De-esterification and Sulfonation in CTMP: Effects on Pulp and Paper Properties

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ABSTRACT

Various tree species and chemicals are today used in chemimechanical pulping. Most CTMP grades are targeted for high bulk and, thus, the use of alkali is minimized. The chemical dosage is, therefore, in most CTMP processes, below that needed for complete de-esterification of methylated and acetylated compounds. Chips were pre-treated with alkaline, sulfite, alkaline sulfite and alkaline peroxide liquors before refining in a small-scale batch refiner. De-esterification and sulfonation reactions were quantified and hand-sheet properties tested. The data were subjected to multivariate analysis and the significance of the chemical reactions towards pulp and paper properties was estimated. The fibre length and width after refining were strongly influenced by lignin sulfonation and pectin demethylation. The deacetylation of galactoglucomannans (GGM) had little influence on preserving fibre dimensions in CTMP refining. The bulk, on the other hand, was found to be negatively influenced by the GGM deacetylation. Peroxide reactions in alkaline peroxide treatments had no significant effect on the pulp and paper properties.

INTRODUCTION

Pre-treatment of chips in CTMP production aims at selective fibre separation. Improved fibre length and a lower proportion of fines and shives, compared to TMP, may be attributed to softening of the middle lamella and primary wall [1]. This enables production of pulps with high freeness. The most important papermaking property of CTMP is, however, its high ratio volume per weight (bulk). Alkaline pre-treatments increase fibre swelling. The fibres then become more flexible and prone to collapse, i.e. loose their rounded shape in the paper sheet, indicated as reduced bulk and lowered light scattering. The most decisive factor for paper strength is the degree of fibre collapse, increasing the total surface contact area between fibres [2, 3, 4]. The internal fibre strength and the size of the fibres, i.e. length and width, will also influence the paper strength [5]. Tear strength is strongly dependent on the preservation of fibre length in refining, while tensile strength mainly is a reflection of the bonding strength, i.e. flexibility and surface properties of the fibres. Good correlations have been demonstrated between formation of additional anionic groups (AGs), fibre swelling and strengthening of mechanical pulps [6, 7]. Another important aspect of mechanical pulping is the specific energy consumption in refining. This is higher for chemically pre-treated softwood chips than for untreated chips, compared at the same freeness level [1, 8]. This observation can be explained by the increased flexibility and compressibility of the long and slender softwood fibres which will limit the maximum energy that can be absorbed in the course of refining [9]. Chemically pre-treated hardwood chips, on the other hand, normally require less refining energy to develop the same freeness levels as untreated chips. Acetyl and methyl de-esterification and sulfonation are the major chemical reactions in chemithermomechanical pulping, but the rate of these reactions is highly dependent on the wood species and pre-treatment conditions. The strong interrelation between galactoglucomannan (GGM) deacetylation and pectin demethylation makes it difficult to distinguish their specific impact on the process characteristics. Some oxidation of lignin structures could also be expected in the case of alkaline peroxide treatments. Sulfonation and demethylation generate new AGs predominantly in the primary wall, leading to a local swelling/tension in this for fibre separation important region.

The role of: (a) deacetylation of galactoglucomannans (GGM) (b) demethylation of pectins, and (c) sulfonation of lignin and (d) other alkali-consuming reactions on the final pulp and paper properties was assessed on laboratory-scale spruce (Picea abies) and aspen (Populus tremula) CTMP’s.

MATERIAL AND METHODS

Pre-steamed spruce and aspen chips (500 g oven dry) were compressed in a cylindrical hydraulic press, to approximately one-third of the initial bed-volume, before adding the impregnation liquor. The impregnation liquors were: alkaline (A), sulfite (S), alkaline sulfite (AS) and alkaline peroxide (AP) [10]. A reference pulp (TMP) was obtained by pre-treatment with only water. The impregnation liquor volume was 3 L (including calculated chip water content). Heat-treatments were performed in a rotating digester for 30 min (excluding heat-up time) at 40, 60 and 80°C.
A Wing defibrator type refiner was used for refining [11]. The chips were pre-heated in the refiner (at 120-130°C for 5 min) to soften the chips before refining (at 125-135°C). The refiner was run for 1.5 to 12 min to reach targeted freeness levels. Pulps were hot-disintegrated (ISO 5263) and screened in a vertical centrifugal screen with 0.15 mm slots. The pulps were homogenized and stored frozen. Hand-sheets (10 cm ×10 cm, 60 g m⁻²) were formed according to a modified ISO 5269-1979 standard. The degree of esterification was determined by complete hydrolysis of the acetyl and methyl ester groups in the pulps [12]. The released acetic acid was quantified using an ion chromatograph equipped with a Metrosep organic acid IC exclusion column. The released methanol was quantified using headspace solid-phase microextraction (SPME) and GC on a polar-phase capillary column [13]. Sulfonation was quantified by quinoline sorption on washed pulp by a spectrophotometric method [14]. Freeness (CSF) of screened pulps was determined according to ISO 5267-2:1980. The average (length weighted) fibre length and width was measured on a Kajaani FibreLab 3.5. The hand-sheet bulk and strength properties were determined according to ISO 5270-1979. Bulk, strength properties and specific energy consumption (SEC) was plotted as function of pulp freeness and compared at a freeness level of 500 ml for spruce and 400 ml for aspen.

RESULTS AND DISCUSSION

**Effect of De-esterification and Sulfonation on Fibre Dimensions**

The effect of the spruce CTMP reactions on the average fibre length is demonstrated in Figure 1. The correlation for the GGM deacetylation was relatively weak ($R^2 = 0.40$). Especially, the considerable increase in fibre length for the S pre-treated pulps (0% NaOH) did not correlate very well with the GGM deacetylation (0-20 µmol g⁻¹). The correlation with pectin demethylation was significantly higher ($R^2 = 0.69$) than that of GGM deacetylation. Introduction of sulfonic groups caused fibre length increment in a linear fashion. This effect was highest in absence of alkali. The sum of demethylation and sulfonation correlated very well ($R^2 = 0.92$) with the fibre length after refining. Accordingly, the impact of pectin demethylation and lignin sulfonation on the fibre dimensions is prominent for spruce CTMP. Low additions of sulfite have been reported to result in high sulfur contents in fines originated from the primary wall region (P). The exposed surfaces of mildly sulfonated fibres were also reported to be composed of primary wall fragments [15]. This supports our interpretation that lignin sulfonation and pectin demethylation have a synergetic effect for an improved fibre separation by increasing the amount of anionic groups in the P region.

![Figure 1. Fibre length of spruce CTMP as function of deacetylation, demethylation, sulfonation, and the sum of demethylation and sulfonation for A and AS pre-treatments at 60°C. White symbols=no NaOH, light grey symbols=1% NaOH (based on o.d. wood) and dark grey symbols=2% NaOH. Circles=no sulfite, triangles=2% sulfite (based on o.d. wood), diamonds=4% sulfite and squares= 6% sulfite.](image)
Figure 2. Fibre length of aspen CTMP as function of deacetylation and the sum of demethylation and sulfonation for TMP and alkaline (circles), alkaline sulfite (triangles) and alkaline peroxide (diamonds) pre-treated pulps. Alkali dosages were 0.5, 1 and 3% NaOH (based on o.d. wood) in alkaline (A) and alkaline sulfite (AS) pre-treatments and 1, 2 and 6% NaOH in alkaline peroxide (AP) pre-treatments.

Sulfonation did not play a very important role for the preservation of fibre length in aspen CTMP refining, in contrast to earlier findings [16]. The sulfonation degree is much lower for aspen than for spruce, due to lower lignin content and differences in lignin composition. Oxidation by peroxide did not affect the defibration. It was not possible to distinguish the significance of deacetylation and demethylation separately for aspen. Both these reactions had approximately the correlation for fibre length. The aspen CTMP fibre length was not better preserved at low degrees of demethylation and sulfonation (Figure 2).

**Effect of De-esterification and Sulfonation on SEC**

Figure 3. Specific energy consumption (SEC) for spruce CTMP as function of (A) deacetylation, (B) demethylation, (C) sulfonation, and (D) the sum of demethylation and sulfonation for A and AS pre-treated at 60°C. See figure 1 for symbol description.

The effect of the CTMP reactions on the SEC of refining is shown in Figure 3. For the A and AS pre-treatments, the correlation between the degree of GGM deacetylation and SEC was modest, $R^2 = 0.45$. Sulfonated samples (indicated with triangles, diamonds and squares) tended to have slightly higher SEC than the non-sulfonated pulps (indicated by circles), compared at the same deacetylation degree. Pectin demethylation correlated slightly better with SEC. Lignin sulfonation resulted in three almost parallel lines,
depending on the alkali dosage. Increasing degrees of lignin sulfonation correlated well with increasing SEC. When calculating the anionic groups formed by adding the degrees of pectin demethylation and lignin sulfonation, the correlation ($R^2 = 0.77$) was significantly improved. Nearly 30% of the dosed alkali is, however, consumed by other reactions than demethylation and deacetylation. Hydrolysis of possible lactone structures in 4-O-methyl-glucuronoxylans or ester-type LCC bonds may also create anionic groups. SEC for aspen CTMP increased when dosing low amounts of alkali, in the same way as for spruce. This phenomenon is probably intensified in the Wing defibrator compared to what could be observed in a full-size disc refiner. However, it seems that the wood material needs a specific alkali dose in order to soften enough for decreased energy demands in refining (Figure 4).

Pulp properties are usually compared at a specific freeness. This is not always an ideal approach since freeness is not necessarily a reflection of the fibre properties. The SEC of the refined spruce pulps was, for this reason, also compared at the same tensile index (20 Nm/g). The conclusions drawn for the correlations of SEC compared at the same freeness also holds for SEC compared at the same tensile index. The correlations of deacetylation and demethylation were, however, slightly higher when calculating SEC at a specific tensile strength than at the same freeness (Figure 5).

Figure 4. Specific energy consumption (SEC) for aspen CTMP as functions of deacetylation and the sum of demethylation and sulfonation for A, AS and AP pre-treatments. See figure 2 for symbol description.

Figure 5. Specific energy consumption (SEC) for spruce CTMP at a tensile strength of 20 Nm$^2$/g for spruce CTMP as function of deacetylation, demethylation, sulfonation, and the sum of demethylation and sulfonation for A and AS pre-treated at 60°C. See figure 1 for symbol description.
Effect of De-esterification and Sulfonation on Bulk and Strength Properties

The bulk property can be considered as an expression of the degree of fibre collapse. It could then be presumed that the bulk should be affected by reactions occurring in the thick secondary cell walls more than in the relatively thin compound middle lamella. The GGM deacetylation had indeed a high correlation with bulk, $R^2 = 0.69$, while the corresponding value for pectin demethylation was slightly lower ($R^2 = 0.54$). The bulk for the sulfonated samples was on the same level as the non-sulfonated, indicating that sulfonation has a low effect on bulk. The sum of the demethylation and sulfonation gave a low linear correlation, $R^2 = 0.38$. Consequently, GGM deacetylation seems to be an important factor for the decrease in hand-sheet bulk. The total amount of GGM in spruce wood is approximately 20% of the wood mass. Splitting of the acetyl groups may result in structural changes and possibly also formation of new hydrogen bonds between the GGM polymer chains, decreasing its specific volume. Other possible alkali-induced reactions, mentioned earlier, could also play a role in the loss of bulk under alkaline conditions.

Paper strength is determined by the bonding strength between fibres, but also by the internal fibre strength and the size of the fibres, i.e. length and width. Both lignin sulfonation and pectin demethylation have a strong influence on the fibre dimensions. It could, therefore, be assumed that these two reactions would have a strong effect also on the strength properties. The fibre length has, by a rule of thumb, a high influence on the tear index. Similar type of correlations was observed for the tear index and the fibre length. The sum of demethylation and sulfonation was significantly better correlated to tear index than deacetylation or demethylation (figures not shown). Generally, it is said that tensile strength is a manifestation of fibre-fibre bonding. The bulk should then be proportional to the tensile index. This is probably the case for pulps with comparable fibre lengths. In this work, however, the tensile index was strongly influenced by sulfonation.

![Figure 6. Bulk for spruce CTMP as function of deacetylation, demethylation, sulfonation and the sum of demethylation and sulfonation for A and AS pre-treated at 60°C. See figure 1 for symbol description.](image)

Effect of Reactions by Peroxide on Pulp and Paper Properties

The effects of AP treatments on the pulp and paper properties are shown in Figure 7. The presence of peroxide will oxidize lignin structures and thus increase the amount of anionic groups. The rate of this reaction was not quantified, but a comparison was made against the degree of de-esterification. The pulps treated with only alkali (circles) are the same as in Figures 1, 3 and 6. Based on these results, peroxide has no effect on any of the pulp and paper properties studied. A good correlation was obtained for the fibre length ($R^2 = 0.90$), and this finding supports the importance of the demethylation on this parameter. It should be noted that these samples contained no sulfonic groups.
Figure 7. Average fibre length, specific energy consumption (SEC), and bulk for spruce CTMP as function of demethylation for A and AP pre-treated at 60°C. Circles = no peroxide, triangles = 2% peroxide (based on o.d. wood), diamonds = 4% peroxide and squares = 6% peroxide.

**Multivariate Analysis**

To mathematically differentiate and single out the significance of the CTMP reactions, the experimental data for spruce pre-treatments at 40, 60 and 80°C were subjected to multivariate analysis. The independent parameters of the models were (1) GGM deacetylation, (2) pectin demethylation, (3) lignin sulfonation, and (4) the unspecified alkali consumption (total alkali consumption with deacetylation and demethylation subtracted).

The dependent parameters were: SEC, fibre length, fibre width, tear index, tensile index, and bulk. The partial least squares (PLS) approach was used for correlation in combination with the leave-one-out approximation for cross validation of the independent parameters. Root-Mean-Square Error of Cross-Validation (RMSECV) was calculated on scaled and centred data with two latent variables integrated into the models. A number of different models were created using different combinations of independent parameters (Table 1). The mean and standard deviation (SD) for the dependent parameters are also presented. Each independent parameter is present in seven of the 11 models. Their individual impact on the dependent parameters can be estimated from the RMSECV values of the models. An “error factor” (Equation 1) was calculated for each independent parameter from the RMSECV values of the models. The RMSECV of the models in which the specific parameter was not present was set to zero. These relative numbers describe the order of significance of the independent parameter on the calculated models. If an independent parameter is significant, the “error factor” for this parameter will be low.

\[
\text{Error Factor} = \sum_{i=1}^{N} \frac{(\text{RMSECV}_i - \text{RMSECV}_{\text{min}})}{N} 
\]  

(1)
In equation 1 is N the total number of models and RMSECV_{min} is the lowest RMSECV value among the models (best fit). The RMSECV_{min} was subtracted from the RMSECV values of the other models. This operation will focus the variation between the models and allow the independent parameters to be compared at the same scale (Figure 8). However, the absolute “error factor” values cannot be compared between the different dependent parameters.

Table 1. Root-Mean-Square Error of Cross-Validation (RMSECV) for calculated models of scaled and centred data obtained from the spruce CTMP trials

<table>
<thead>
<tr>
<th>Independent Parameters</th>
<th>SEC, MWh/ton (2.93, 0.57)</th>
<th>Length, mm (2.42, 0.08)</th>
<th>Width, µm (32.12, 0.36)</th>
<th>Tear, mN/m²/g (7.30, 0.80)</th>
<th>Tensile, Nm/g (18.73, 1,44)</th>
<th>Bulk, m³/ton (3.96, 0.21)</th>
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<td>0.69</td>
<td>0.95</td>
<td>0.96</td>
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</tr>
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<td>0.86</td>
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<td>0.94</td>
<td>0.78</td>
</tr>
<tr>
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<td>0.41</td>
<td>0.81</td>
<td>0.88</td>
<td>0.87</td>
<td>0.83</td>
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<td>0.84</td>
<td>0.88</td>
<td>0.89</td>
<td>0.81</td>
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<td>0.70</td>
<td>0.97</td>
<td>0.96</td>
<td>0.96</td>
<td>0.79</td>
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<td>0.45</td>
<td>0.84</td>
<td>0.89</td>
<td>0.87</td>
<td>0.79</td>
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<tr>
<td>2, 3, 4</td>
<td>0.50</td>
<td>0.30</td>
<td>0.84</td>
<td>0.87</td>
<td>0.88</td>
<td>0.79</td>
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<tr>
<td>1, 2, 3, 4</td>
<td>0.49</td>
<td>0.36</td>
<td>0.83</td>
<td>0.88</td>
<td>0.88</td>
<td>0.78</td>
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</table>

Parameters: (1) Deacetylation, (2) demethylation, (3) sulfonation, (4) unspecified alkali consumption

The fibre length and width and the tear index were found to be highly dependent on sulfonation, followed by pectin demethylation, while GGM deacetylation had the lowest impact (Figure 8). The close relationship between fibre length and tear index could thus be confirmed. The order of significance for tensile index and tear index differed in some aspects. Sulfonation seemed to be most significant for the tensile index, probably because of its strong effect on fibre length. In contrast to the tear index, the significance of deacetylation and the unspecified alkali consumption was higher than demethylation for the tensile index. Sulfonation had the highest impact on SEC, followed by the unspecified alkali consumption, and deacetylation. The impact of demethylation was the lowest. The hand-sheet bulk was mostly dependent on the deacetylation and the unspecified alkali consumption, whereas sulfonation had the lowest impact.

Figure 8. Calculated error factors, showing the significance of the different reactions in spruce CTMP. A low value indicates a high significance on the pulp property determined. Unspecified alkali consumption is the total alkali consumption with the de-esterification reactions subtracted. It should be noted that the absolute error factor values cannot be compared between different dependent parameters.
CONCLUSIONS

De-esterification and sulfonation reactions, creating new anionic groups in the middle lamella and primary wall layers, are the key chemical reactions in spruce chemithermomechanical pulping. The fibre length was considerably better preserved even at low additions of sulfite compared to TMP. The specific energy consumption (SEC) in refining was significantly increased by sulfonation. The unspecified alkali consuming reactions (other than deacetylation and demethylation) also increased the SEC. Formation of AGs in the secondary walls might increase the fibre flexibility and compressibility, which in turn will result in increased SEC. The strong correlation between fibre length and tear index was confirmed. GGM deacetylation was more significant for the tensile strength than pectin demethylation. The bulk decreased linearly with the degree of deacetylation. Splitting of the voluminous (bulky) acetyl groups of GGM, primarily in the secondary wall, seems to be an important factor for fibre collapse. The loss in bulk enables increased fibre-fibre contact areas resulting in improved tensile indices of the paper.

ACKNOWLEDGEMENTS

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References

De-esterification and sulfonation in CTMP: Effects on pulp and paper properties

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- Finnish Funding Agency for Technology and Innovations (Tekes)
- Academy of Finland - Finnish Centre of Excellence Programme (2000-2011)
Background

- Highly acetylated *galactoglucomannans* (GGM) in spruce or *xylans* in aspen mainly located in the S-wall

- *Pectins* (highly methylated galacturonic acids) mainly located in the thin P-wall

- Lignin concentration highest in the ML, but *coniferyl alcohol* and *coniferylaldehyde* units mainly located in the P-wall region
Key reactions in CTMP?

- **Deacetylation** of GGM in softwoods and xylans in hardwoods by alkali.
- **Demethylation** of pectins by alkali.
- **Sulphonation** of lignin structures by sulphite.
- **Oxidation** of lignin by peroxide.
- Other alkali consuming reactions?
Aims

Assessing the role and significance of the key CTMP reactions towards the final pulp and paper properties
Lab-scale spruce CTMP

- Spruce CTMP pre-treatment liquors

<table>
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<tr>
<th>Chemical dosages</th>
<th>NaOH, %</th>
<th>Na$_2$SO$_3$, %</th>
<th>H$_2$O$_2$, %</th>
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<td>Water (TMP) and Alkaline (A)</td>
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<td>Sulfite (S) and Alkaline Sulfite (AS):</td>
<td>0 / 1 / 2</td>
<td>2 / 4 / 6</td>
<td>-</td>
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<tr>
<td>Alkaline Peroxide (AP)</td>
<td>1 / 2</td>
<td>-</td>
<td>2 / 4 / 6</td>
</tr>
</tbody>
</table>

- Heat-treatment for 30 min at 40°C, 60°C or 80°C
## Lab-scale aspen CTMP

### Aspen CTMP pre-treatment liquors

<table>
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<th>Chemical dosages</th>
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<th>H$_2$O$_2$, %</th>
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<tr>
<td>Water (TMP) and Alkaline (A)</td>
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<tr>
<td>Alkaline Sulfite (AS):</td>
<td>0.5 / 1 / 3</td>
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<tr>
<td>Alkaline Peroxide (AP)</td>
<td>0.5 / 1 / 3</td>
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</table>

### Heat-treatment for 30 min at 60°C
Lab-scale CTMP of spruce and aspen

- **Refining** in a “Wing Defibrator” batch refiner

![Refining in a “Wing Defibrator” batch refiner](www.tkk.fi/Units/Pulp/equipment.html)
Chemical analysis of pulps

- **De-esterification (residual methyl-esters and acetyl groups)**
  - Alkaline hydrolysis of wood and pulps
  - Chromatographic quantification of released methanol and acetic acid

- **Sulphonation (Sulphonic groups)**
  - Quinoline sorption

- **Total alkali consumption**
  - Acid titration of residual alkali
Determined pulps and paper properties

- Specific energy consumption (SEC)
- Freeness (CSF)
- Fibre dimensions (Kajaani FibreLab)
  - Fibre length and width
- Testing of hand-sheets
  - Tear and tensile index
  - Bulk
  - (Light scattering)
CTMP reactions vs. pulp and paper properties

- Correlation analysis in x-y diagrams through $R^2$-values
- Multivariate analysis
Results
Pulp and paper properties vs. Freeness

- Specific energy consumption, MWh ton⁻¹
- Average fibre length, mm
- Bulk, m³ ton⁻¹
- Tear index, nNm² g⁻¹
Fibre length for spruce CTMP

Demethylation

- 1% NaOH
- 2% NaOH

“TMP”
Fibre length for spruce CTMP

Demeth. + Sulf.

- 6% Na₂SO₃
- 4% Na₂SO₃
- 2% Na₂SO₃

No alkali !!
Fibre length for spruce CTMP

Demeth. + Sulf.

- 6% Na$_2$SO$_3$
- 4% Na$_2$SO$_3$
- 2% Na$_2$SO$_3$
- 1% NaOH

Demethylation and sulfonation, µmol/g
Fibre length for spruce CTMP

Demethylation and sulfonation, µmol/g

2.0 2.2 2.4 2.6 2.8
0 20 40 60 80 100

+ 2% NaOH

+ 2% NaOH

4% Na₂SO₃

6% Na₂SO₃

2% Na₂SO₃

Demeth. + Sulf.
Fibre length for spruce CTMP

![Graph showing fibre length for spruce CTMP with a linear regression line and an R^2 value of 0.92.](image)

Demethylation and sulfonation, µmol/g

Demeth. + Sulf.
Fibre length for spruce CTMP

Deacetylation

Demethylation

Sulfonation

Demeth. + Sulf.

De-esterification and sulfonation, µmol/g
Specific energy consumption, MWh/ton

Deacetylation $R^2 = 0.45$

Demethylation $R^2 = 0.56$

Sulfonation $R^2 = 0.77$

De-esterification and sulfonation, µmol/g
Bulk, m³/ton

Deacetylation
R² = 0.69

Demethylation
R² = 0.54

Sulfonation
R² = 0.38

De-esterification and sulfonation, µmol/g
Multivariate analysis for spruce CTMP

Root-Mean-Square Error of Cross-Validation (RMSECV) was calculated on scaled and centred data

<table>
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<tr>
<th>Independent parameters</th>
<th>SEC, MWh ton⁻¹</th>
<th>Fibre length, mm</th>
<th>Fibre width, µm</th>
<th>Tear index, mNm² g⁻¹</th>
<th>Tensile index, Nm g⁻¹</th>
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<td><strong>0.35</strong></td>
<td>0.87</td>
<td><strong>0.86</strong></td>
<td>0.900</td>
<td>0.826</td>
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<tr>
<td>2, 4</td>
<td>0.78</td>
<td>0.67</td>
<td>0.98</td>
<td>0.93</td>
<td>0.942</td>
<td>0.784</td>
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<td>3, 4</td>
<td>0.48</td>
<td>0.41</td>
<td>0.81</td>
<td>0.88</td>
<td>0.869</td>
<td>0.830</td>
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<td>1, 2, 3</td>
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<td>0.39</td>
<td>0.84</td>
<td>0.88</td>
<td>0.888</td>
<td>0.806</td>
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<td>1, 2, 4</td>
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<td>0.70</td>
<td>0.97</td>
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<td>0.788</td>
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<td>1, 3, 4</td>
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<td>0.45</td>
<td>0.84</td>
<td>0.89</td>
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<td>0.790</td>
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<tr>
<td>2, 3, 4</td>
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<td><strong>0.30</strong></td>
<td>0.84</td>
<td><strong>0.87</strong></td>
<td>0.882</td>
<td>0.794</td>
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<tr>
<td>1, 2, 3, 4</td>
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<td>0.36</td>
<td>0.83</td>
<td>0.88</td>
<td>0.882</td>
<td>0.783</td>
</tr>
</tbody>
</table>

(1) Deacetylation, (2) demethylation, (3) sulphonation, (4) unspecified alkali consumption
Multivariate analysis for spruce CTMP

Error Factor = \sum_{i=1}^{N} \left( \frac{\text{RMSECV}_i - \text{RMSECV}_{\text{min}}}{N} \right)

Error factor

- Deacetylation
- Demethylation
- Unspecified
- Sulfonation

Alkali consuming reactions

SEC

Fibre length

Fibre width

Tear index

Tensile index

Bulk

Sulfonation
Conclusions

- **Fibre length, fibre width and tear index:**
  sulphonation > demethylation > unspecified alkali consumption > deacetylation

- **Tensile index and SEC:**
  sulphonation > unspecified alkali consumption > deacetylation > demethylation

- **Bulk:**
  deacetylation > unspecified alkali consumption > demethylation > sulphonation