Statistical modeling and sizing determination guides for dispersed rosin sizes

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ABSTRACT: Four cationic dispersed rosin sizes were studied in terms of their performance when pH, temperature, and water hardness were varied. Three of the sizes were based on fortified rosin with different concentrations of fumaric acid, and the fourth size was based on esterified rosin. Statistical tools are used to refine and simplify an earlier model proposed by Nitzman and Royappa, who first examined the relationship between sizing and the factors of pH, temperature, water hardness, and fortification. The simplified models provide some insight into the differences between esterified sizes and fortified sizes in terms of paper sizing. Based on the algorithmic modeling approach, guidelines are proposed for choosing different levels of pH, temperature, and water hardness for use with different rosin sizes.

Application: Guidelines for the values of pH, temperature, dosages, and water hardness can be used to help control sizing in paper mills.

Paper sizing is determined by several factors, including pH, water hardness, and temperature. Based on a study of these three factors on cationic dispersed rosin sizes [1], Nitzman and Royappa proposed two models for the two different types of sizes, esterified sizes and fortified sizes. The two models fit the data reasonably well and revealed some important patterns in the relationship between sizing and the factors examined.

However, the models have two drawbacks. First, the sizing evaluated by an HST value is always positive whereas the prediction range of linear regression models is from $-\infty$ to $+\infty$. Consequently, the regression models could provide bad predictions of sizing for some combination of factor levels and therefore are not appropriate for some situations. Second, each model is a full, second-order polynomial regression model. The full model for the esterified sizes has 15 terms, and the model for the fortified sizes has 20 terms. In many situations, a full model is not needed, and a smaller model can provide a good fit to the data.

Here, we refine this model by addressing these two issues. If one can predict sizing for certain levels of factors, then the paper sizing process can be brought under more rational control. Based on this consideration, we also provide guidelines for controlling sizing by setting restrictions on the range of variation for each factor.

BACKGROUND

In the earlier study, Nitzman and Royappa conducted experiments on four cationic dispersed rosin sizes to examine the effects of pH, water hardness, and temperature [1]. One size was based on esterified rosin. They selected esterified rosin size because its paper sizing is expected to be robust at higher pH values [2, 3]. The other three sizes were based on fortified rosin with three concentrations of fumaric acid, from 3% to 15%. Cationic dispersed sizes were selected because they are known to be efficient over a wide range of pH.

For each factor, they considered three different levels. Three levels of acidity, three temperatures, three dosage levels, and levels of hardness were used, all of which are listed in **Table I** as independent values. Nitzman and Royappa evaluated the paper sizing and studied the dependence of sizing on these various factors. Sizing was evaluated with a Hercules Sizing Tester (HST).

A first-order and a second-order polynomial linear regression model were proposed for each of the two different types of sizes [1]— fortified rosin sizes and esterified size. Although we do not consider the first-order models here, the format for the second-order model is given in Eq. 1:

$$\begin{aligned}\hat{HST} = {} & c_0 + c_1x_1 + c_2x_2 + c_3x_3 + c_4x_4(+c_5x_5) \\ & + (c_6x_1^2 + c_7x_2^2 + c_8x_3^2 + c_9x_4^2(+c_{10}x_5^2)) \\ & + (c_{11}x_1x_2 + c_{12}x_1x_3 + c_{13}x_1x_4(+c_{14}x_1x_5) \\ & + c_{15}x_2x_3 + c_{16}x_2x_4(+c_{17}x_2x_5) \\ & + c_{18}x_3x_4(+c_{19}x_3x_5 + c_{20}x_4x_5)) \qquad (1)\end{aligned}$$

where

- x_1 = temperature, °C
- x_2 = dosage, %
- x_3 = pH
- x_4 = hardness, ppm
- x_5 = fortification, % (where applicable).

Also, c_0 is the intercept, c_i, with i = 1, ... 20, are the coefficients, and *HST* with a caret over it stands for the estimated HST values for a combination of factor levels. The coefficients for these two cases are shown in **Table II**.

RESULTS AND DISCUSSION

Model refinement

As mentioned, we found two drawbacks. First, the model is not appropriate for some situations, when a combination of factor levels indicates a value on the negative side of a range. Second, a smaller model is more appropriate for those situations in which a full model is not needed. Therefore, we can refine the model by providing a proper range for predicting sizing and then simplifying the model.

To solve the first problem, we considered a mathematical transformation of the data. Here, we use the natural logarithmic transform. When we express HST values in the natural log scale, the transformed HST values vary from $-\infty$ to $+\infty$, which eliminates the problem discussed earlier. Furthermore, since this transformation is monotonically increasing, it does not change the pattern of sizing. We have used transformed HST values throughout the rest of this section.

pH	Temp., °C	Dosage %	Dosage lb/ton	Hardness, ppm $CaCO_3$
5	40	0.35	7	135
6	50	0.50	10	270
7	60	0.65	13	600

I. Independent experimental levels for each factor.

Coeffs.	Fortified size	Esterified size
c_0	1952	–11.254
c_1	–41.279	20.826
c_2	3480	2441
c_3	–298.483	–125.721
c_4	–0.869	–0.493
c_5	38.923	—
c_6	–0.03791	–0.21422
c_7	477.531	1028
c_8	–8.235	9.389
c_9	1.017×10^{-3}	8.948×10^{-4}
c_{10}	–2.972	—
c_{11}	–5.459	–33.600
c_{12}	7.029	0.384
c_{13}	-2.917×10^{-3}	-4.607×10^{-3}
c_{14}	0.101	—
c_{15}	–386.586	–173.315
c_{16}	–0.343	0.04729
c_{17}	–44.876	—
c_{18}	0.04212	4.820×10^{-3}
c_{19}	2.714	—
c_{20}	4.824×10^{-3}	—

II. Coefficients for the second-order polynomial model for the two types of sizes (5).

	Esterified size	Fortified sizes
Test statistics	0.4140	0.1995
Degrees of freedom		
Numerator	8	7
Denominator	81	243
P value	>0.9	>0.9

III. Results of the goodness-of-fit test.

The general plan of attack for solving the second problem was to use a simplified model having fewer terms than the full model has. Whether or not to include a term in the model was determined by the contribution of the term toward the explanation of variation in sizing. This procedure is called "model selection" and was done with a statistical analysis system.

There are different ways to select a model. There is backward model selection, which starts from the full model, with one insignificant term deleted in each step until all the terms are significantly effective. There is also forward model selection, which starts from a model having only the intercept, with one significant term added in each step until no more terms can be added. Finally, there is stepwise model selection, in which each step adds or deletes a term based on how significant the term is. The models selected using different methods are then judged by a commonly used statistical measure called "Mallows C_p" [4]. This measure gives the total squared errors. For an unbiased model, as indicated by Mallows [4], C_p should be close to or smaller than the number of terms in the model. Following this rule, the model with the smallest value of C_p is then selected as the final model fitting the data.

Equations 2 and 3 are the two models selected with Mallows C_p values of 2.3120 and 5.5728, respectively. Equation 2 is for the esterified size, and Eq. 3 is for the fortified rosin size.

$$\hat{S} = -34.7581 + 1.4602\times T - 9.8132\times D + 4.1244\times P - 0.01183\times T^2 - 0.1040\times T\times P + 0.3134\times T\times D \quad (2)$$

$$\hat{S} = -10.30294 - 0.23777\times T - 13.3754\times D + 8.38897\times P + 0.00115\times H + 1.17609\times F - 1.01113\times P^2 + 4.76\times 10^{-6}\times H^2 - 0.02589\times F^2 + 0.03794\times T\times P + 3.20548\times D\times P - 0.00099556\times P\times H - 0.1476\times P\times F \quad (3)$$

where S with a caret over it denotes the fitted sizing (in the scale of natural logarithm of HST values) for a combination of different factor levels. Also in these two simplified models, we use the first letter of each factor name to denote different factors: T is for temperature, D is for dosage, P is for pH, F is for fortification, and H is for hardness.

We noticed that in the model for the esterified size, water hardness is absent. Based on the model, this absence can be explained in that this factor's contribution to sizing variation is negligible according to the information from the data set we have. This phenomenon can be seen in the profile plot in **Fig. 1**. This profile is plotted as the values averaged across all other factor levels for each level of hardness. The average sizing first decreases and then increases as hardness increases. There is not much difference between the two larger HST values, and this pattern reveals that water hardness may not have a significant effect on sizing.

We can speculate on the chemical significance of this finding. Fortification increases the carboxylic acid groups on the rosin molecule; conversely, esterification decreases free carboxylic acid groups. Water hardness, which is caused by the presence of divalent calcium and magnesium ions, can precipitate nonsizing forms of rosin salts. Compared to fortified sizes, esterified sizes can have half the number of carboxylic acid groups, and thus the ester sizes are less affected by water hardness. The insignificant effect of water hardness means that we will have to look at a wider range of water hardness levels if we are to see its effects.

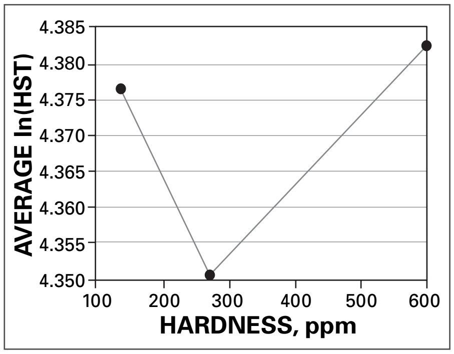
As we have seen from Eq. 1, the number of terms in the full models was 15 for the data on the esterified size, whereas the reduced model has 7 terms. There are 20 terms for the data of the fortified sizes, as opposed to 13 terms in the reduced model. The reduced models are therefore considerably simpler than the full models. Of course, a simplified model is not as good as the full model. Whether or not to accept a reduced model is determined by the amount of information lost upon simplification. If the loss is minor, one can use the reduced model to draw conclusions; otherwise, the full model must be used.

Whether the amount of loss is significant or not is determined by a goodness-of-fit test, which checks whether the reduction of the sum of squares of errors is significant or not. Let N denote the total number of observations, and let S_i, where $i = 1, ..., N$, be the HST value (in natural log scale) for i^{th} observation. The sum of squares of errors is then defined as:

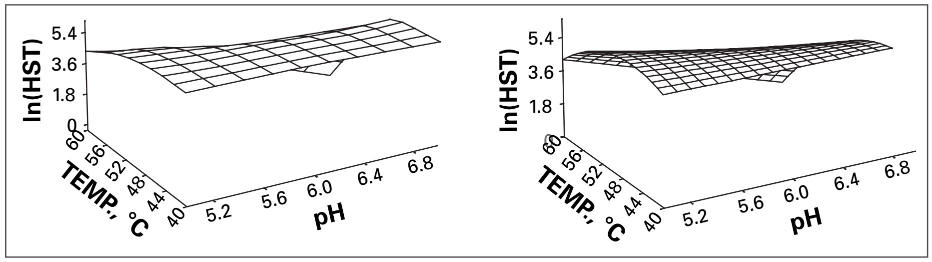
$$SSE = \sum_{i=1}^{N}(S_i - \hat{S}_i)^2, \quad (4)$$

in other words, the sum of squared differences between the observed HST values (in natural log scale) and the predicted HST values (in natural log scale).

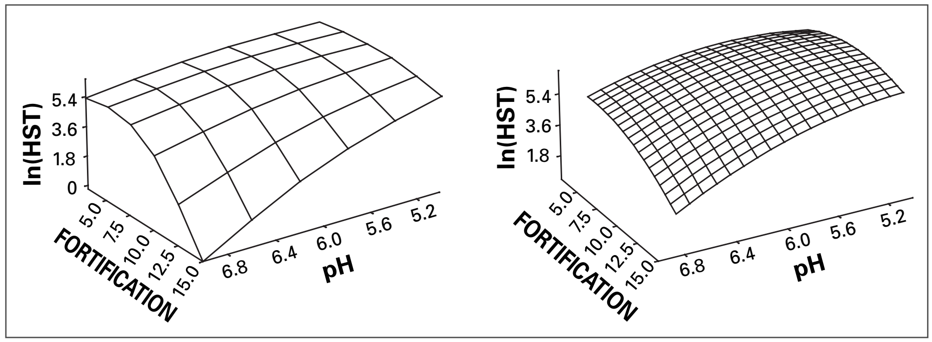
The null hypothesis is that the two models are equivalent, and the alternative hypothesis is that the full model is



1. The effect of hardness on sizing.



2. Relationship between temperature, pH, and ln(HST) for esterified size for experimental data (left) and fitted model (right).



3. Relationship between fortification, pH, and ln(HST) for fortified sizes for experimental data (left) and fitted model (right).

better than the simpler model. We use a test statistic to help determine whether or not we can reject the null hypothesis. The test statistic is calculated as:

$$F = \frac{(SSE_{\text{full}} - SSE_{\text{reduced}})/(n_{\text{full}} - n_{\text{reduced}})}{MSE_{\text{full}}} \quad (5)$$

where

SSE_{full}= sum of squares of errors (Eq. 4, summing over all N observations) obtained from the full model

$SSE_{reduced}$= sum of squares of errors (Eq. 4) obtained from the reduced (simpler) model

MSE_{full}= mean square errors for the full model with n_{full} terms, obtained by dividing SSE_{full} by $(N - n_{full})$

n_{reduced}= the number of terms in the reduced model.

Under the null hypothesis, the distribution of F is a central F distribution with numerator degrees of freedom $n_{\text{full}} - n_{\text{reduced}}$ and denominator degrees of freedom $N - n_{\text{full}}$. We use the P value method to draw conclusions about the hypothesis testing. The P model is defined to be the probability of getting a test statistic that is at least as extreme as the test statistic from the experiment data if the null hypothesis is true. If the P value is higher than a pre-specified significance level, then we reject the null hypothesis at the specified significance level. The commonly used significance levels are 0.01, 0.05, and 0.1.

Table III gives the summary of the goodness-of-fit test. The first row is for the test statistics based on the experimental data and calculated by Eq. 5. The second and third rows are for the degrees of freedom of the numerator and denominator of the test statistic for each situation, calculated as ($n_{\text{full}} - n_{\text{reduced}}$, $N - n_{\text{full}}$). From the P values indicated in the last row, we cannot reject the null hypothesis based on any commonly used significance levels. Therefore, the two reduced models are competitive with the two corresponding full models.

To visualize the fit of the two models to our data, we compared the patterns revealed by the data for the two sizes to the patterns revealed by the fitted model. The left graph in **Fig. 2** is from the data for the esterified size when the dosage was 0.50%. It reflects the relationship between pH values, temperature, and the natural logarithm of the HST values. The right graph is from the fitted model, Eq. 1, also at a dosage of 0.50%. The patterns shown by these two figures are quite similar, reflecting a good fit of the model to the data.

The graphs in **Fig. 3** are for the fortified sizes. The left graph is based on the data, and the right graph is derived from our model. The two figures reflect the relationship between fortification, pH, and the natural logarithm of HST with all other factor levels fixed. The values were fixed at 0.50% for dosage, 135 ppm for hardness, and 50°C for temperature. Again, the two figures reflected quite similar patterns, indicating the close fit of our model to the actual data.

Interpretation of results from the refined model

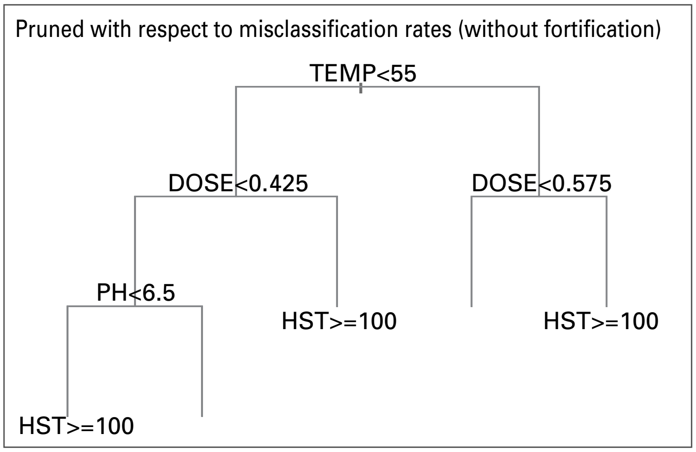
The interpretation of the results includes two parts. The first part is the coincidence between the full models and the reduced models, and the second part describes some patterns that we are not able to see if we are using full models.

As shown in Table III, the reduced model fits the data as well as the full model did. In other words, the reduced model revealed the same general patterns of sizing as the full model. The coincidence between the two models can be brought to light from (a) the relationship between sizing and each factor and (b) the relationship between a factor and the sizing with another factor involved.

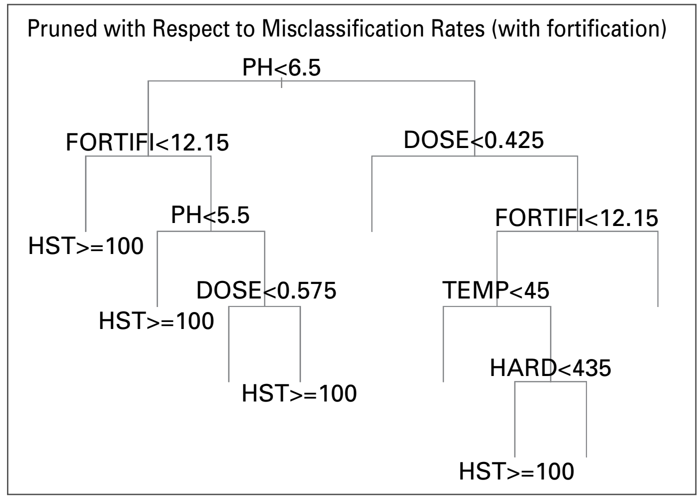
The relationship between sizing and each factor revealed by the reduced model is the same as that derived from the full model. The relationships presented here are the relationships between sizing and pH, sizing and dosage, and sizing and fortification. The relationships for the remaining factors can be examined similarly.

Sizing generally decreases with increasing pH and increases quickly with increasing dosage. The right graphs in Figs. 2 and 3 illustrate the first pattern. As the pH increases, the sizing decreases, but it decreases more quickly for fortified sizes. The relationship between sizing and dosage can be directly evaluated based on the newly fitted models by fixing the levels of the other factors.

For example, arbitrarily picking a temperature of 50°C and taking all the other



4. Classification tree for the esterified size.



5. Classification tree for the fortified sizes.

factors to be constant, the relationship found between sizing and dosage level from the reduced model is:

$$\begin{aligned}\hat{S} &= \text{constant} - 9.8132 \times D + 0.3134 \times 50 \times \mathrm{D} \\ &= \text{constant} + 5.8568 \times D \qquad (6)\end{aligned}$$

This relationship between dosage and sizing is clearly positive.

Similarly, for the fortified sizes, with all other factor levels fixed, the relationship between dosage and sizing is as follows, with pH taken to be 6:

$$\begin{aligned}\hat{S} &= \text{constant} - 13.3754 \times D + 3.2055 \times 6 \times D \\ &= \text{constant} + 5.8576 \times \mathrm{D} \qquad (7)\end{aligned}$$

Again, this is a positive relationship.

The reduced model also predicted the same pattern as that described by the full model for the relationship between sizing and fortification. Both models indicated that best sizing was obtained in the middle range of fortification, and as the pH rises, high fortifications yield low sizing.

The relationship between a factor and the sizing with another factor involved (i.e., the interaction) revealed from the reduced model is the same as that derived from the full model. Here we examine some relationships mentioned earlier [1].

The full model revealed that sizing was resistant to increasing pH when temperature was low, but it dropped quickly as pH increased when the temperature was high. The reduced model reflected the same pattern (Fig. 2, right graph). When the temperature is low, the plane is almost flat as the pH gets higher. This outcome indicates the resistance of sizing to the change in pH. When the temperature is high (higher than 50°C), the HST values (in log scale) decrease quickly with increasing pH. This result can be seen from the tilted plane for higher temperature.

Figure 3, right graph, shows that the effect from fortification is minor when pH is low but that it decreases quickly as pH gets larger.

Terms and trends

The reduced model also predicted the same pattern as that described by the full model for the relationship between sizing and fortification. Both models indicated that best sizing was obtained in the middle range of fortification, and as the pH rises, high fortifications yield low sizing.

In Eq. 2, only the temperature factor has a quadratic term. What does this imply? For esterified sizes, the relationship between sizing and any factor except temperature is linear when the rest of the factors are kept constant. On the other hand, the relationship between sizing and temperature with other factors kept constant is quadratic and has a maximum point for ln(HST) values. However, this quadratic pattern for the factor of temperature does not exist in the fortified sizes, as reflected by Eq. 3.

Why is the esterified size so much more dependent upon temperature than the fortified size? Presumably, the chemical bonds between the rosin and the cationic resins used to emulsify the size are stronger for the fortified size than for the esterified size. The added carboxylic acid groups in fortified sizes are stronger acids than the original carboxylic acid on the rosin. Consequently, fewer and weaker acid groups would be left after esterification. Therefore, the interactions between the rosins and cationic resins are less susceptible to disruption by higher temperatures for fortified rosins than for esterified rosins.

By comparing Eqs. 2 and 3, we find an interesting trend in the relationship between sizing and dosage. Generally this relationship is not affected by pH values for the esterified sizes, although it is affected by pH for the fortified sizes. For the fortified sizes, the larger the pH values, the more important the dosage becomes. This trend can be understood by considering that with increasing pH, there is greater ionization of the carboxylic acid groups; to counteract this occurrence, a higher dosage is needed to achieve the same sizing.

Size controlling guide

A guide for controlling size allows us to visualize the relationship between HST values and the different factor levels by setting up what is known as a "classification tree." For example, one may want to know what the values of pH, dosage, and temperature should be in order to make papers with an HST value greater than 100. Here, we provide guidelines for the ranges of factor levels to obtain an HST value of at least 100, which is a common level of sizing. Classification trees can be set up for other HST values as well.

The method for setting up the size controlling guide is different from the one we used for model refinement. According to Breiman, there are two "cultures" in using statistical modeling to draw conclusions from raw data [5]. In the first culture, or practice, the data are assumed to be generated from a stochastic data model, which Breiman refers to as "data modeling." This practice underlies model refinement. The other practice uses the data *per se* and treats the mechanism of data generation as unknown, a practice Breiman refers to as "algorithmic modeling."

As we have seen, data models can provide insight into prediction and can reveal overall trends in the data. However, since the algorithmic modeling approach does not rest on any assumptions regarding the data-generating mechanism, it can provide easily understood insights into experimental outcomes. Specifically, based on a statistical criterion (maximum reduction of deviance), it classifies each HST value in the data into one of k groups ($k > 0$) using the measurements of pH, temperature, etc.A tree is then built to display the relationships between the classified HST values and factor levels.

The tree is built based on the maximum reduction of deviance at every node in the tree. At any node in the tree, the split that maximally reduces the deviance in the left and the right branches is selected. Splitting continues until nodes are pure or data are too sparse. This type of tree is called a "regression tree" [6].

Figure 4 is the tree built for the esterified size, and **Figure 5** is for the fortified sizes. For a condition indicated at each node, if it is satisfied, then the left branch is applied; otherwise, the right branch is taken.

Figure 4 indicates that there are three approaches to get sizing with an HST value of at least 100 for the esterified size:

1. Set the temperature between 40° and 55°C and the dosage between 0.425% and 0.65%, with no restrictions on pH.
2. Set the temperature between 40° and 55°C, the dosage between 0.35% and 0.425%, and the pH between 5.0 and 6.5.
3. Set the temperature between 55° and 60°C and the dosage at no less than 0.575%, with no restrictions on pH.

Figure 5 indicates four approaches for obtaining sizing with an HST value of at least 100 for the fortified sizes:

1. Set the pH lower than 6.5 but higher than 5.0, and set the fortification between 3% and 12.15%, with no restrictions on the other factors.
2. Set the pH between 5.5 and 6.5 and the fortification between 12.15% and 15%, with no restriction on the other factors.
3. Set the pH between 5.5 and 6.5 and the dosage higher than 0.575%, with no restrictions on other factors.
4. Set the pH between 6.5 and 7.0, the dosage higher than 0.425%, the fortification between 3% and 12.15%, the temperature between 45° and 60°C, and the hardness less than 435 ppm $CaCO_3$.

Since the trees are set up based on the information from an experimental data set, extrapolating to HST values outside the data range is fraught with uncertainty. For the dosage, the sizing always increases as the dosage level gets higher. However, for other factors, the relationship between sizing and the factor levels outside the data range is not clear. Therefore, upper and lower limits have been established for each factor except dosage.

In Fig. 4, the factors used to classify HST values are temperature, dosage, and pH. Note that the hardness factor is not included. This figure indicates that hardness is not an important factor in determining sizing, as we have seen in our discussion of refining the model.

The misclassification rate can be evaluated by applying the tree to the data and dividing the number of observations classified correctly and those classified incorrectly into a group. **Table IV** indicates the misclassification rates for the two trees. For example, the numbers 3 and 34 in the second row mean that 34 HST values for the esterified size are correctly classified into the HST > 100 group, but 3 HST values were misclassified. Therefore the misclassification rate for this group is 0.081.

The highest misclassification rate in the table is 0.21, which corresponds to the numbers 19 and 5 in the first row of the table. This higher misclassification rate is due to the small number of observations in this category for HST ≤ 100. This rate would decrease substantially if we had more data. All the misclassification rates in the table are acceptable, indicating that the constructed trees fit the data reasonably well.

	From tree classification	
From data	**HST ≤ 100**	**HST > 100**
Esterified size		
HST ≤ 100	19	5
HST > 100	3	34
Fortified sizes		
HST ≤ 100	78	17
HST > 100	5	143

IV. Misclassification rates as the number of data values.

Limitation on the application of results

The linear regression models and the sizing control guides we propose are obtained based on experimental data. From all the test results, we can see that the proposed models and control guides work well for interpolation, or predicting the sizing for factors levels within the scope of the factors suggested by the data. However, as for any statistical models, one should always be cautious when attempting to extrapolate the data and predict the sizing for factors levels outside the data range.

CONCLUSIONS

We have proposed simplified statistical models to describe the relationship between sizing and pH, temperature, water hardness, size dosage, and fortification (when applicable). The simplified model is appropriate, as shown by examples such as the decrease of sizing with an increase in pH and the variation of sizing that occurs with increasing fortification.

Based on statistical tests, we conclude that the simplified models are good substitutes for the full models proposed by Nitzman and Royappa. From the simplified models, we are also able to see some different patterns between the esterified sizes and the fortified sizes for the relationship between paper sizing and related factors.

We also propose some guidelines that can be used, with caution, to control sizing during paper manufacturing. These guidelines are not entirely foolproof. For some cases, for example, misclassification rates are not low enough. Nevertheless, the guidelines are useful for the determining factor ranges needed to obtain a certain level of sizing. **TJ**

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INSIGHTS FROM THE AUTHORS

This research was a continuation of our previous project. The models we used in our previous research were too complicated and hard to interpret; therefore, we felt that simplified models were needed. Further, from our experience, we realized that it would be good to provide some guidance to paper manufacturers about the selection of process conditions in order to make desired papers.

One difficult aspect of this research was to select appropriate process variables. We finally solved this problem by using different model selection methods plus knowledge with respect to different process variables.

Based on statistical tests, we concluded that the simplified models were a good substitute for the models proposed by our previous research. Further, from the simplified models, we were able to see some different patterns between the esterified sizes and the fortified sizes for the relationship between paper sizing and related factors. Surprisingly, the factor of water hardness has no effect toward sizing for the esterified sizes. We have also proposed a general procedure for establishing sizing control guidelines for, e.g., paper mills, that can be used—with caution—to control sizing during paper manufacturing.

The simplified linear regression models enable papermakers to reveal different patterns between sizing and interested process factors. The proposed guidelines help guide mills seeking to control sizing. On the other hand, the proposed linear regression models and the sizing control guides are obtained based on experimental data. Therefore, as for any statistical results, one should always be cautious when attempting extrapolation (sizing prediction for factors levels outside the range of the factors in the data).

In this research, we found that the factor of water hardness is not effective for the esterified sizes, but does affect the sizing for the fortified sizes. Further investigation of this factor is needed. Also, there are some other important process variables that have not been studied, such as hard wood and soft wood fiber sources.

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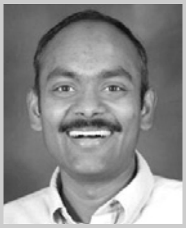
Nitzman



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