MODELING THE PROPERTIES OF HEMICELLULOSE PREEXTRACTED HARDWOOD KRAFT PULPS IN BIOREFINERY PROCESSES

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Abstract

Pretreatment of hardwood can dissolve some of its hemicellulose, which can be used as a feedstock solution for biofuels within the context of a wood based biorefinery. It is well known that most pretreatment methods accelerate subsequent pulping and bleaching reactions. This study reports models developed for predicting several aspects of the impact of pretreatment on the properties of unbleached kraft pulps produced from sample hardwoods: sugar maple (A. saccharum) and eucalyptus (E. globulus). The kappa number was correlated with the severity of pretreatment using a first order approximation of the delignification kinetics. The resulting correlation could be applied to the delignification of pretreated hardwood chips of both the species. Other properties of pulps were modeled with pretreatment and pulping variables using principal component analysis. Multivariable linear regression (MVLR) models were established for the pulp yield, viscosity, composition, cationic demand of fibers, tensile index, tear index, stiffness and air resistance.

Keywords: Fiber lengths, Hot Water Extraction, Kraft Fiber Properties, Zeta Potential of pulp, cationic demand, water retention.

Introduction

Rising gas prices and higher environmental awareness have contributed to the pursuit of alternative clean energy sources. The biorefinery is a concept that is analogous with the petroleum refinery, differing only in the initial raw material to be used. In this case, one or several biomass feedstocks are used to produce a mixture of products, including transportation fuels, heat, energy, chemicals and materials. Lignocellulosic materials such as wood constitute an important natural resource for the production of biofuels and biodegradable plastics and can be a component for sustainable industrial development [1]. Current pulp mills are considered first generation of biorefineries since they produce energy and pulp/paper from a renewable resource. Therefore, they can be adapted and converted into second-generation biorefineries, producing biofuels and/or an array of other products (acetic acid, bioplastics, etc), while still producing paper [2-3].

Several researchers are investigating possible processes to convert existing pulp/paper mills into integrated second-generation biorefineries [4, 5]. The idea behind this concept is to better utilize the lignocellulosic material, by manufacturing value added products from the low value hemicelluloses. In order for success, two crucial aspects need to be guaranteed;

1. Paper production and quality is not hindered
2. Hemicellulose isolation and processing needs to be technically and economically feasible.

The purpose of this study was to use statistical modeling tools to try to better understand how a hot water extraction based biorefinery will affect the pulp quality. Can these tools give us more insight (and hopefully foresight) about the processes and phenomena in play? To answer this question one needs to identify which parameters affect critical pulp properties and assess their significance. For this purpose, the well-known method of principal component analysis was chosen. The statistical analysis and modeling was performed using the software The Unscrambler® from Camo. The main techniques applied to our experimental data were: Principal Components Analysis (PCA), Multivariate Curve Resolution (MCR) and Partial Least Squares (PLS) Regression.

In the first stage of our analysis, we used the pretreatment and pulping data to predict the impact of extraction followed by kraft cooking on the kappa number, yield and composition of the pulp. Models to predict some of the pulps' properties are also presented, using as input the pulps' composition and the conditions that led to that composition. In the second stage of correlation development, the fiber properties (in conjunction with information about the process) are used to predict the end product properties, i.e., the paper properties. Some of the experimental data (sugar maple) and mechanistic explanations for kappa number and pulp viscosity were presented earlier [6, 7]. Modeling can be extremely useful, not only to predict new experiments' outcome, but also to help explain the results obtained. However, it is recognized that correlational models describe data in a statistical sense and offer

some insight into the significant variables. Mechanistic models of paper structure [8] and its impact on paper properties offer better prediction tools but need too many detailed input data.

Experimental

Two wood species were used in this work, Sugar Maple (*Acer saccharum*) and Eucalyptus (*E. globulus*). The former was obtained, in logs, from Heiberg Forest (from SUNY ESF in Tully, NY, USA), and the second was supplied by a Portuguese pulp and paper mill. The Sugar Maple logs were manually debarked and chipped using a Carthage chipper. All chips (Eucalyptus and Sugar Maple) were air dried and screened through a series of screens with circular opening of 9/8, 7/8/ 5/8 and 3/8 inch in diameter. The chips retained in the 7/8 and 5/8 in were considered accepts and used in the laboratory experiments [9]. The extractions and cooks were carried out in a 4.5 liter M&K Digester, using 500 g oven-dried chips. Dionized water was added in order to reach 4:1 liquid to wood ratio. Extractions were carried out at 160 ºC, with a heating ramp time of 30 min and the time at temperature varied from 30, 60, 90 to 120 minutes. The Kraft cooks were performed similar to the extractions. The white liquor was prepared in order to have 16% active alkali (AA) and 25% sulfidity, while maintaining 4:1 L:W ratio. The heating up time for the cooks was 60 min and the H-factor varied in order to achieve three different kappa numbers – 15, 25 and 35. Cooks were performed with all of the extracted chips (after 30, 60, 90 and 120 min extraction), as well as with unextracted chips (control) for comparison. When performing a Kraft cook on extracted chips, the cook was done right after the extraction and therefore the chips were never dried. Two washes with DI water at 80ºC for 15 min where performed between the extraction and the cook. In these cases, experiments were done until two pulps with similar kappa ($\pm$ 2) were obtained.

The zeta potential was determined using a Brookhaven (BIC) Zeta Potential Analyzer (ZetaPlus®). Since zeta potential is determined by measuring the electrophoretic mobility of particles, these need to be small enough not to be affected by gravity. Therefore, to avoid sedimentation (in the time frame of the measurements) this analysis was performed with the fine fraction of the pulps that were able to pass through a paper machine wire. Each value reported is the average of 10 measurements.

Lignin was quantified in all the initial chips, extracted chips and pulps. For the chips, both Klason (or Acid Insoluble) Lignin and Acid Soluble Lignin tests were performed, according to the respective TAPPI Standard T222 and TAPPI Useful Method 250. For the acid soluble lignin, a PerkinElmer Lambda 650 UV/Vis Spectrophotometer was used. For the pulps, the residual lignin was measured via an indirect method [10], by measuring the Kappa Number of the pulps, according to TAPPI Standard T 236. Klason lignin was performed in duplicates. Acid Soluble lignin was performed in triplicate

^{1}H NMR analysis was used to determine the cellulose and hemicellulose content (from the quantification of monomeric sugars – glucan, xylan, mannan, arabinan, rhamnose and galactan) of wood chips,

extracted wood chips and pulp samples. The NMR methods used in this research are described in detail earlier [11-13]. The wood and pulp samples (milled using a Wiley Mill with a 60 mesh screen) were first digested to yield sugars and then analyzed using ^{1}H NMR. In a first digestion stage, a 50 mg OD sample (milled wood/pulp) is dispersed in 16 ml of 72% sulfuric acid at room temperature for 2 hours, stirring it every 15 minutes to ensure proper dissolution. In a second stage, 21 ml of DI water are added to the mixture, bringing the acid content down to 40%. This mixture is then placed in a water bath at 80ºC for one hour, being shaken every 15 minutes. The tubes are then cooled down and kept in the refrigerator overnight, for the residual solid matter to precipitate. When necessary the tubes are centrifuged at 2500 rpm for 7 min to further settle the solid matter and allow the collection of 1 ml of the clean supernatant, which is transferred to a NMR tube and mixed with 0.1 ml of a standard solution. The standard solution is a mixture of known amounts of tri-methylamine hydrochloride (TMA) and glucosamine. This analysis was done in duplicate.

The cationic demand of pulps was measured using a Mütek Particle Charge Detector (PCD-02) with an automatic titrator (PCD-T2). A known amount (approximately 0.8 g) of pulp was dispersed in 100 ml of water and an aliquot of 10 ml was used per test. The pulp was allowed to reach a steady streaming potential for 3 minutes and then it was titrated against a commercial solution of poly-DADMAC with a concentration of 0.001 N. The reported value is an average of three measurements.

The pore size distributions were measured at the Labgran – Granulometry Laboratory and the University of Coimbra, Portugal. The pore size distribution measurements were performed in duplicate using an AutoPore IV Mercury Porosimeter from micromeritics, in Norcross, GA, USA. The fiber analysis and the Water Retention Value (WRV) measurements were done at the Specialty Minerals Research Center facilities in Allentown, PA. The first was done using an OpTestHiRes Fiber Quality Analyzer (FQA) from OpTest Equipment Inc, Hawkesbury, ON, Canada. The analysis provided a fiber length distribution (different length averages, fines content, among others) as well as fiber curl and kink information. The operating procedure consists of a series of dilutions in order to obtain a representative sample at very low consistency (0.04%). The dilution was done once and triplicate aliquots were taken for measurement. The methodology used for the WRV was similar to TAPPI Useful Method T256. 1.94 OD g of pulp where weighed and transferred into the crucibles (forming a 1400 g/m^{2} pad), with the assistance of a vacuum to ensure a neat pulp pad at the bottom of the crucible. The crucibles were then placed in the centrifuge for 30 min and 2500 rpm's (900 G's). After the centrifugation the crucibles and pulp were weighed and placed in an oven at 105ºC for drying. Once dried, they were weighed again in order to determine the weight of the dry pulp. Due to time constrains, not all of these tests were performed in duplicates. Roughly 60% of the tests were carried out in duplicate to ensure that the variability between them was small enough.

The viscosities of the pulps were determined in duplicates, using TAPPI Standard T230, with the exception that no nitrogen purge was used. Since this method is only valid for lignin amounts below 4%, the pulps with kappa 35 were not tested. Handsheets were prepared and tested according to the standard TAPPI Methods. Only non-extracted pulps (control pulps) and 120 minutes extracted pulps (for all kappa levels) were used for paper testing.

Results and Discussion

Extraction and Pulping

The simplest model (Figure 1) correlates the mass removal for both the Eucalyptus and Sugar Maples species based on the extraction time at a temperature of 160ºC and a ramp time of 30 min. From the extracted chips' composition [6,7] and mass removal data it is possible to see that the dissolution of cellulose is practically inexistent and the dissolution of lignin is only a minor part of the mass removal. Therefore neglecting the cellulose and lignin dissolution (which is true for cellulose) the mass removal is proportional to the hemicellulose removal and therefore to its concentration in the wood chip. Assuming that the hemicellulose dissolution follows first order kinetics, the following equation can be written for *M*, the mass removed

$$M = M_0[1 - \exp(-bt)] \qquad (1)$$

where M_0 represents the fraction of dissolvable material (i.e. hemicellulose) in the chip and *b* is the kinetic rate coefficient. This model was used to fit the data, with very high regression coefficients for both species. The coefficients are given in Figure 1. With all the data available it was possible to build several multi-variable linear regression models that help explain and predict the outcome of extraction and pulping stages. They have the general form:

$$Y = b_0 + \sum_{i=0}^{n} b_i X_i \qquad (2)$$

where:
Y – Output Variable
X_i – Input Variables
b_i – Regression Coefficients

Insert Figure 1

The set of parameters we used for modeling are described in Table 1. Parameters such as the total yield, pulp viscosity, pulp composition, cationic demand and zeta potential were modeled based on different extraction and cooking parameters and pulp composition.

Total Yield

Two models were created to explain the behavior of total yield. One took into account the alkali used and the second did not. Although the first presented a slightly better fit (0.966 compared to 0.957 for Sugar Maple), the second one was able to explain 91% of the output variance instead of 88%. Furthermore, the second model is capable of predicting the total yield, without actually having to do the extraction and cook in order to measure the alkali used. One needs only to know the mass removal, which can be estimated via equation 1.

Figure 2 shows the correlation loadings and predicted vs. measured plots for the total yield models for Sugar Maple (plots for eucalyptus are given in Figure S1 in the supporting information). From the correlation loadings plot it can be observed that the variance of the input variables is almost completely explained by the principal components (99% and 97% for Sugar Maple and Eucalyptus respectively) and that the variance of the output variable is also well explained (91% and 93%, respectively). The predicted vs. measured plots show excellent fits between the real data and the data predicted by the model, with correlation as high as 0.997 for eucalyptus and 0.957 for Sugar Maple. Table 2 gives the raw and weighted coefficients for the total yield regression model are given. The raw coefficients correspond to the raw data values, whereas the weighted coefficients correspond to the weighted data values and are a good indication of the importance of each input variable for the output variable. In other words, the weighted coefficients allow for a direct comparison of the importance of each variable. The weighting is done by dividing the raw data by its standard deviation.

Insert Figure 2 and Table 2

Pulps' Viscosity

As for pulps' viscosity, several models were tried. Initially, models using the chip composition (after extraction), H-factor and alkali consumption were developed. However, there was no significant gain in using the alkali consumption in the models, as the results obtained with and without it were similar. Therefore, the final model chosen used only the chip composition and the H-factor. Since according to TAPPI Standard T230, the viscosity for pulps with lignin content higher than 4%(which corresponds roughly to kappa 27) is not reliable and cannot be taken as a measurement of the pulps' degree of polymerization, viscosity data for pulps with kappa 35 were not used.

It is possible to accurately model the viscosity of the pulps using the chip composition and the H-Factor as input, with higher explanation percentage (88%) and better correlation coefficients (R=0.935) for Sugar

Maple than Eucalyptus (83% and R=0.916). The model coefficients are given in Table 3 and its performance shown in Figure S2.

Insert Table 3

Pulps' Composition

Finally, the pulp composition can be modeled for cellulose and hemicellulose content. It is not possible to model the lignin content of the pulps using MVL regression. However, a different model was used to estimate the kappa number of the pulp, and consequently have an idea of the residual lignin content. Assuming that kappa number and lignin are linearly proportional it is possible to derive a model that correlates kappa number with H-Factor and P-Factor (used as a reaction coordinate by [14-16] and with a similar algebraic expression to the H-Factor). This model is given in equation 4 and the derivation of this model can be found elsewhere [6].

$$k = aL_0 \exp\left[-\left(bH + cP + dH.P\right)\right] \qquad (3)$$

where *a*, *b*, *c* and *d* are constants used to fit the data. Table 4 gives these coefficients and Figure 3 shows how the predicted values correlate with the experimental values.

Insert Table 4 and Figure 3

For cellulose and hemicellulose the models done using MVLR fit the data extremely well. For Sugar Maple, the model for cellulose is able to explain 93% of the output variable's variance, having a correlation of ≈0.966. For eucalyptus, the results are even better, being able to explain 95% of the variance in the data and fitting it with a coefficient of ≈0.974. The input variables that provided the best fit for the cellulose content were the total yield, the mass removal (it is intuitive why these two variables translate to the amount of cellulose) and the extracted chip composition in terms of lignin and hemicellulose. Curiously, the extracted chip cellulose content did not help fitting the data. Another curious observation is that for Sugar Maple, the most "important" parameter is total yield, followed by the mass removal whereas for Eucalyptus it is the extracted chip lignin content followed by extracted chip hemicellulose content. Table 5 presents the model parameters for the cellulose model for Sugar Maple and Eucalyptus and Figures S3 and S4 their respective performance.

Insert Table 5

In the case of hemicellulose, the models also fit the data extremely well, but in this case one more input variable, H-Factor, was used. Although it is not as important as the other variables, it still improved the

model slightly. This, combined with the fact that it is an easily calculated variable, is the reason why it is incorporated in the model. If it was a parameter difficult to measure (or time consuming), the gain of using it in the model would not be worth the extra work. This model explains 98% and 99% of the output variable's variance for Sugar Maple and Eucalyptus respectively with correlation coefficients close to unity (0.987 and 0.997 respectively – see Figures S5 and S6. Table 6 presents the regression coefficient values for these models.

Insert Table 6

Cationic Demand

The cationic demand of the pulps is not only a function of their composition, but also of their specific surface area, which becomes clear after analyzing the correlation loadings for these variables, where the surface area is reflected by the fiber length and fines content.

The model fits the data for Eucalyptus somewhat better than for Sugar Maple with a correlation of 0.952, opposed to 0.854 and explains 89% of variance of the output variable instead of 73%. Table 7 presents the regression coefficient values for these models.

Insert Table 7

Paper Properties

In this section, pulp properties will be used to try to explain and predict some of the most important paper properties. The paper property most commonly used to quantify paper quality is the tensile index. The model built to describe the tensile index is very successful in doing so. It uses as input variables pulp properties such as fiber length, fiber composition – cellulose and hemicellulose content and kappa number (roughly equivalent to lignin content), kink index and fines in the pulp suspension. The retention was assumed to be constant between the pulps. For some control pulps (identified as those without fines), the fines were removed and added to the extracted pulps with the same kappa (extracted with extra fines). It is assumed that all fines were removed from the control samples (meaning that theses samples have zero fines) and that all the fines were added to the extracted samples (meaning that these have their initial amount plus the amount of the control pulps or a fraction of this sum). These assumptions seem reasonable accordingly to visual observations and model results. As seen from Figures S7 and S8 although the model is very good for both species, the model for Eucalyptus fits slightly better than the one for Sugar Maple, with 94% of variance explained (as opposed to 89%) and a correlation coefficient of 0.968 instead of 0.942. This can be due to the fines fraction on each pulp. As can be observed from the correlation loadings plots, the fines have a smaller contribution to the model in the case of Sugar Maple than the Eucalyptus. There may be a larger error in the fines removal/addition in case of the Sugar Maple, as they are harder to remove than in the case of Eucalyptus. Another

interesting observation is that the fiber length seems to have a smaller impact on the tensile index in the case of Sugar Maple than in the case of Eucalyptus (as can be seen from both the correlation loadings graph and the weighted coefficients in Table 8. The fact that for Sugar Maple the fiber length coefficient is negative, it does not necessarily imply that the fiber length correlates negatively with the tensile index. In fact, as shown in the correlation loadings, the tensile index and the fiber length correlate positively via PC1 and negatively via PC2. However for Sugar Maple the fiber length barely changes with extraction time, and therefore its impact in the model is small (as is the fines content), as seen by a very small weighed coefficient. In fact, these two parameters can be set to zero, and the results will remain virtually unaffected.

Insert Table 8

Another very important property is the tear index. It is possible to describe the behavior of this property using simpler models, since it is influenced by less input variables than most other properties. Indeed, it is possible to very accurately describe the tear index of these pulps using only two input variables, the hemicellulose content and the fiber length. It is easily understandable why these two parameters should describe the tear index. Fiber length allows for the energy of a tear to be dispersed over more fibers, thus decreasing the individual load on each fiber and consequently increasing the tear resistance. The hemicellulose content must translate a measure of inter-fiber bonding [17] and therefore indicates how strongly one fiber is attached to another. Indeed, the Bonding Index (which is the ratio between tensile strength and zero-span tensile strength) correlates well with the hemicellulose content (see Figure 4). Indeed, for Sugar Maple, if the extracted pulp with kappa 15 is neglected, the R^2 increased to 0.912. Analogously for Eucalyptus, if the control pulp with kappa 15 is neglected then the R^2 increased to 0.910, which clearly showing the correlation between the two, as expected and previously referred. Despite the fact that bonding index correlates well with tear index, it is not used in the model, since it is a result of paper properties and not a fundamental fiber property. For this reason, the model was done with the fundamental fiber properties and not the bonding index.

Although these two fiber properties (hemicellulose content and fiber length) are sufficient to model the Tear Index, the incorporation of a third variable (fines content) was advantageous to improve the model slightly (Figures S9 and S10). However, its contribution is, by far, the least important, as it can be seen by the weighed coefficient shown in Table 9. Indeed, if not used, it will barely affect the result of both this model and the tensile index model. This suggests that the retention of fines during handsheet preparation was poor, as it is expected that fines in the paper contribute to inter-fiber bonding and therefore to both tensile and tear indexes.

Insert Figure 4 and Table 9

Stiffness was the next important paper property modeled. Unlike in other models, where only fundamental fiber properties were used, in this model, the sheet's thickness was taken into account, as it is a crucial parameter for stiffness. Actually, bulk was used instead of thickness, since the differences in thickness for the handsheets were very small (in the order of 0.01 mm) and when associated with the variance in grammage, the bulk became a better descriptor of stiffness than thickness. The model for Sugar Maple explains 82% of the variance in stiffness whereas for Eucalyptus it only explains 76%. However, in the case of Sugar Maple two samples had to be discarded as outliers. Table 10 and Figure S11 show the model's performance. It is possible to see from this table that both species behave differently. For Sugar Maple, the fiber length is virtually unimportant and bulk plays the most important role. In Eucalyptus, kappa number and bulk are the two main variables.

Insert Table 10

Three remaining paper properties were modeled: burst index, zero-span, and Gurley's air resistance. For these, the model information is compiled in Tables 11 to 13. The models for all these properties were able to fit the data almost perfectly. It is curious to see, once again, how Sugar Maple and Eucalyptus behave differently. For burst index model, the fiber length is almost unimportant for Sugar Maple, whereas for Eucalyptus it is fiber width that barely influences the model. For zero-span, the differences between the species are in kappa number and fiber width. One final remark is due regarding the models for Gurley air resistance, as they were performed with only 11 of the 12 samples, as both species had one value considered to be an outlier.

Insert Table 11, Table 12 and Table 13

Prediction of Paper Properties

In the previous section, models were created to help explain and predict the properties of paper produced from pulps with kappa numbers in the range of 15 to 35, and extraction times comprised between 0 and 120 min. Like all models, these are only valid within the range of values for which they were performed. This means that all the input variables need to be within the range of the ones used for building the model. Since the models were based on the extrema of the range of conditions, all the extraction levels have input values that fall within the range of validity of the model, with very few exceptions (namely in the fiber width). In these cases, care is needed, as the model is being used to extrapolate. Nonetheless, the results obtained make sense and are a good initial estimate for the paper properties (of handsheets).

Tables S1 and S2 provide the predicted paper properties, as well as the real data (available for the control and the 120 minutes extracted) for the Sugar Maple and Eucalyptus pulps, respectively. In both tables, the grey cells are the cases where the real data is within 68.2% of the prediction (± one standard deviation). All others are within the 95.4 % confidence interval (± two standard deviation). As expected the

model works better for the control and 120 minutes extracted pulps, which is evidenced by the smaller deviations for these. The reason for the better performance is that this data was actually used to build the models.

Conclusions

This work allowed to verify that the extracted fibers (and paper produced thereof) have significant different properties than those from the control. Therefore, unless there are some other changes to the papermaking process (e.g. different concentration of the pulping chemicals), these fibers are not viable to produce the same grades of papers that they are typically used for without significant loss of quality.

Nevertheless, the models built can explain very well the majority of properties presented for both species and provide a good tool for predicting them, as long as the models are used within their validity range. Moreover, the variables used to build those models have a very good physical explanation and it is easy to understand why they are important in explaining a given property.

Additionally, the modeling of the different pulp and paper properties was especially useful, not only as a predicting tool, but also as an explaining tool. It allowed a clear description of which are the most important variables that affect the outcome of a given property, which would otherwise be a complicated task, since there are several parameters changing at any given time.

Future work should focus on expanding the validity range of the models (by using different chemical cooking conditions) as well as their further validation.

References

1. Ragauskas, A. J.; Williams, C. K.; Davidson, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. *Science*, **2006**, *311*, 484.

2. S. Liu, T. E.Amidon, R. C. Francis, B. V. Ramarao, Y. Z. Lai and G. M. Scott. From forest biomass to chemicals and energy. Industrial Biotechnology, **2006**, 2, 113-120.

3. Goyal, G.; Tan, Z.; Yin, C.; Marsolan, N.; Amidon, T. Biorefinery – An Overview. In *Proceedings of the 3rd International Colloquium on Eucalyptus Pulp*: Belo Horizonte, Brazil, 2007.

4. Mittal, A. K. Kinetics of Hemicellulose Extraction During Autohydrolysis of Sugar Maple Wood, Ph.D. Diss., State University of New York, Coll. of Env. Science and Forestry, 2006.

5. Barber, V. Extraction of Hemicellulose from Sugar Maple Chips after Biotreatment with Ceriporiopsissubvermispora, Ph.D. Diss., State University of New York, Col. of Env. Science and Forestry, 2007.

6. Duarte, G.V.; Ramarao, B.V.; Amidon, T.E.; Ferreira, P.T. Effect of Hot Water Extraction on Hardwood Kraft Pulp Fibers (Acer Saccharum, Sugar Maple). Ind. Eng. Chem. Res., **2011**, 50 (17), 9949–9959.

7. Duarte, G. V. Gamelas, J.A.F., Ramarao, B. V.; Amidon T. E. Ferreira, P.J. Properties of extracted Eucalyptus globulus kraft pulps, TAPPI Journal, 2012, 11 (4), 47.

8. Lavrykov, S.; Lindstrom, S. B.; Singh, K. M.; Ramarao, B. V. 3D network simulations of paper structure. Nordic Pulp Pap. Res. J., **2012**, 2, 184-196.

9. Smook, G. Handbook for Pulp and Paper Technologists, 3rd Ed., Angus Wilde Publications, 2002.

10. Carvalho, M.G.V; Martins, A.A.; Figueiredo, M.M.L. Kraft pulping of Portuguese *Eucalyptus globulus*: effect of process conditions on yield and pulp properties. Appita J. **2003**, *56*(4), 267-274.

11. Bolton, T. Hardwood Cell Wall Modifications by Acid Hydrolysis and Their Effects on Alkaline Delignification, Ph.D. Diss., State University of New York, Coll. of Env. Science and Forestry, 2008.

12. Bose, S.K.; Barber, V.A.; Alves, E.F.; Kiemle, D.J.; Stipanovic, A.J.; Francis, R.C. Improved method for the hydrolysis of hardwood carbohydrates to monomers, Carbohydrate Polymers, **2009**, 78, 396-401.

13. Alves, E.F.; Bose, S.K.; Francis, R.C.; Colodette, J.L.; Iakovlev, M.; Heiningen, A.V. Carbohydrate composition of eucalyptus, bagasse and bamboo by a combination of methods, Barbohydrate Polymers, **2010**, 82, 1097-1101.

14. Testova, L.; Vilonen, K.; Pynnonen, H.; Tenkanen, M.; Sixta, H. Isolation of hemicelluloses from birchwood: distribution of wood components and preliminary trials in dehydration of hemicelluloses. Lenz. Berichte, **2009**, 87, 58.

15. Sixta, H. Chemical Pulping Processes. In Handbook of Pulp; Sixta, H., Ed.; Wiley-VCH Verlag Publishing, Germany, Weinheim, **2006**, 4, 109-409.

16. Tunc, M. S.; Lawoko, M.; van Heiningen, A. Understanding the limitations of removal of hemicelluloses during the auto-hydrolysis of a mixture of southern hardwoods. Bioresources, **2010**, 5 (1), 356.

17. Yoon, S.; Van Heiningen, A. Kraft pulping and papermaking properties of hot-water pre-extracted loblolly pines in an integrated forest products biorefinery, TAPPI Journal, **2008**, 22-27.

Table 1 – Parameters modeled by multiple variable linear regression.

Property	Variables
Pulp Yield	Time, H factor, mass removal
Pulp viscosity	H factor, composition (cellulose, hemicellulose and lignin)
Pulp kappa number	Predicted according to semi-empirical model of equation (3) relating P and H factors
Cationic charge density	Time, Fines fraction, fiber length, fines fraction, fiber composition (X_c, X_H, X_L).
Tensile Index	Fiber length, fines fraction, Kink index, fiber composition (X_c, X_H, κ number or X_L).
Tear Index	Fiber length, fines fraction, Kink index, fiber composition (X_c, X_H, κ number or X_L).
Burst Index	Fiber length, fines fraction, Kink index, fiber composition (X_c, X_H, κ number or X_L).
Z-Span	Fiber length, fines fraction, Kink index, fiber composition (X_c, X_H, κ number or X_L).
Gurley Air Resistance	Fiber length, fines fraction, Kink index, fiber composition (X_c, X_H, κ number or X_L).

Table 2 - Total yield model regression coefficients for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Extraction Time	-5.439×10^{-2}	-0.499
	H-Factor	-3.451×10^{-3}	-0.248
	Mass Removal	-0.369	-0.608
	b_0	56.442833	11.789495
Eucalyptus	Extraction Time	-5.433×10^{-2}	-0.422
	H-Factor	-1.141×10^{-2}	-0.213
	Mass Removal	-0.508	-0.699
	b_0	58.528797	10.775261

Table 3 – Viscosity (cP) models' regression coefficients for Sugar Maple and Eucalyptus

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	H-Factor	-2.614×10^{-2}	-1.240
	Ext. Chip Cellulose	-0.235	-0.118
	Ext. Chip Hemicellulose	0.472	0.205
	Ext. Chip Lignin	-0.874	-0.226
	b_0	89.137672	11.830536
Eucalyptus	H-Factor	-1.804×10^{-2}	-0.368
	Ext. Chip Cellulose	-0.302	-0.185
	Ext. Chip Hemicellulose	-1.648	-0.962
	Ext. Chip Lignin	-10.708	-0.801
	b_0	387.782227	41.246063

Table 4– Coefficients in Eq. (3) via multiple linear regression. Standard errors of regression estimates are also provided.

Species	Parameter	Estimate	Standard Error of estimated coefficient
Sugar Maple	a.L0	44.5351	1.1117
	b	7.3064×10^{-4}	1.445×10^{-4}
	c	-5.2345×10^{-5}	2.741×10^{-5}
	d	2.682×10^{-6}	4.096×10^{-7}
	R^2	0.9436	
Eucalyptus	a.L0	44.0955	1.1406
	b	1.4464×10^{-3}	3.3082×10^{-4}
	c	2.2924×10^{-4}	3.261×10^{-4}
	d	1.1716×10^{-5}	1.7985×10^{-6}
	R^2	0.8694	

Table 5 – Coefficients for Cellulose Content Model for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Total Yield	-1.394	-1.064
	Mass Removal	0.315	0.396
	Ext. Chip Hemi	0.418	0.214
	Ext. Chip Lignin	-1.394	-0.318
	b_0	165.975845	26.465090
Eucalyptus	Total Yield	-0.226	-0.207
	Mass Removal	0.109	0.144
	Ext. Chip Hemi	-0.284	-0.245
	Ext. Chip Lignin	-2.076	-0.465
	b_0	155.5000	24.95678

Table 6 - Regression Coefficients for Hemicellulose Content Model for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	H-Factor	2.065×10^{-3}	0.114
	Ext. Chip Cellulose	0.331	0.196
	Ext. Chip Hemi	0.273	0.140
	Ext. Chip Lignin	-0.355	-0.109
	Total Yield	0.643	0.495
	Mass Removal	-0.287	-0.363
	b_0	-28.827423	-4.627396
Eucalyptus	H-Factor	1.788×10^{-3}	4.429×10^{-2}
	Ext. Chip Cellulose	-0.139	-0.127
	Ext. Chip Hemi	0.307	0.235
	Ext. Chip Lignin	0.307	0.245
	Total Yield	0.303	0.246
	Mass Removal	-0.181	-0.211
	b_0	-35.097664	-4.989467

Table 7 - Regression coefficients for cationic demand model for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Cellulose	-0.456	-0.743
	Hemicellulose	0.179	0.288
	Lignin	1.205	0.397
	Fines	-0.885	-0.483
	Fiber Length	-8.237	-3.222×10^{-2}
	Extraction Time	7.393×10^{-3}	8.35×10^{-2}
	b_0	64.948723	16.704809
Eucalyptus	Cellulose	-7.177×10^{-2}	-0.220
	Hemicellulose	5.238×10^{-2}	0.181
	Lignin	0.688	0.424
	Fines	-0.235	-0.110
	Fiber Length	11.184	0.202
	Extraction Time	-6.555×10^{-3}	-0.141
	b_0	17.389416	8.539732

Table 8 - Regression coefficients for tensile index model for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Fiber Length	-18.518	-3.281×10^{-2}
	Fines	1.496×10^{-3}	1.554×10^{-3}
	Kink Index	-6.418	-0.323
	Cellulose	-0.298	-0.281
	Hemicellulose	0.320	0.313
	Kappa	-0.386	-0.324
	b_0	80.798820	9.640932
Eucalyptus	Fiber Length	38.446	0.176
	Fines	-0.177	-0.102
	Kink Index	-4.311	-0.239
	Cellulose	-0.315	-0.198
	Hemicellulose	0.294	0.239
	Kappa	-0.514	-0.409
	b_0	55.476791	4.833528

Table 9 - Regression coefficients for tear index model for Sugar Maple and Eucalyptus.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Fiber Length	-5.806	-6.087×10^{-2}
	Fines	1.774×10^{-2}	0.109
	Hemicellulose	0.181	1.047
	b_0	5.610810	3.961387
Eucalyptus	Fiber Length	13.028	0.499
	Fines	6.571×10^{-3}	3.153×10^{-2}
	Hemicellulose	7.054×10^{-2}	0.481
	b_0	-2.426474	-1.770043

Table 10 - Regression coefficients for stiffness model for Sugar Maple.

Species	X Variables	Raw Coefficient	Weighed Coefficient
Sugar Maple	Bulk	-0.623	-0.303
	Fiber Length	-0.336	-2.724×10^{-2}
	Kink Index	-9.521×10^{-2}	-0.223
	Cellulose	-4.554×10^{-3}	-0.206
	Hemicellulose	4.627×10^{-3}	0.218
	Kappa	-5.153×10^{-3}	-0.206
	b_0	3.969152	23.199474
Eucalyptus	Bulk	-0.761	-0.343
	Fiber Length	0.711	0.156
	Kink Index	-7.358×10^{-2}	-0.195
	Cellulose	-5.685×10^{-3}	-0.171
	Hemicellulose	5.228×10^{-3}	0.203
	Kappa	-9.321×10^{-3}	-0.355
	b_0	4.056526	16.899523

Table 11 - Regression coefficients for burst index models for Sugar Maple and Eucalyptus (* - first value is the explained variance of the output variable and the second value is the regression coefficient.)

Specie	X Variables	Raw Coefficient	Weighed Coefficient	Model Fitting
Sugar Maple	Fiber Length	1.065	3.352×10^{-2}	95 % 0.975
	Kink Index	-0.316	-0.282	
	Fiber Width	-0.264	-0.257	
	Cellulose	-1.556×10^{-2}	-0.261	
	Hemicellulose	1.643×10^{-2}	0.289	
	Kappa	-1.345×10^{-2}	-0.200	
	b_0	6.932002	14.692238	
Eucalyptus	Fiber Length	3.007	0.204	95 % 0.977
	Kink Index	-0.346	-0.284	
	Fiber Width	-0.163	-9.428×10^{-2}	
	Cellulose	-2.461×10^{-2}	-0.229	
	Hemicellulose	2.277×10^{-2}	0.274	
	Kappa	-3.582×10^{-2}	-0.422	
	b_0	5.523162	7.119149	

Table 12 - Regression coefficients for zero-span tensile models for Sugar Maple and Eucalyptus(* - first value is the explained variance of the output variable and the second value is the regression coefficient.)

Specie	X Variables	Raw Coefficient	Weighed Coefficient	Model Fitting
Sugar Maple	Kink Index	-14.601	-0.291	86 % 0.921
	Fiber Width	-6.899	-0.150	
	Cellulose	-0.768	-0.288	
	Hemicellulose	0.773	0.300	
	Kappa	-0.251	-8.359×10^{-2}	
	b_0	353.39874	16.725544	
Eucalyptus	Kink Index	-7.904	-0.332	96 % 0.981
	Fiber Width	1.84	5.462×10^{-2}	
	Cellulose	-0.544	-0.259	
	Hemicellulose	0.528	0.325	
	Kappa	-0.675	-0.406	
	b_0	198.14450	13.07437	

Table 13 - Regression coefficients for Gurley air resistance model for Sugar Maple and Eucalyptus.

Specie	X Variables	Raw Coefficient	Weighed Coefficient	Model Fitting*
Sugar Maple	Fiber Length	-5.861	-0.308	86% 0.925
	Fines	1.352×10^{-2}	0.417	
	Fiber Width	-0.168	-0.253	
	Kappa	-1.123×10^{-2}	-0.260	
	b_0	7.725764	26.105104	
Eucalyptus	Fiber Length	-1.912	-0.307	93% 0.935
	Fines	1.689×10^{-2}	0.314	
	Fiber Width	-0.202	-0.283	
	Kappa	-7.900×10^{-3}	-0.210	
	b_0	6.164769	18.346464	

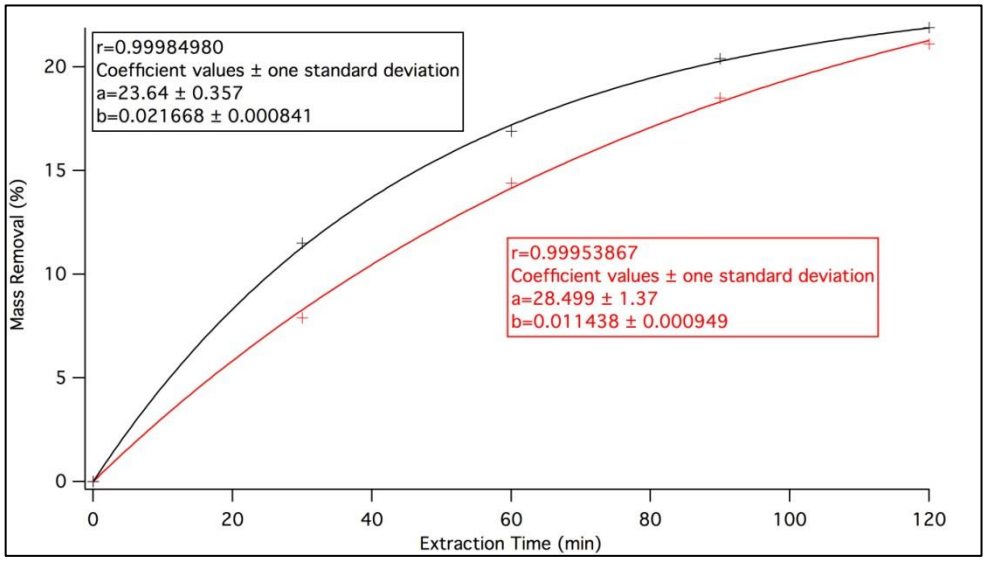


Figure 1 – Correlation between extraction time and mass removal. Black – Eucalyptus; Red – Sugar Maple.

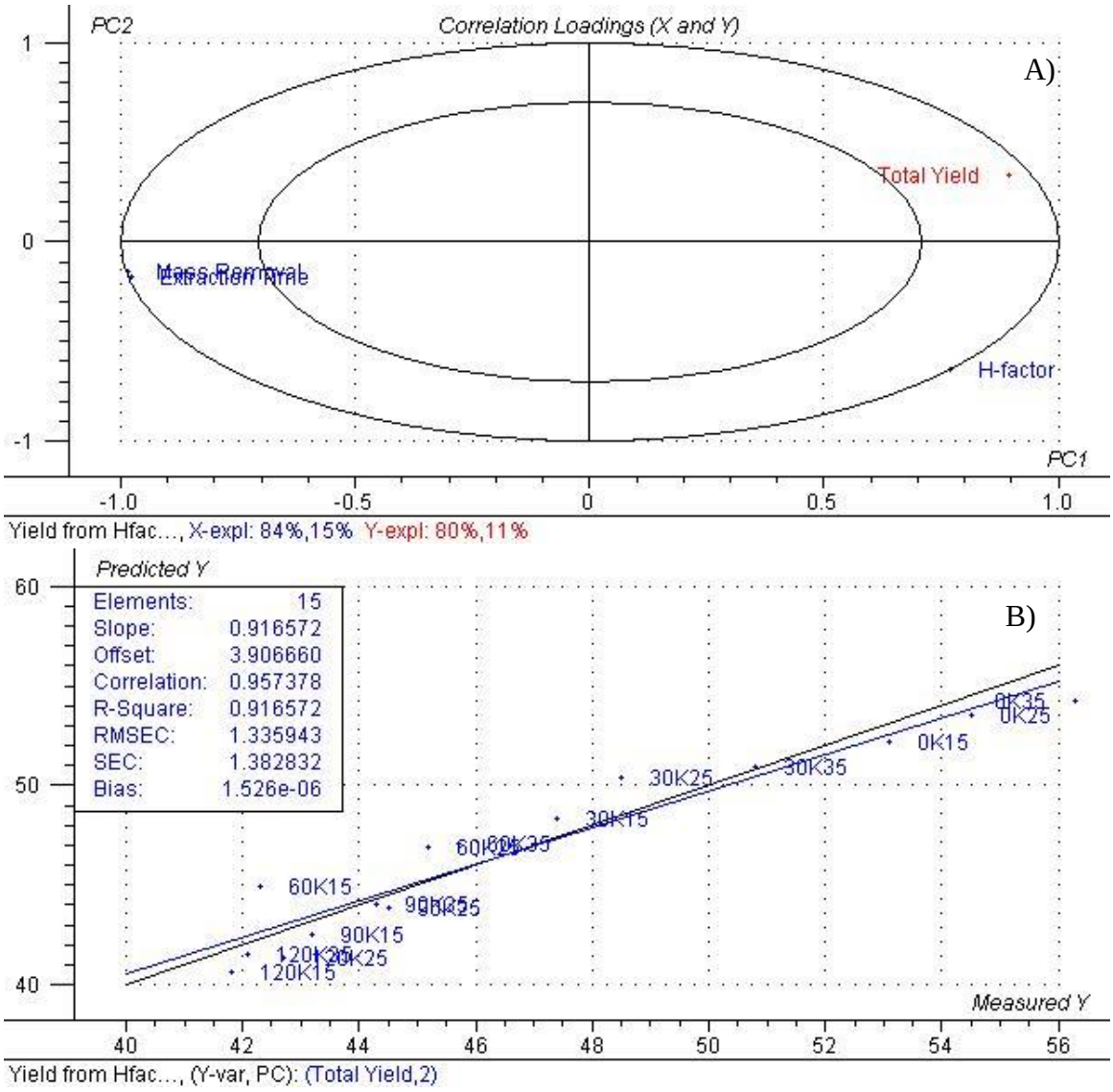


Figure 2 - Results for Yield model based on H-Factor, Mass Removal and Extraction Time for Sugar Maple. A) Correlation Loadings; B) Predicted vs. Measured

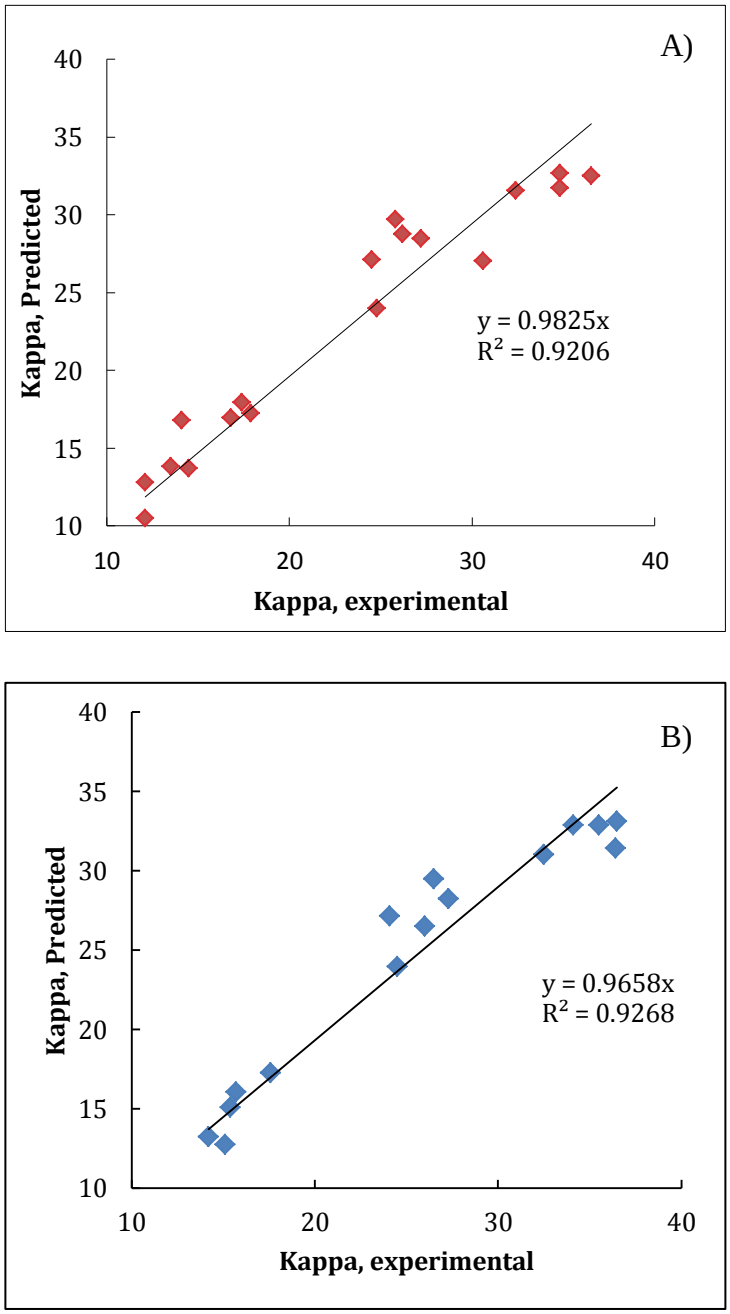


Figure 3 – Comparison of the predicted versus measure Kappa # for Sugar Maple (A) and Eucalyptus (B) extracted pulps.

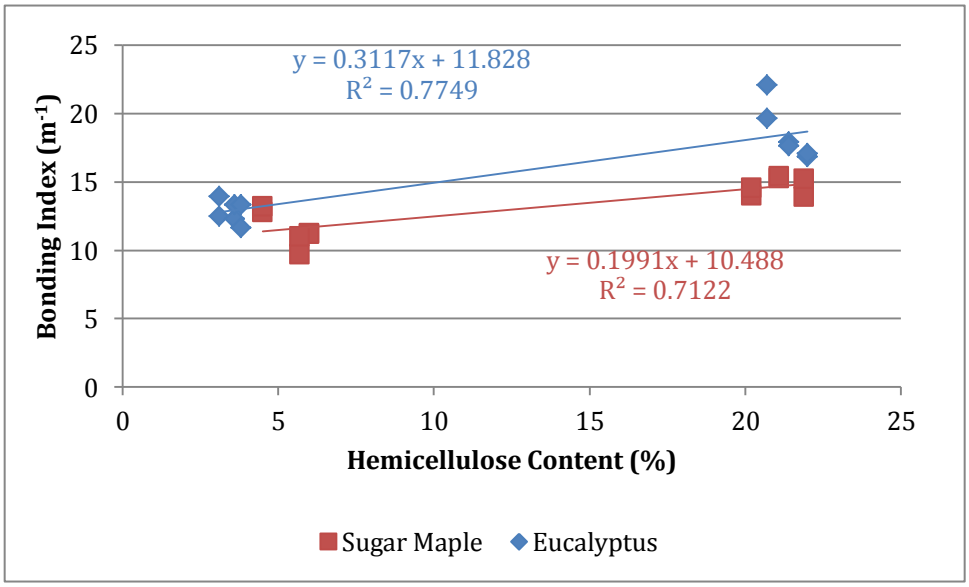


Figure 4 – Effect of pulps' hemicellulose content on papers' bonding index.

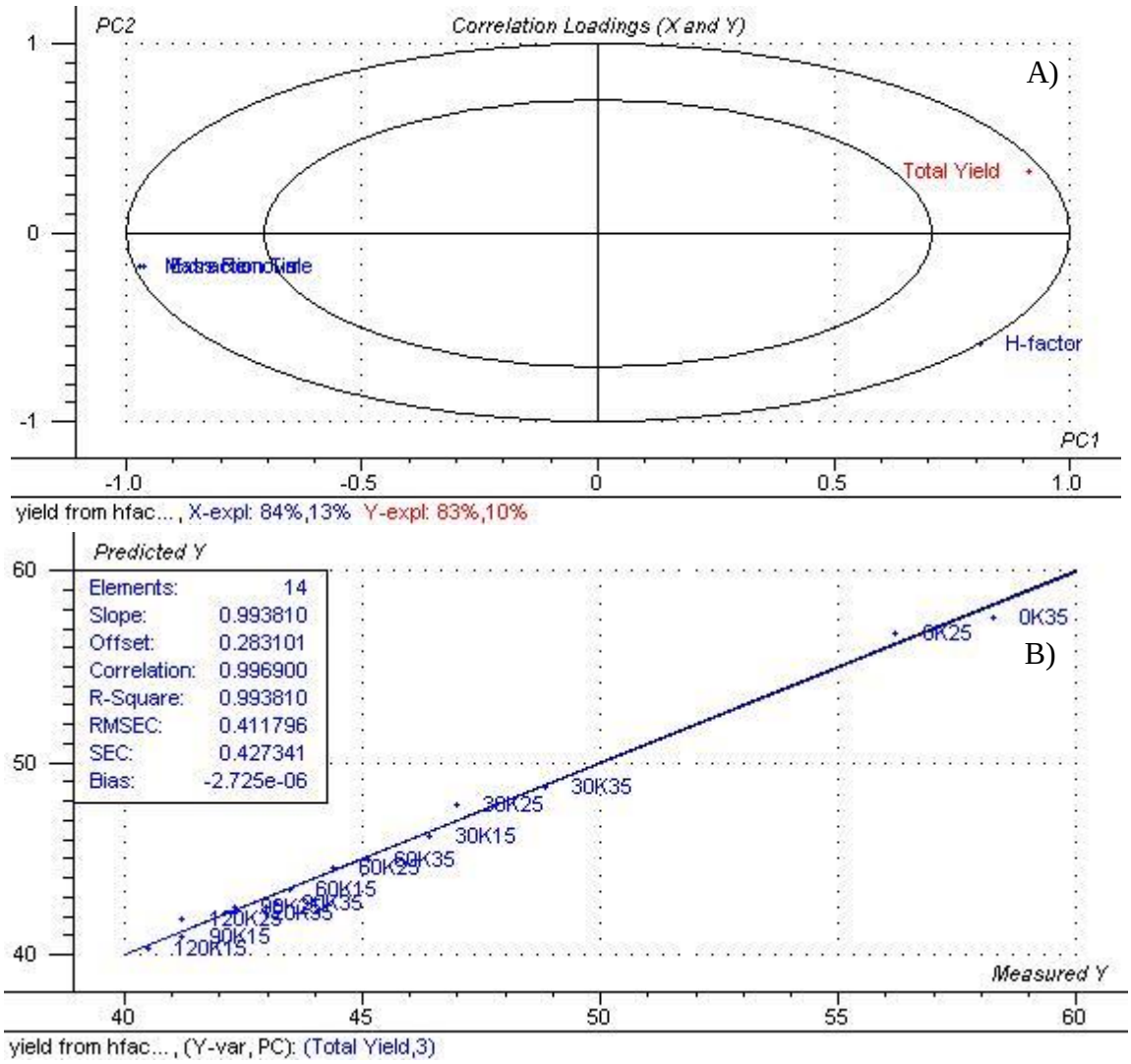


Figure S5 - Results for Yield model based on H-Factor, Mass Removal and Extraction Time for Eucalyptus. A) Correlation Loadings; B) Predicted vs. Measured

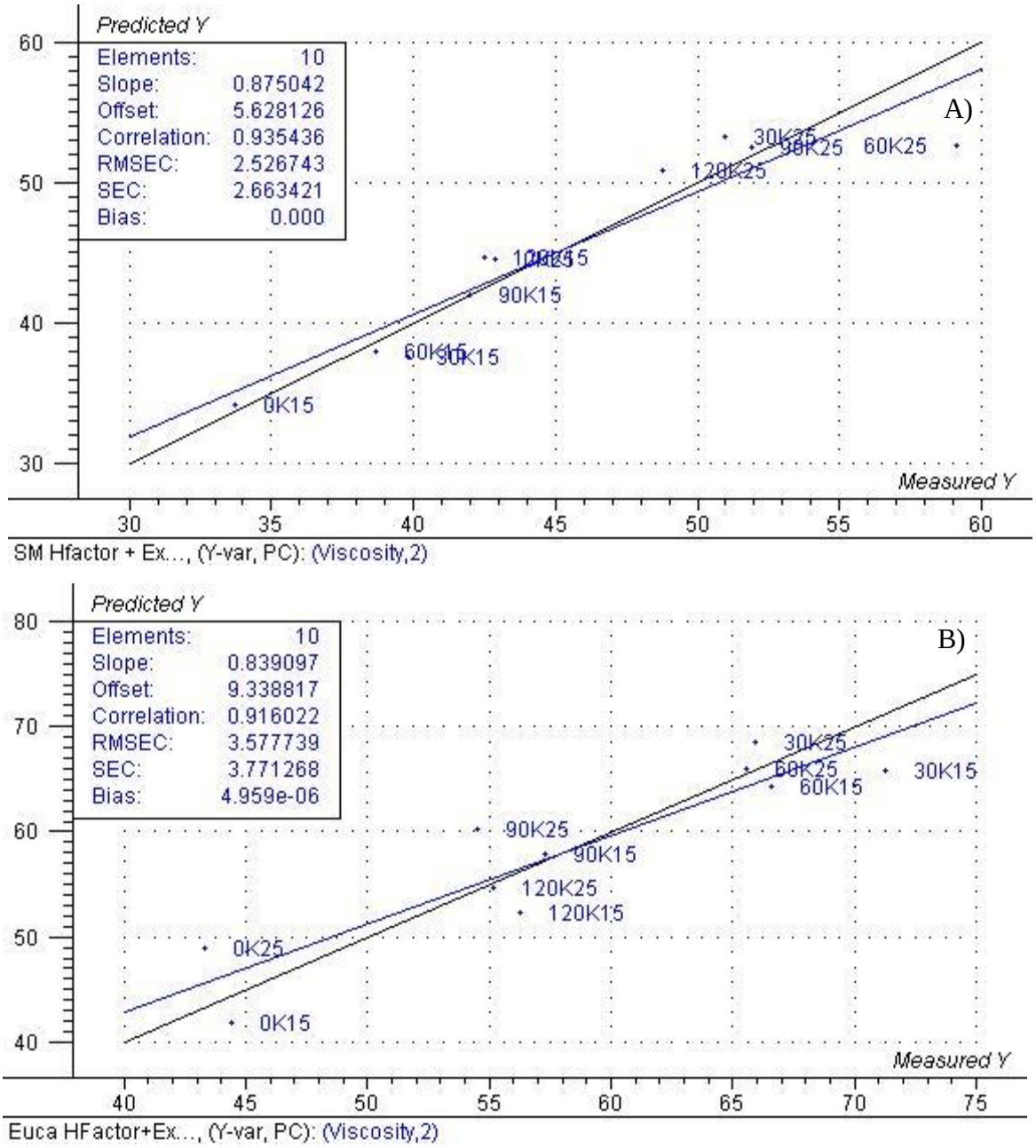


Figure S6 - Results for Viscosity model.A) Sugar Maple; B) Eucalyptus

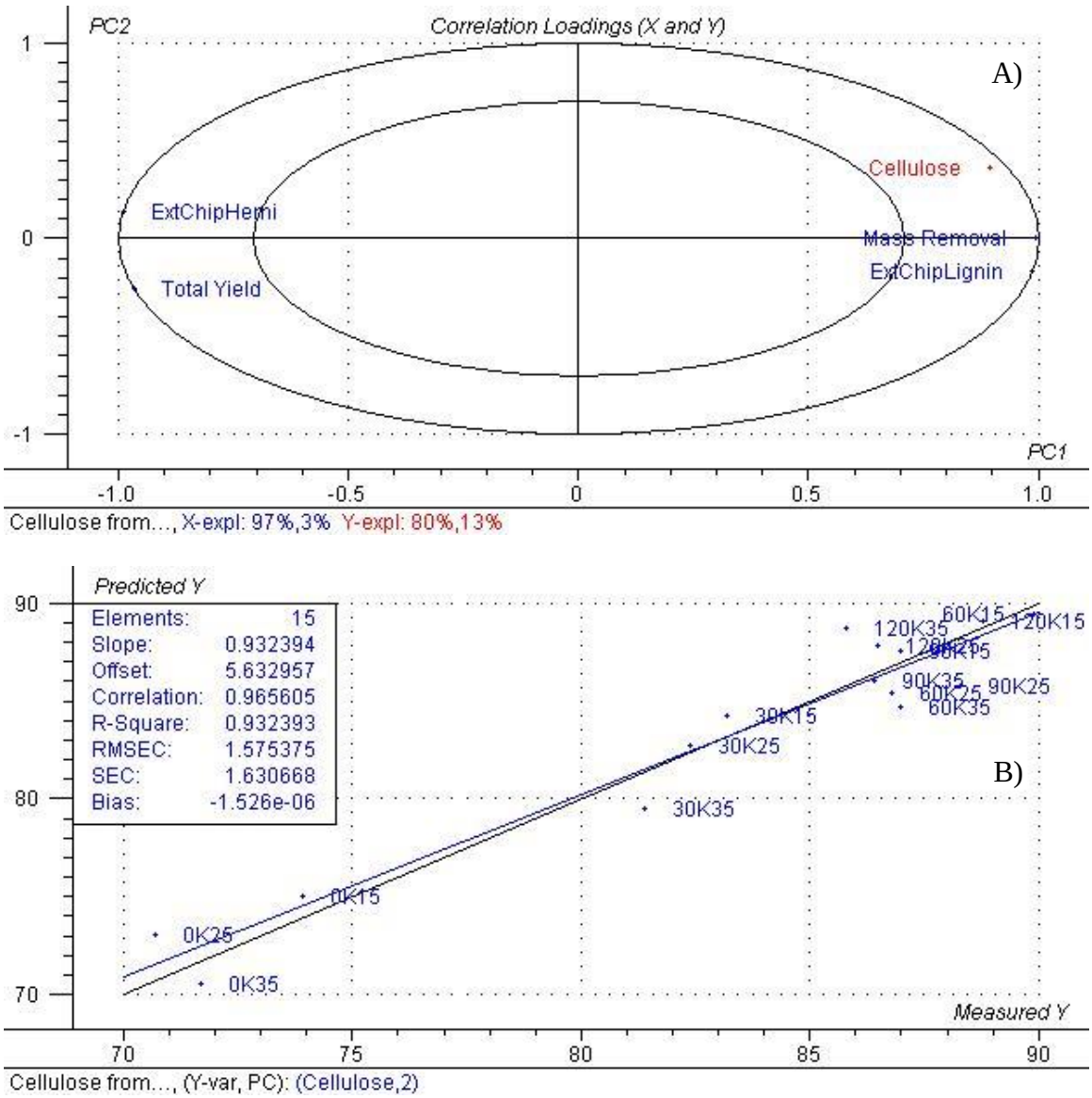


Figure S7 – Model Results for Pulp's Cellulose Content for Sugar Maple. A) Correlation Loadings. B) Predicted vs. Measured

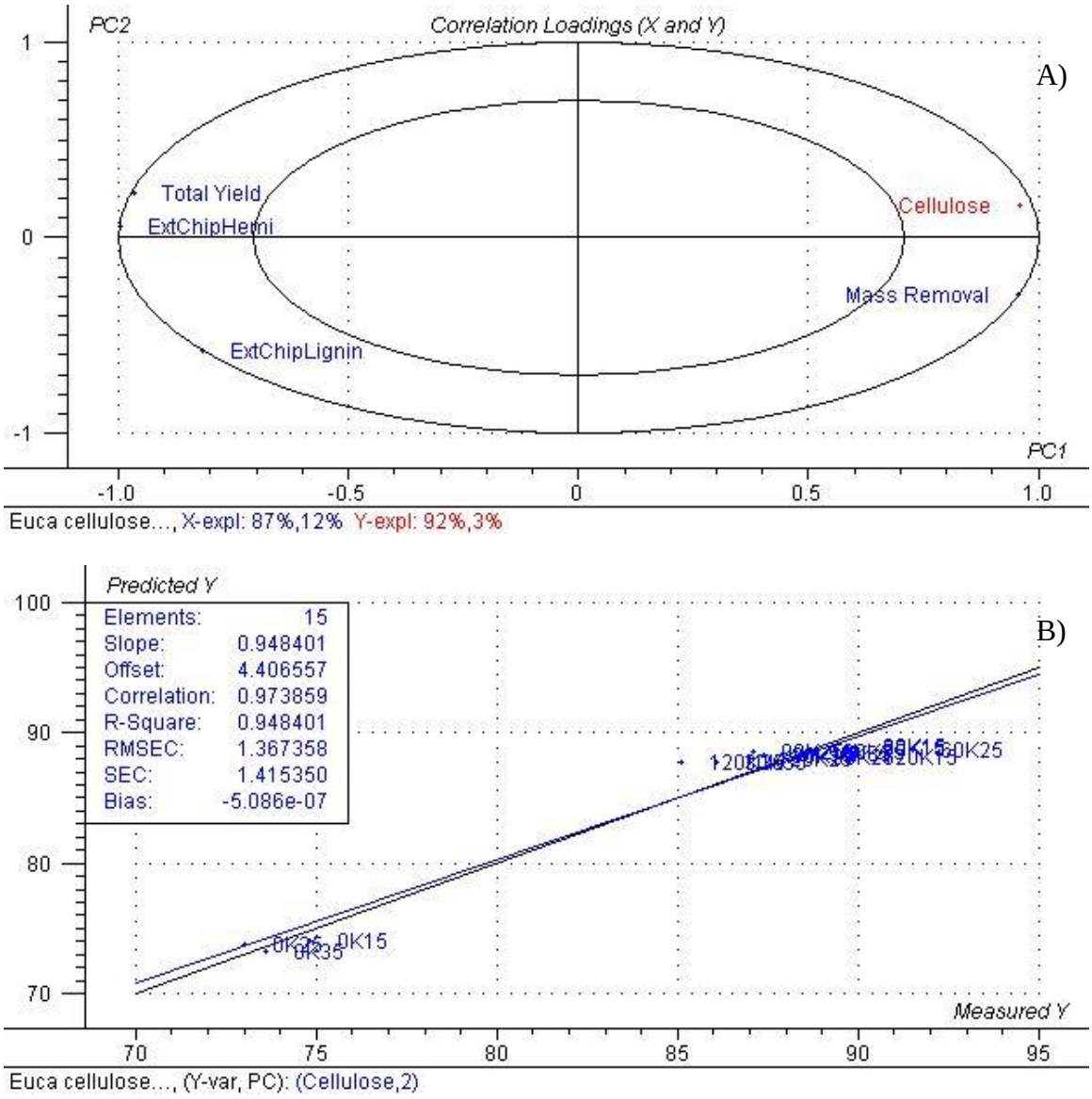
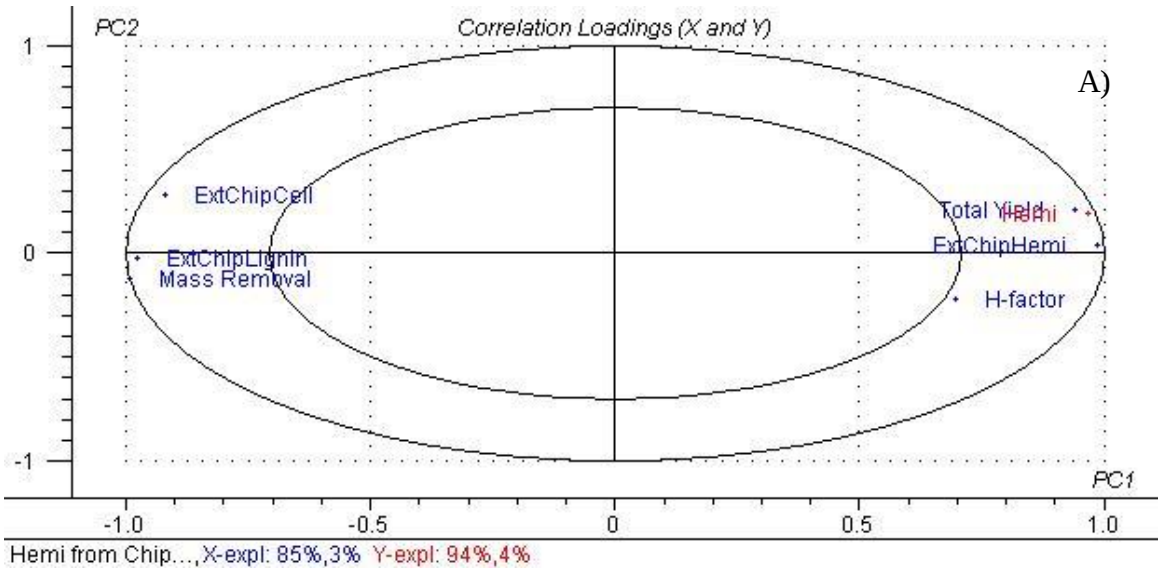


Figure S8 - Model Results for Pulp's Cellulose Content for Eucalyptus. A) Correlation Loadings. B) Predicted vs. Measured



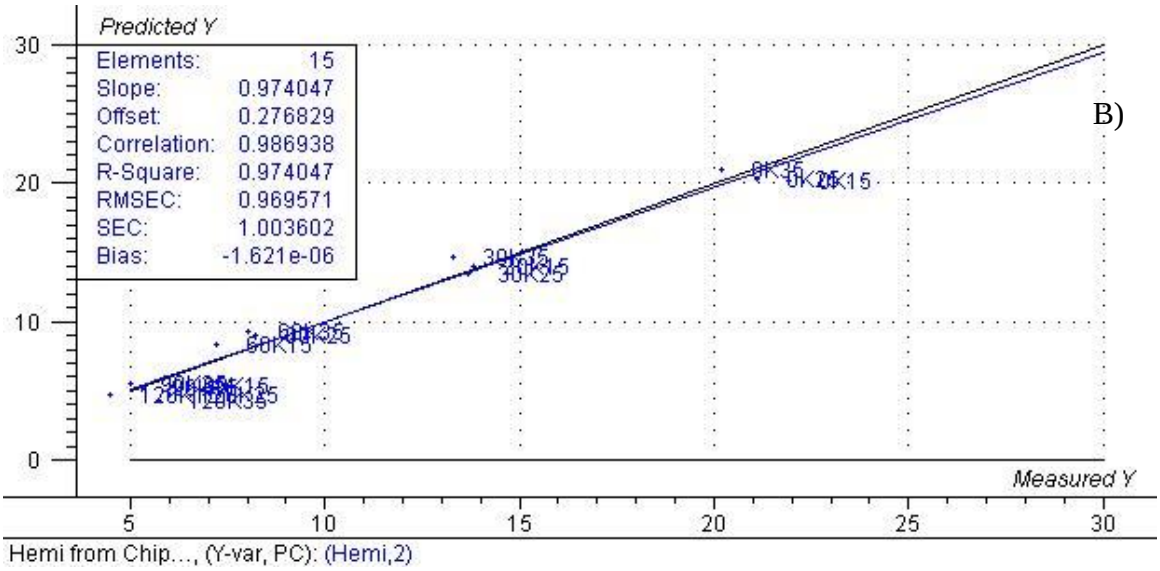


Figure S9 - Model Results for Pulp's Hemicellulose Content for Sugar Maple.A) Correlation Loadings. B) Predicted vs. Measured

B)

A)

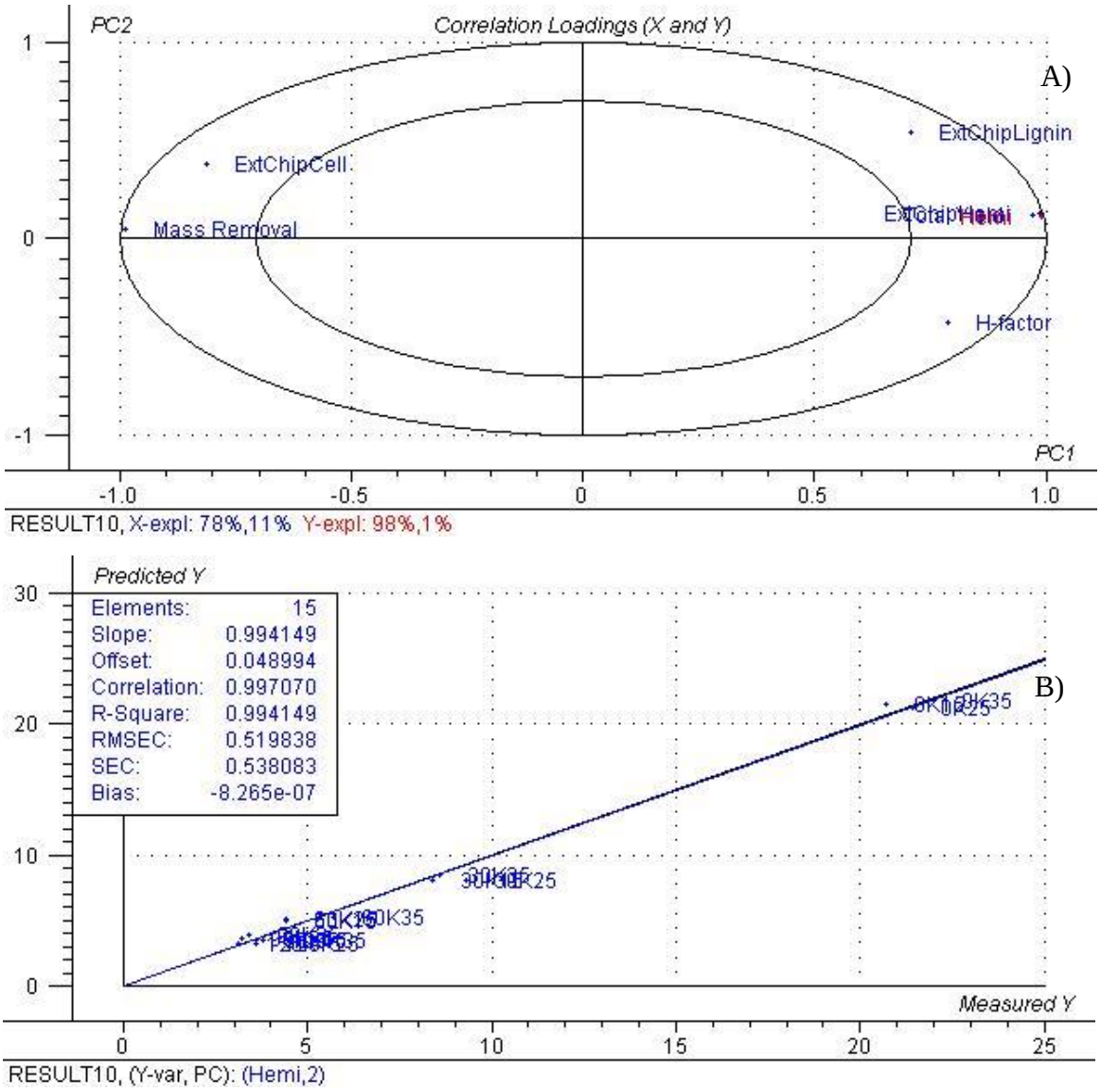


Figure S10 – Model Results for Pulp's Hemicellulose Content for Eucalyptus.A) Correlation Loadings. B) Predicted vs. Measured

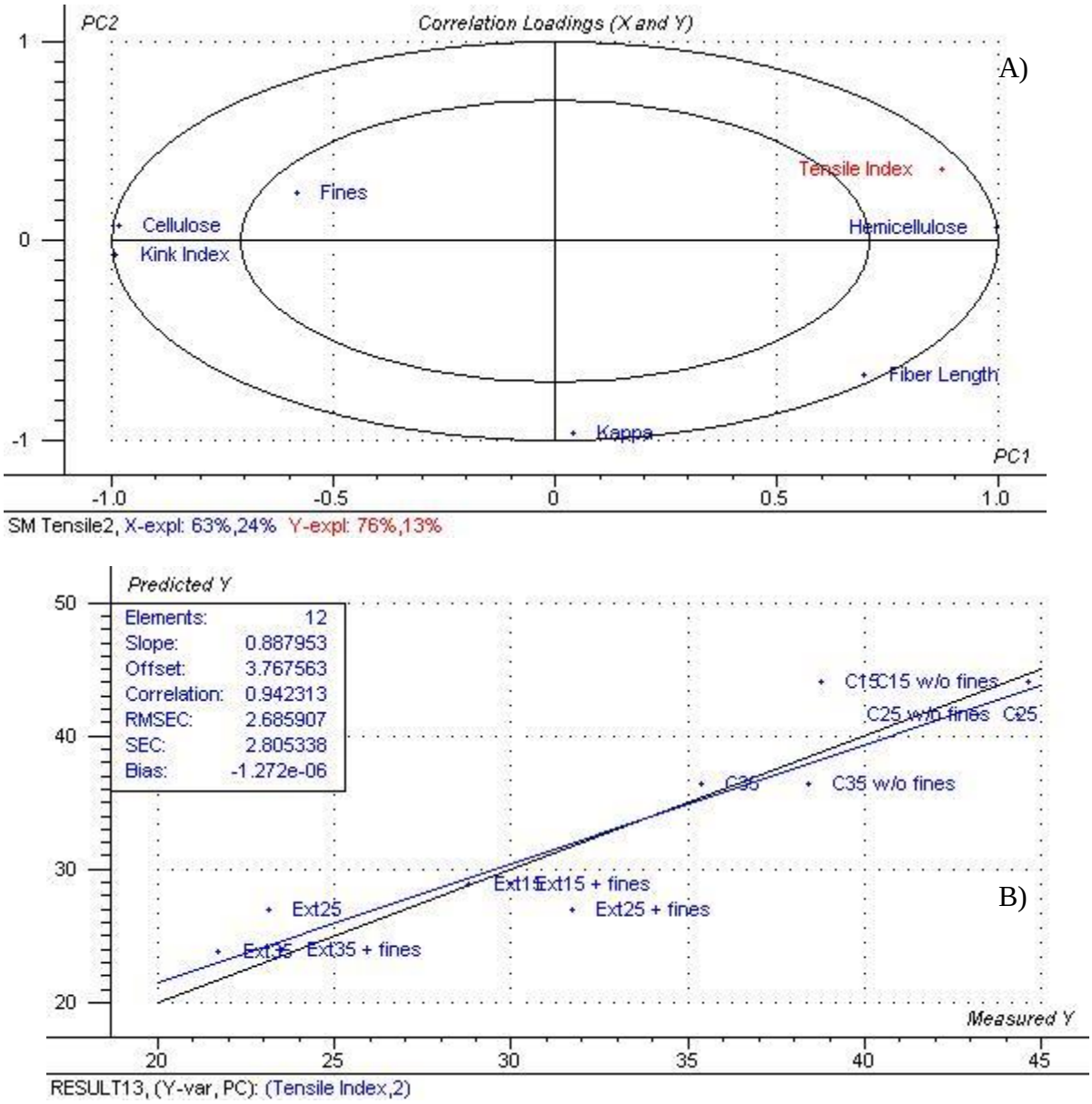
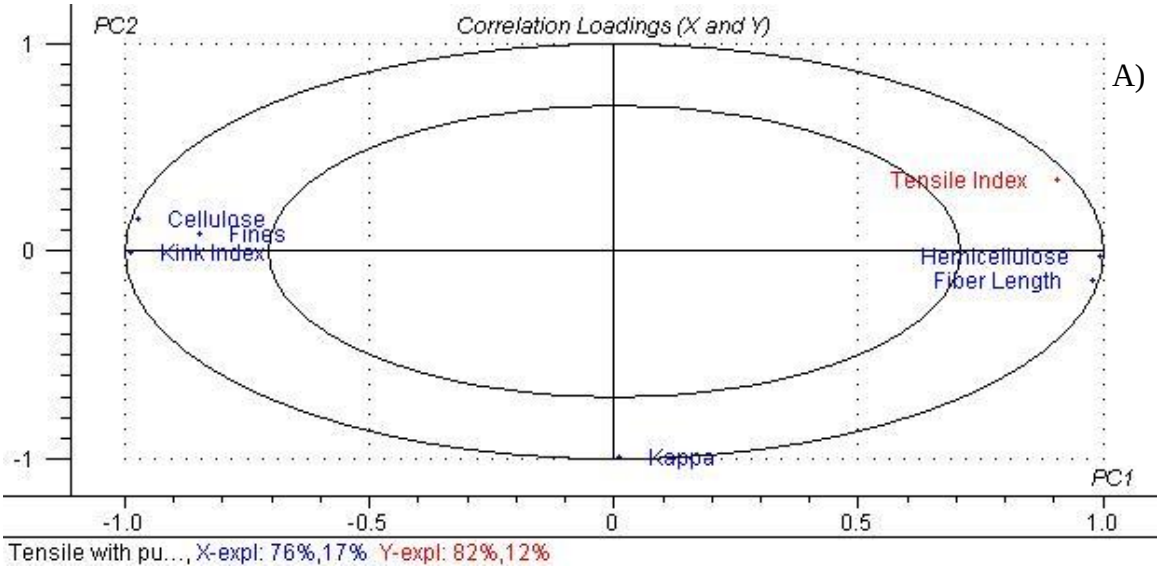


Figure S11 - Model Results for Tensile Index (N.m/g) for Sugar Maple. A) Correlation Loadings. B) Predicted vs. Measured



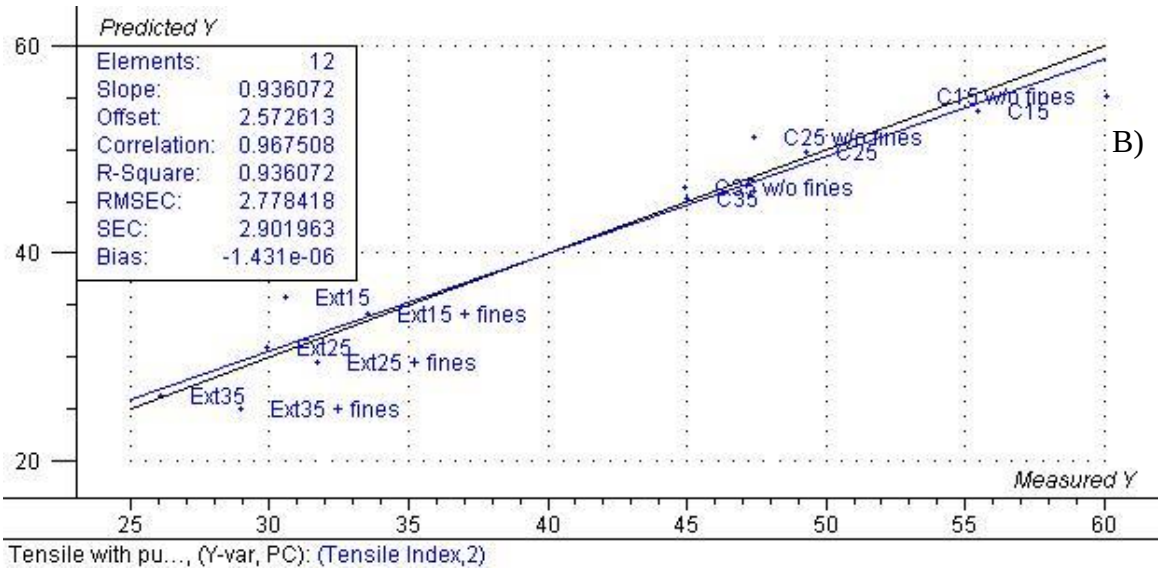
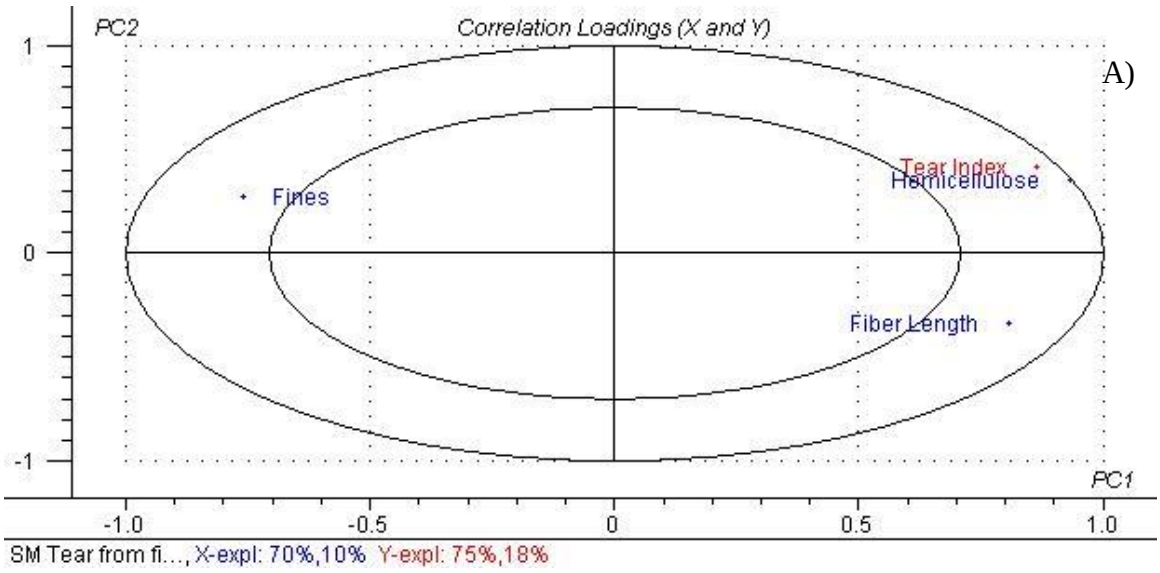


Figure S12 - Model Results for Tensile Index (N.m/g) for Eucalyptus. A) Correlation Loadings. B) Predicted vs. Measured



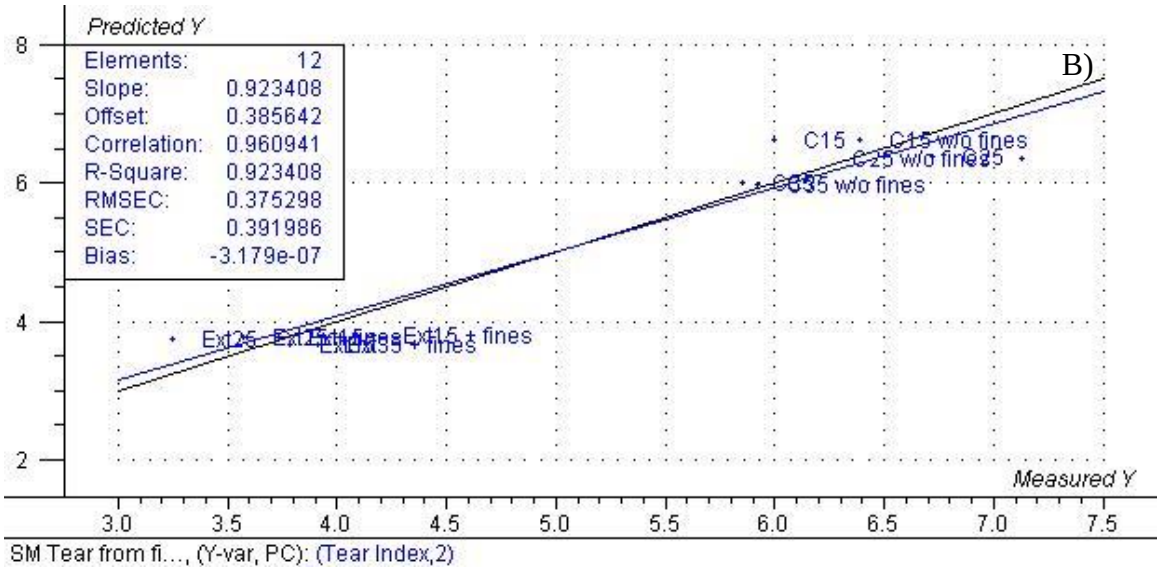


Figure S13 - Model Results for Tear Index (mN.m^2/g) for Sugar Maple. A) Correlation Loadings. B) Predicted vs. Measured

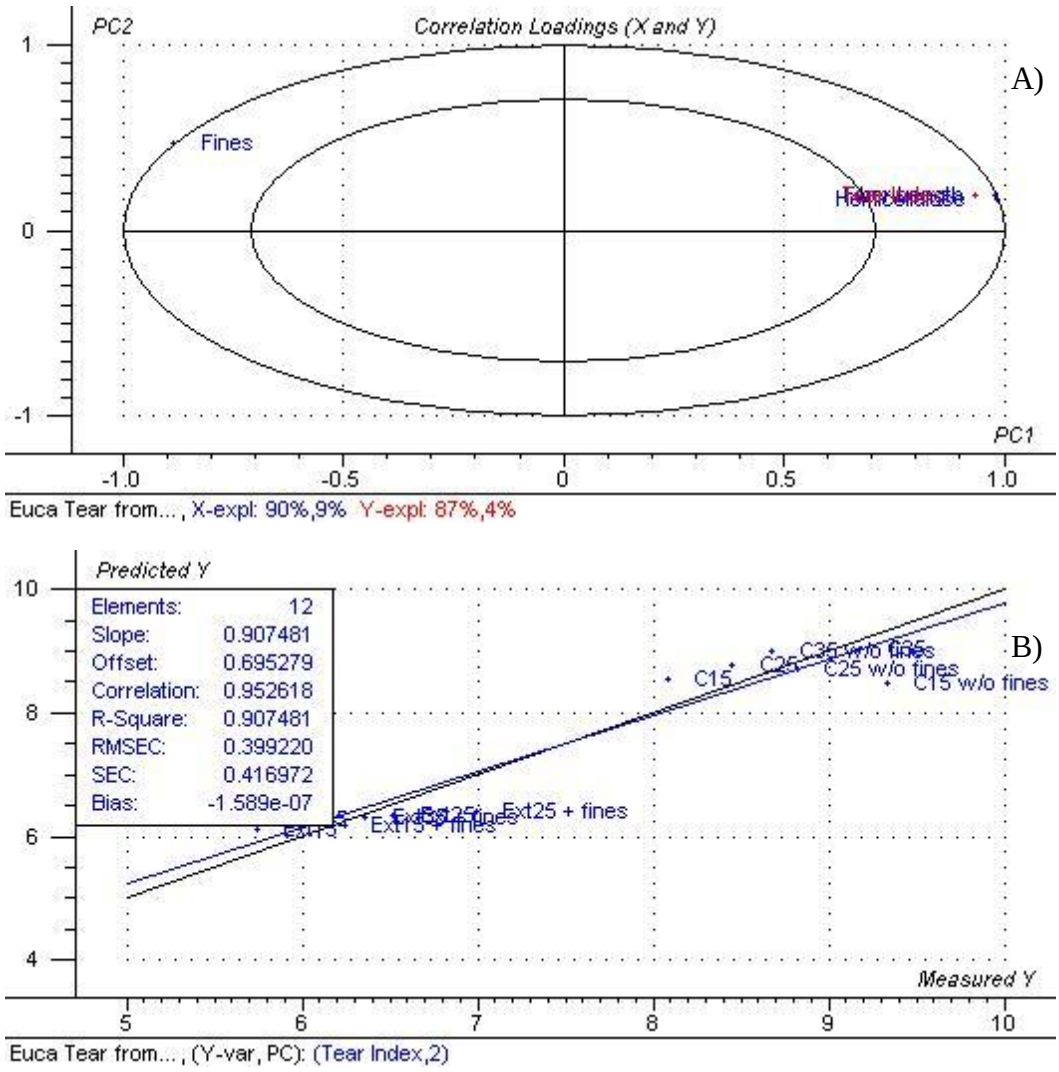


Figure S14 - Model Results for Tear Index (mN.m^2/g) for Eucalyptus. A) Correlation Loadings. B) Predicted vs. Measured

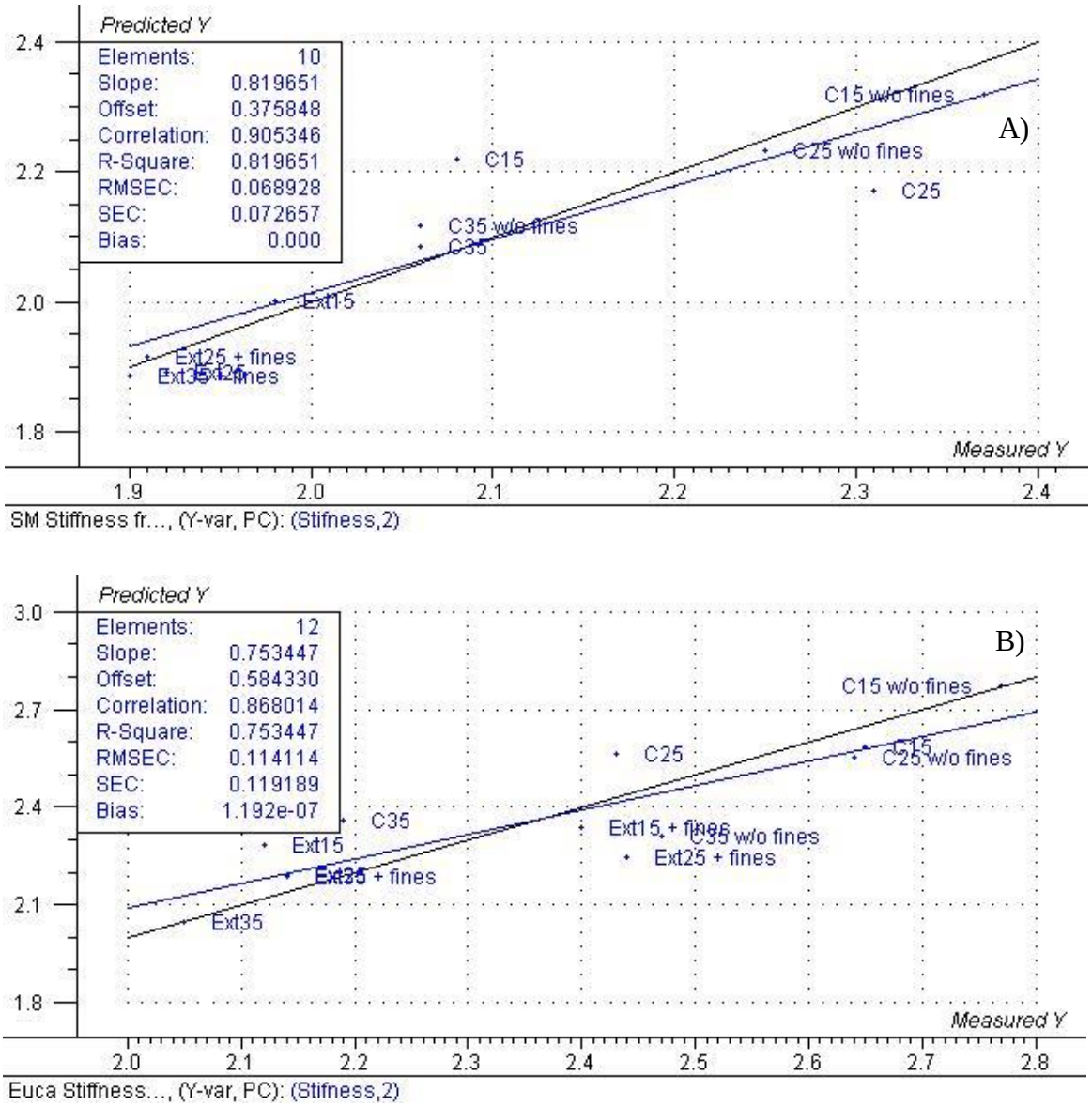


Figure S15 - Model Results for Stiffness Resistance (SU).A) Sugar Maple B) Eucalyptus

Table S14 – Sugar Maple's real and predicted paper properties with a confidence interval of 68.2 % (± standard deviation).

Sample	Tensile Index (N.m/g)		Tear Index ($mN.m^2/g$)		Stiffness (SU)		Burst Index ($kPa.m^2/g$)		Zero Span Strength (N)		Air Resistance (s)	
	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real
0K15	44.06 ± 2.29	38.74	6.62 ± 0.33	6.00	2.22 ± 0.11	2.08	1.92 ± 0.10	1.77	184.81 ± 8.33	174.79	1.70 ± 0.23	1.16
120K15	28.82 ± 4.47	28.82	3.53 ± 0.75	3.73	2.00 ± 0.07	1.98	1.10 ± 0.10	1.09	146.64 ± 12.4	147.12	1.78 ± 0.17	1.64
0K15 w/o fines	44.04 ± 2.82	44.60	6.46 ± 0.53	6.39	2.32 ± 0.09	2.37	1.92 ± 0.10	1.99	184.81 ± 8.33	195.35	1.58 ± 0.16	1.62
120K15 + fines	28.85 ± 2.93	30.00	3.86 ± 0.36	4.17	2.03 ± 0.09	2.35	1.10 ± 0.10	1.09	146.64 ± 12.4	152.71	2.03 ± 0.13	2.26
0K25	41.62 ± 2.54	43.20	6.44 ± 0.28	6.72	2.17 ± 0.08	2.31	1.76 ± 0.10	1.73	181.74 ± 4.73	185.20	1.51 ± 0.17	1.40
120K25	26.93 ± 3.15	23.12	3.66 ± 0.33	3.25	1.89 ± 0.07	1.92	0.87 ± 0.16	0.76	143.82 ± 5.12	130.78	1.37 ± 0.20	1.32
0K25 w/o fines	41.60 ± 2.13	44.32	6.27 ± 0.33	7.13	2.23 ± 0.06	2.25	1.76 ± 0.10	1.98	181.74 ± 4.73	185.20	1.38 ± 0.11	1.38
120K25 + fines	26.95 ± 3.76	31.70	3.99 ± 0.57	3.57	1.92 ± 0.05	1.91	0.87 ± 0.16	0.89	143.82 ± 5.12	139.71	1.63 ± 0.12	1.54
0K35	36.45 ± 2.82	35.36	6.15 ± 0.54	5.85	2.09 ± 0.05	2.06	1.43 ± 0.08	1.32	172.41 ± 11.2	163.88	1.18 ± 0.15	1.22
120K35	23.86 ± 3.16	21.72	3.58 ± 0.32	3.78	1.85 ± 0.06	2.18	0.73 ± 0.09	0.71	139.64 ± 7.14	153.98	1.28 ± 0.21	1.28
0K35 w/o fines	36.43 ± 2.21	38.40	6.00 ± 0.35	5.92	2.12 ± 0.07	2.06	1.43 ± 0.08	1.42	172.41 ± 11.2	172.14	1.07 ± 0.11	1.22
120K35 + fines	23.89 ± 3.47	23.52	3.89 ± 0.58	3.91	1.89 ± 0.08	1.90	0.73 ± 0.09	0.86	139.64 ± 7.14	137.27	1.51 ± 0.12	1.44
30K15	38.60 ± 2.88	-	5.19 ± 0.31	-	2.13 ± 0.11	-	1.55 ± 0.38	-	167.07 ± 11.1	-	1.75 ± 0.22	-
60K15	33.28 ± 4.2	-	4.01 ± 0.51	-	2.05 ± 0.12	-	1.31 ± 0.36	-	154.18 ± 14.6	-	1.82 ± 0.17	-
90K15	32.42 ± 3.84	-	3.81 ± 0.62	-	2.03 ± 0.08	-	1.14 ± 0.42	-	150.33 ± 10.5	-	1.72 ± 0.30	-
30K25	34.24 ± 2.56	-	5.07 ± 0.31	-	2.07 ± 0.10	-	1.17 ± 0.54	-	157.94 ± 8.44	-	1.35 ± 0.28	-
60K25	28.81 ± 2.52	-	4.09 ± 0.26	-	1.99 ± 0.08	-	0.78 ± 0.68	-	142.70 ± 12.0	-	1.29 ± 0.44	-
90K25	26.25 ± 3.10	-	3.51 ± 0.31	-	1.95 ± 0.07	-	0.72 ± 0.44	-	138.71 ± 8.44	-	1.34 ± 0.35	-
30K35	29.77 ± 4.02	-	4.88 ± 0.90	-	2.01 ± 0.15	-	0.89 ± 0.55	-	151.09 ± 16.6	-	1.01 ± 0.29	-
60K35	23.51 ± 2.74	-	3.99 ± 0.47	-	1.91 ± 0.12	-	0.50 ± 0.51	-	135.04 ± 17.6	-	1.04 ± 0.40	-

90K35	22.46 ± 3.08	-	3.56 ± 0.30	-	1.89 ± 0.11	-	0.48 ± 0.43	-	132.97 ± 13.7	-	1.18 ± 0.45	-

Table S15 – Eucalyptus' real and predicted paper properties with a confidence interval of 68.2 % (± standard deviation).

Sample	Tensile Index (N.m/g)		Tear Index ($mN.m^2/g$)		Stiffness (SU)		Burst Index ($kPa.m^2/g$)		Zero Span Strength (N)		Air Resistance (s)	
	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real	Predicted	Real
0K15	53.62± 3.39	55.44	8.55± 0.63	8.08	2.59± 0.16	2.65	2.84± 0.14	3.15	183.47± 2.61	184.52	1.42± 0.16	1.48
120K15	35.98± 3.94	30.54	6.13± 0.32	5.74	2.28±0.17	2.12	1.55± 0.14	1.35	157.38± 2.39	156.77	1.72± 0.14	1.56
0K15 w/o fines	55.12± 3.50	60.12	8.49± 0.57	9.33	2.78± 0.14	2.77	2.84± 0.14	2.90	183.47± 2.61	181.81	1.27± 0.21	1.76
120K15 + fines	34.48± 3.17	33.53	6.18± 0.35	6.24	2.34± 0.12	2.40	1.55± 0.14	1.37	157.38± 2.39	157.11	1.86± 0.10	1.82
0K25	49.32± 3.37	49.30	8.76± 0.32	8.45	2.57± 0.10	2.43	2.47± 0.10	2.47	178.46± 1.78	177.58	1.19± 0.08	1.28
120K25	30.60± 3.24	29.92	6.35± 0.45	6.52	2.19± 0.08	2.14	1.07± 0.25	1.08	150.99± 4.61	155.90	1.47± 0.08	1.70
0K25 w/o fines	50.73± 2.78	47.40	8.71± 0.28	8.82	2.55± 0.08	2.64	2.47± 0.10	2.29	178.46± 1.78	178.77	1.06± 0.11	1.02
120K25 + fines	29.20± 3.10	31.70	6.40± 0.40	6.99	2.25± 0.10	2.44	1.07± 0.25	1.15	150.99± 4.61	152.03	1.60± 0.12	1.74
0K35	45.61± 3.38	44.98	9.03± 0.58	9.18	2.36± 0.09	2.19	2.15± 0.14	2.21	173.03± 2.44	170.98	1.00± 0.10	0.98
120K35	26.32± 3.15	26.10	6.27± 0.26	5.79	2.05± 0.10	2.05	0.84± 0.26	0.97	145.62± 4.47	147.77	1.48± 0.15	1.36
0K35 w/o fines	46.82± 2.94	44.90	8.99± 0.63	8.68	2.31± 0.12	2.47	2.15± 0.28	1.91	173.03± 2.44	175.81	0.89± 0.09	0.80
120K35 + fines	25.12± 3.14	28.98	6.32± 0.27	6.36	2.19± 0.21	2.14	0.84± 0.29	0.96	145.62± 4.47	138.83	1.60± 0.17	1.54
30K15	41.79± 4.25	-	7.29± 1.28	-	2.40± 0.18	-	1.95± 0.28	-	163.61± 2.75	-	1.53± 0.15	-
60K15	37.25± 4.65	-	6.75± 1.41	-	2.31± 0.17	-	1.64± 0.29	-	157.26± 3.40	-	1.60± 0.14	-
90K15	37.17± 3.72	-	6.34± 0.41	-	2.32± 0.16	-	1.66± 0.19	-	158.47± 3.05	-	1.72± 0.15	-
30K25	36.98± 4.48	-	7.35± 1.05	-	2.31± 0.16	-	1.60± 0.32	-	157.53± 4.08	-	1.44± 0.09	-
60K25	33.16± 5.25	-	6.76± 1.46	-	2.24± 0.17	-	1.32± 0.33	-	151.90± 4.20	-	1.51± 0.09	-
90K25	31.46± 3.42	-	6.41± 0.84	-	2.21± 0.08	-	1.20± 0.16	-	150.93± 2.44	-	1.54± 0.09	-

30K35	33.51± 4.16	-	7.44± 1.72	-	2.25± 0.15	-	1.30± 0.28	-	153.18± 2.92	-	1.27± 0.07	-
60K35	28.97± 4.70	-	7.00± 1.61	-	2.16± 0.16	-	1.04± 0.42	-	146.36± 5.85	-	1.39± 0.14	-
90K35	27.21± 3.81	-	6.50± 1.04	-	2.13± 0.11	-	0.88± 0.20	-	145.26± 2.83	-	1.43± 0.11	-