwood pulp, the energy reduction was somewhat smaller, up to 20%, when the pulp was refined in the Na⁺-form rather than in the Ca²⁺-form. The results are in agreement with those reported in previous laboratory (Hammar et al. 2000) and pilot scale (Bäckström et al. 2009) studies on unbleached softwood kraft pulps. The energy saving was, as expected, lower for the bleached softwood fibres and this may be explained as being due to the smaller amount of charged groups in the pulp, 45 mmol/kg for the softwood pulp compared to 95 mmol/kg for the hardwood pulp. The bleached hardwood pulp had approximately the same amount of charged groups as the unbleached softwood pulps (see e.g Hammar et al. 2000; Bäckström et al. 2009) and also the same energy reduction potential.

The improved refinability for fibres in Na⁺-form shows the importance of the swelling capacity for the refinability of pulps. If the ionic form of the fibres is changed, then the swelling behavior will change as well as the pore distribution within the fibre wall (Salmén and Berthold 1997).

The more energy-efficient refining of pulps in the Na⁺-form may be explained as a co-operation between a higher osmotic pressure in the fibre wall and the mechanical stress applied during refining. A schematic drawing of this is shown in Fig. 8. When mechanical forces are applied on the fibre and the fibre wall, the electrostatic repulsion forces due to the ionization act as an additional aid to increase the swelling, and this in

turn helps to delaminate the fibre wall. Gellerstedt et al. (2000) have shown that it is possible, by the introduction of additional charges on the fibres, to increase the osmotic pressure above the cell-wall elasticity and to delaminate the cell-wall without the application of any mechanical force.

To illustrate this co-operation, refining of fibres in the H^+ -form can be regarded as the case when there is no electrostatic interaction, since most of the charged groups in the fibres are undissociated and only mechanical energy is transferred to the fibres (see Fig. 8, denoted “ H^+ -form, WRV in H^+ -form”). Laine (1994) showed, however, that at a pH-level of 5 there are still some dissociated groups present. On the other hand, the Donnan equilibrium calculations done by Grignon and Scallan (1980) show that the pH is much lower within the fibre wall than in the surrounding media, especially at a low ionic strength as in this case.

When the fibres are transferred into the Na^+ -form, the charged groups in the matrix are ionized and, as the mechanical energy is transferred by the refiner, the electrostatic nature of the matrix co-operates with the mechanical stresses to delaminate the fibre, so called “electrostatic repulsion-assisted refining” (see Fig. 8, denoted “ Na^+ -form, WRV in Na^+ -form”). The help of this interaction can be regarded as the difference in WRV when the WRV is determined in the Na^+ -form and the value obtained after the pulp has been reconverted back to the H^+ -form (see Fig. 8, denoted “ Na^+ -form, WRV in H^+ -form”). The analysis of our results are in harmony with the interpretation made by Laivins and Scallan (2000) on how the effects of chemical and mechanical processes are additive under alkaline conditions.

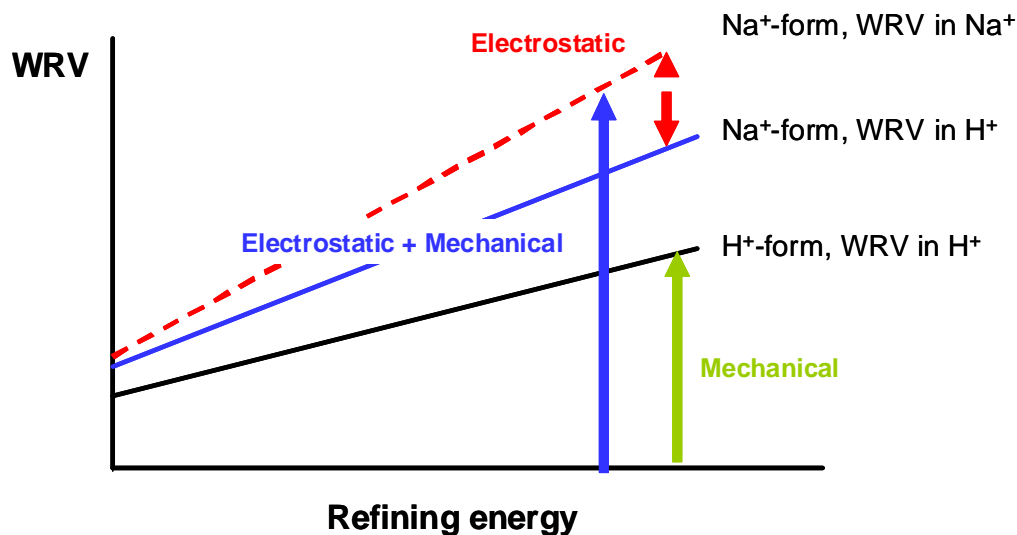


Fig. 8. A schematic drawing of the development of WRV during the refining of fibres in the H^+ -form and the Na^+ -form

Our results show that the refinability can be improved if the fibres are converted into the Na^+ -form prior to refining. If the effect were solely a reduction in energy requirement, the relationship between strength properties and WRV or density would be unchanged.

The pulps that were refined and sheet moulded in the Na⁺-form had a lower tensile index at a given WRV than the other ionic forms (Figs. 4 and 7). So the higher water uptake did not lead to a sheet with a higher tensile index.

During the sheet moulding of the fibres in the Na⁺-form, electrostatic interactions occur within the fibres and as well as between the fibres. The WRV does not give any information as to where the water is located, so no differences can be distinguished between water at the fibre surface or water within the fibre wall. In this study, we conclude that the increase in WRV due to refining was not recovered in strength properties. It is possible that refining in different ionic forms leads to different fibrillation patterns and differences in the ratio of bulk swelling to surface swelling. Laine et al. (2003) attempted to distinguish between the bulk swelling and the surface swelling by measuring the WRV in different ionic forms and blocking the surface charge with a high molecular weight polymer on CMC-grafted unrefined pulp fibres.

In the present study on the bleached hardwood pulps, the ionic form did affect the tensile index-density relation (Fig. 4d). A significantly higher tensile index at a given density was obtained for the pulps refined in the Na⁺-form. This is consistent with the findings where unbleached pulps refined in the Na⁺-form had a higher tensile strength than the pulp refined in the Ca²⁺-form (Hammar et al. 2000; Bäckström et al. 2009). However, there was no difference in the relationship if the sheet moulding was done in the Ca²⁺-form or in the Na⁺-form, indicating that the improved tensile - density relation was due not to the consolidation process but to the refining process.

CONCLUSIONS

Refining of bleached hardwood pulps and bleached softwood pulps having different counter-ions to the charged groups within the fibres was studied. The results show that an energy reduction of 50% can be achieved for the hardwood pulps and 20% for the softwood pulp if the fibres are converted into the Na⁺-form prior to refining.

The results obtained in the present study also support the hypothesis that the refinability is improved when electrostatic interactions co-operate with the mechanical stresses in the refining process.

It can also be concluded that the amount of charged groups in the fibres is important for the refinability, since the refining efficiency was much lower for bleached softwood fibres, which have a much smaller amount of charged groups than bleached hardwood pulp.

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