Prediction of important sulphite pulp properties from NIR spectra

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Introduction

Borregaard Industries Ltd. produces sulphite pulp in a wide range of qualities from Norway Spruce. These pulps are mainly used as raw material in the manufacture of cellulose derivatives such as cellulose ethers, esters, nitrocellulose and viscose, as well as for microcrystalline cellulose. In the process of transforming wood chips to the desired products, the first steps take place in batch reactors. While the wood chips are being processed in the reactors, there is at present time no possibility to measure the properties of the solid phase contents. Such information would be very useful for the decision of when the cook should be ended, and thereby lower chemical composition variation of unbleached pulp produced.

The pulp and paper industry has used near infrared (NIR) spectroscopy as a tool for predicting important process parameters for several years. The parameters are often difficult and time consuming to analyse by traditional wet chemical methods, so there is a need for robust, online measurements. NIR spectroscopy can provide this, but spectroscopic predictions require robust calibration models. Other advantages with NIR are accurate measurements and the possibilities for remote data transfer.

In this study prediction of pulp properties with NIR spectroscopy on cooking liquor and pulp for spruce sulphite cooking has been investigated. The main focus has been to investigate if there is potential for using NIR measurements on the cooking liquor. If so, NIR-spectroscopy can be used to make decisions in the mill operation.

Much of earlier work with NIR spectroscopy in pulp and paper research has been prediction of pulp properties based on NIR spectra on pulp.[1-4] NIR spectroscopy has also been investigated substantially for prediction of chemical parameters in kraft cooking liquor.[5-8] The chemical composition of cooking liquor serves as a fingerprint of the associated pulp. Some investigations have been made to predict kraft pulp properties with spectroscopic methods on the cooking liquor.[9,10]

At Borregaard, wood chips and cooking acid is mixed in batch reactors at a certain ratio. The mixture is then heated and pressurized according to specific recipes. During the cooking procedure, the chemical compounds in the wood, i.e. lignin, hemicellulose and cellulose, are continuously decomposing and the molecular fractions dissolve into the cooking liquor. The amount of organic material removed from the chips is therefore directly correlated to the amounts in the cooking

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liquor. The idea that NIR spectra on cooking liquor can be used to predict sulphite pulp properties should therefore be promising.

Predicted process parameters

Viscosity and Kappa No. are two important parameters of the produced pulp. Viscosity is a measure of the chain length of the carbohydrates in the pulp and the Kappa No. is an indirect method for measuring the remaining lignin content in the pulp. The balance between cellulose- and lignin degradation is critical to the process, and the degree of success will dependent on the differences in degradation kinetics for the two compounds.

Experimental

The experiment was constructed as a 2^2*8 factorial design, without replicates.[11] The factors were chip quality, cooking recipe and time at top temperature (eight levels). The experiment was performed in an autoclave digester system at the laboratory at Borregaard, in order to avoid irrelevant noise from the mill operation.

In the design of the experiment a large range for both viscosity and Kappa No. was chosen. Viscosity and Kappa No. were measured according to standard SCAN procedures.[12,13] NIR spectra were measured on both pulp and cooking liquor produced in the autoclave reactors. The NIR instrument used was Spectrum One NTS, FT-NIR Spectrometer (PerkinElmer, UK). The wavelength range for both pulp and liquor was 1000–2500 nm. The liquor samples from the first autoclave cook were however measured at the range 1100–2500.

The data was treated by the Unscrambler, ver. 7.6, Camo, Norway, and prediction models, based on NIR spectra on the cooking liquor and pulp, were developed for the pulp qualities. Three different regression methods were investigated; principal component regression (PCR) and partial least square with one or more responses (PLS1 and PLS2).[14]

The NIR spectra on the cooking liquor were measured on unfiltered samples, which means they contained some particles. Inhomogeneity was also a problem with the pulp samples. Some of these effects were filtered off by removal of the additive and/or multiplicative effects. The additive effects were removed by using the first derivative of the NIR spectra, and the multiplicative effects were removed by the second derivative. Both effects were filtered off by the multiplicative scatter correction (MSC).[14]

The models were evaluated based on root mean square error of prediction (*RMSEP*), for full cross validation. In addition the correlation coefficient between the measured and predicted responses were studied. The principal components was interpreted based on the score plot form the Unscrambler and analysis of variance (ANOVA) in Minitab, ver. 13.32, Minitab Inc., UK.

Results

The most important result from this investigation is that there is good potential for prediction of pulp viscosity and Kappa No. using NIR spectra on cooking liquor. This is documented in Table 1. The investigation showed that PLS1 on 1st derivatives of the NIR spectra generally gave the lowest RMSEP, highest correlation coefficient and the lowest number of principal components.

Response ranges

In the design of the experiment a large range for both viscosity and Kappa No. was chosen.

Table 1. Trial range for Kappa no. and viscosity, with average.

	Minimum:	Maximum:	Average:
Kappa. no*	3,46	102	39,1
Viskosity, ml g^{-1}	150	1634	985,2

*The Kappa No. has no specific unit, but is defined as "the number of millilitres of 0,1 N $KMnO_4$ solution which is absorbed by 1 g of moister free pulp under certain specified and carefully controlled conditions".[15]

RMSEP and correlation

Table 2 presents the prediction results for viscosity and Kappa No. in pulp based on NIR spectra on the pulp itself.

Table 2. Results for PLS1 calibration models on 1st derivatives of NIR spectra for cooking liquor and pulp.

Response	RMSEP, 1 derived	Corr., y - y_{pred}	Number of principal components
Viscosity, NIR on cooking liquor	110,6	0,98	6
Viscosity, NIR on pulp	138,2	0,97	2
Kappa No., NIR on cooking liquor	9,0	0,96	4
Kappa No., NIR on pulp	3,1	0,99	3

It is interesting to observe that the prediction of viscosity gives a slightly lower RMSEP and higher correlation between measured and predicted values when NIR spectra of cooking liquor are used, compared to NIR on dried pulp. One should expect the opposite, since the viscosity is measured on the pulp itself. This observation must be verified in new experiments. However, the number of principal components dropped from six to two, which indicates that even though the model has a slightly lower predictive ability, there are fewer sources of variation included in the models when NIR is measured directly on the pulp.

The NIR spectra of the cooking liquor were measured in the range 1000–2500 nm for the last three cooks. The first cook was however measured at a slightly smaller range, 1100–2500 nm. Due to instrument failure, the two ranges had different resolution. In the best possible way this was adjusted for, but the difference still dominated the first principal component. This led to at least one extra principal component in the models. The second principal component seems largely made up of recipe, cooking time and temperature.

During each cook the autoclaves were taken out at different times and instantly cooled to room temperature. This drop in temperature should stop the cleavage of the cellulose chains and degradation of lignin.

Bias effects between predicted and measured response

The quality range of the pulp tested in this experiment is quite large. It is therefore interesting to see if there are bias effects between predicted and measured values over this range. This can be illustrated in Bland–Altmann diagrams. In such a diagram the x-axis indicates the average between the measured and predicted response, and the y-axis the difference between the two. In Figure 1 the Bland–Altmann diagram for viscosity and NIR spectra of the corresponding liquor and pulp is given. As shown, the bias does not increase with increasing viscosity.

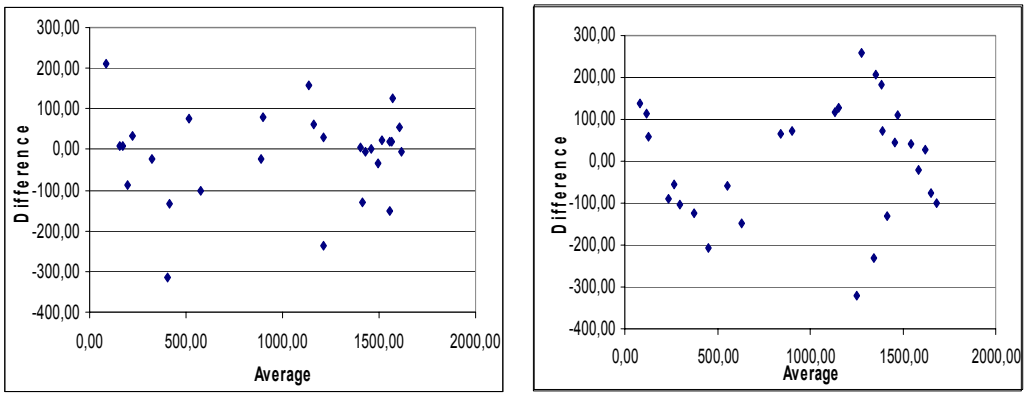

Figure 1. Bland-Altmann diagram for viscosity and NIR on the corresponding (a) liquor and (b) pulp.

Figure 1(b) indicates that there is an increasing bias with increasing viscosity when the predictions are based on NIR on pulp. This is different from what is observed when using NIR on the cooking liquor [Figure 1(a)]. The difference may be explained by the number of principal components used in the models. The model with NIR on the cooking liquor is based on six PC's, whilst the one on pulp is based on only two. This indicates that more of the variation is included in the model with cooking liquor. Due to high content of lignin in the pulps with viscosity above 1300 –1400 ml g^{-1}, these samples were bleached in the laboratory. This introduces a variance that may be included in the model with six PC's, and not the in the one with two.

In Figure 2(a) the Bland–Altmann diagram for Kappa No. and NIR on cooking liquor is shown.The bias is relatively stable over the Kappa No. range, with differences varying from –10 to 10. The diagram reveals some outliers.

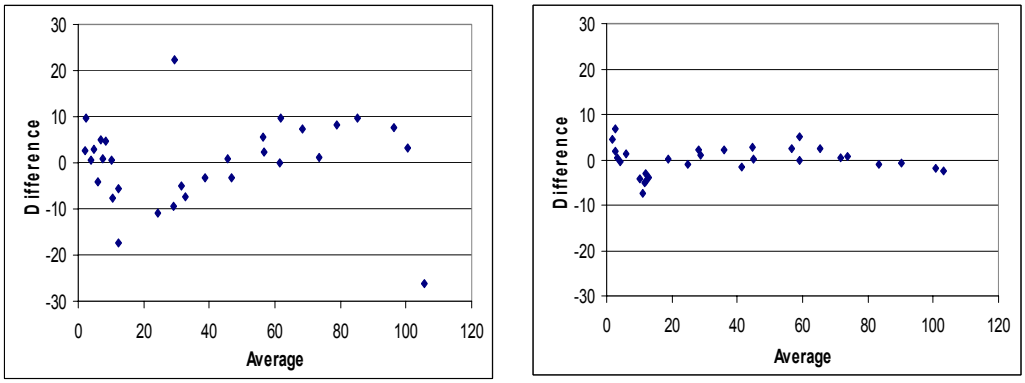

Figure 2. Bland–Altmann diagram for Kappa No. and NIR on the corresponding (a) liquor and (b) pulp.

Figure 2(b) shows the Bland–Altmann diagram for the Kappa No. and NIR on pulp. As shown, there is less bias when the Kappa No. model is based on NIR on pulp than with NIR on cooking liquor. The cooking liquor was cooled down before measuring NIR spectra, which may have caused this. NIR spectra are dependent on temperature and the character of the cooking liquor changes considerably when cooled down. This may be because of condensation reactions of dissolved lignin. Accordingly the correlation between the liquor and the pulp became less than when NIR were measured on the pulp. The character of the pulp does not change significantly with temperature. This is probably why the model with NIR on cooking liquor gave larger bias than the one based on NIR of pulp. This effect was not seen in the viscosity plot, but may have been disguised by the much larger difference between measured and predicted values.

Discussion and conclusions

Some of the important results from this investigation are the root mean square of prediction (*RMSEP*), correlation between predicted and measured responses and explained variance. In Table 2 one can see that the *RMSEP* are relatively low and the correlation is high (0.96–0.99) for the PLS models. The methodology therefore seems very promising.

The models were however established on a relatively small data set, in an autoclave digester system in the laboratory. They must therefore be tested and expanded in order to make good, robust models. This can be done both by repeating the test already performed, but also by spreading out the variation in new directions that have not yet been tested. These directions may be season variation in wood chips, geographical variation from where the timber comes from, variation in wood chip shape, etc. Possibilities also lie in the prediction of other pulp qualities than the ones used in this investigation, that may have large impact on the mill operation. Finally, the real challenge comes in scaling up from the laboratory to the mill.

If good, robust prediction models for sulphite pulp quality based on NIR spectra of the cooking liquor can be established, Borregaard will have a new powerful tool for controlling the pulp quality in the mill digesters. This will help mill operators to stop the cooking process in time, and thereby raise the amount of pulp produced within specification. This will stabilise the production line through the bleaching plant, and lead to more controlled operation all the way to the final product.

In conclusion, the results from this investigation indicate that there is potential for establishing good prediction models for the measurement of viscosity and Kappa No. of spruce sulphite pulps by using NIR on cooking liquor and pulp in the chip digesters at Borregaard.

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