Project Title: Defining Kraft Pulping Spectrum for Southern Loblolly Pine

GT Project Staff:

Principal Investigator: Art Ragauskas

PROGRAM OBJECTIVE:

A key asset for the US pulp and paper industry is its access to vast reserves of low-cost southern pine that provides an excellent pulp for variety of applications especially where strength properties are an important component of the product. This two year project seeks to develop a project directed at developing a comprehensive description of how kraft pulping parameters influence brownstock chemical and physical properties. This industry directed program addresses a key research need of the Pulp and Paper Industry, as described in the Agenda 2020 Technology Platform and by industry leaders. The results of this study will address the industry's need to optimize kraft pulping for optimal pulp properties.

PROJECT BACKGROUND:

Kraft pulping is a complex technology involving both chemical and physical processes. The relationships between these processes, the wood and pulping liquor composition, and the temperature profile determine how the kraft pulping system responds to changes in process variables such as effective alkali, sulfidity, time, and the maximum cooking temperature. A recent study by Ragauskas and Dyer dealt with establishing a relationship between pulp kappa number, pulp color and the process variables of effective alkali, % sulfidity, maximum cooking temperature, and H-factor.[1]

Employing screened southern pine (*Pinus taeda*) wood chips, a rotatable central composite design was carried out with a specific goal of being able to precisely and accurately predict the pulp kappa number under certain pulping conditions. This Phase I central composite design was composed of a 2^3 factorial, with 6 axial points and 6 center points. The effective alkali was varied from 11-21%; the % sulfidity was varied from 5-55%; and the maximum cooking temperature was varied from 162-178ºC. The H-factor for these kraft pulping conditions varied from 400-2200. This Phase I central composite design involved 120 different pulping conditions. Table 1 summarizes some of the effective alkali, % sulfidity, and maximum cooking temperature for each pulping condition in this recent investigation.

Table 1. Summary of the effective alkali, sulfidity, and maximum temperature pulping conditions for Phase I of this research employing unextracted softwood chips.

Sample	% EA	% Sulfidity	Temperature (°C)
1	13.0	15.2	165.0
2	19.0	15.2	165.0
3	13.0	44.8	165.0
4	19.0	44.8	165.0
5	13.0	15.2	175.0
6	19.0	15.2	175.0
7	13.0	44.8	175.0
8	19.0	44.8	175.0
9	11.0	30.0	170.0
10	21.1	30.0	170.0
11	16.0	5.1	170.0
12	16.0	54.9	170.0
13	16.0	30.0	161.6
14	16.0	30.0	178.4
15	16.0	30.0	170.0
16	16.0	30.0	170.0
17	16.0	30.0	170.0
18	16.0	30.0	170.0
19	16.0	30.0	170.0
20	16.0	30.0	170.0

The independent variables were coded and entered into a statistical analysis program known as NCSS. One of the capabilities of this statistical software is that it is able to develop multiple linear regression models to fit data. Based on this information, a model was developed to predict the kappa number of pulps. The format of this model was similar to that used by McDonough in his multiple linear regression model for kraft-anthraquinone pulping of southern pine.[2] The results of the model developed are summarized in the following equation in terms of uncoded variables:

$$\log_{10} K = 4.872 - 0.169EA - 0.029S - 9.909\times10^{-4}H + 0.003EA^2 + 2.680\times10^{-6}SH + 2.257\times10^{-4}S^2 + 2.247\times10^{-7}H^2 \quad \textbf{Equation 1}$$

$$R^2 = 0.98$$

where K is the kappa number; EA is the percent effective alkali charged on oven-dried wood; S is the percent sulfidity; and H is the H-factor. The high multiple correlation coefficient (R^2) indicates that there is a low percent error (2%) in the model. The kappa number in this model varied from 15-116, while the independent variables ranged according to the conditions listed above in Table I. One interesting observation is that the maximum cooking temperature was not statistically significant at the 95% confidence interval in predicting the kappa number of these pulps. Therefore, this variable did not appear in the regression equation. In addition, there are some first-order interactions as well as second order terms in the equation.

However, each of these terms was found to be statistically significant at the 95% confidence interval.

The model developed to predict the pulp kappa number is entirely empirical and has limitations, including the fact that the model cannot be expected to predict the effect of changing the independent variables in such a way that they lie outside the ranges used in the experiments outlined above. However, the specific goal of this phase of the investigation was to accurately and precisely predict the pulp kappa number under a given set of conditions. In order to do this, the model must be validated. Another set of experiments were designed in an attempt to validate the model developed in Phase I. For these experiments, southern pine (*Pinus taeda*) wood chips were collected from various member company mills and cooked in an M-K digester system under varying effective alkali, % sulfidity, maximum temperature, and H-factor. The dependent variable, kappa number, was measured and recorded. Finally, the model from Phase I was used to predict the pulp kappa number under the varying conditions applied to the M-K digester system. The results indicate that there is a good correlation between the predicted and observed kappa numbers from the M-K digesters. In fact, the multiple correlation coefficient (R^2) value was 0.97, indicating that the model was very good at predicting the kappa number obtained from the pulps produced in the M-K digesters. Figure 2 shows the predicted kappa numbers from the regression equation of Phase I vs. the observed kappa numbers from the M-K digesters. Therefore, we are able to conclude that the model developed is indeed a good model for predicting the kappa number, as long as the conditions of effective alkali, sulfidity, and H-factor that one is investigating are within the range that was employed when developing the regression equation. In addition, the model was valid using both the electrically-heated, rotating, multi-unit digester system as well as the M-K digesters. The model was also valid using a wide array of southern pine wood chips and not just those from one site or plantation.

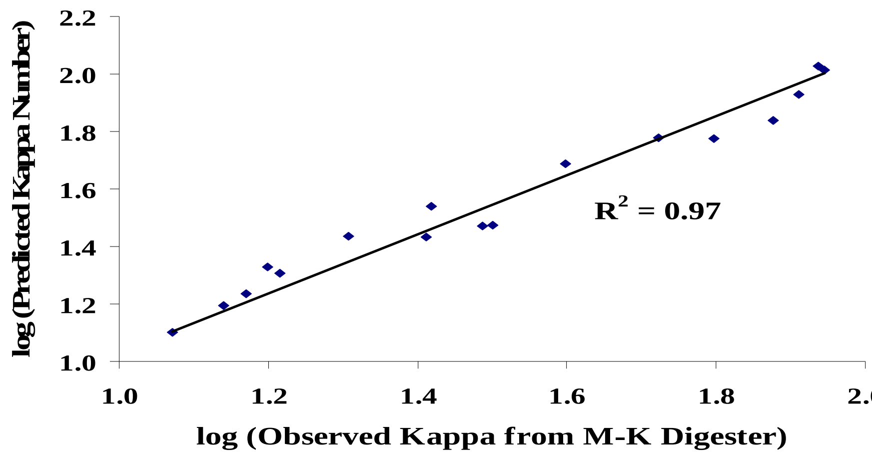

Figure 2. Predicted kappa by the model vs. observed kappa from the M-K digester experiments to validate the model.

This program will develop a comparable relationship to develop global models correlating kraft cooking conditions to fiber chemistry (i.e., kappa#, viscosity, fiber charge, klasen lignin/hexA, carbohydrate profiles) and strength properties (i.e., tensile, tear, burst)

OVERALL PROGRAM DELIVERABLES:

Research activities for this program will provide program sponsors an integrated evaluation of how kraft pulping influences the chemical and physical properties of Loblolly kraft pulps for mature and thinning wood. In year I our studies would focus on a mature wood sample (i.e., 25 year) and year II will be directed on a juvenile Loblolly resource. Although, older work exists in this field most lack some part of the complete picture that this program will address, especially with respect to correlating strength properties. At the completion of this project, program sponsors will receive a final report that highlights how kraft pulping can be used to control paper strength properties.

PROJECT APPROACH:

Pulping studies will be conducted to study the impact of the following variables using a central composite design:

Effective Alkali charge:	11-21%
Sulfidity:	5-40%
Cooking Temperature:	155-175^{o}C
H Factor:	400-2200

This study will be conducted on mature wood and it will be extended to juvenile wood. Ten trees of mature southern pine will be harvested. The trees will be cut in a manner to separate the mature wood form the juvenile wood. Mature wood from the trees will chipped together and screened, using a William Laboratory Classifier. Chips that passed through a 1-inch screen and retained by a 3/8-inch screen will be used for the kraft pulping experiments. After pulping, the pulps will be dinsintegrated using a refiner operating at a gap of .008 inches.

The research parameters to be acquired will include: total and screened yield, kappa number and chlorited viscosity. The analysis of the pulp chemistry and physical properties will be accomplished at IPST@GT. These studies are proposed to include:

Fiber Chemistry	Fiber/Paper Strength Properties
Klasen #	Tensile
Fiber Charge	Tear or TEA
HexA	Burst
Sugar Profile	(unrefined/PFI refined)

- A select subgroup of pulps will be bleached D(E+P+O)DD, brightness 87 and re-analyzed for physical/optical properties.

Regression models will be developed using SAS to correlate the impact of various pulping variables on the properties.

REFERENCES

[1] Deconvoluting chromophore formation and removal during kraft pulping: influence of metal cations. Dyer, T.J. .; Ragauskas, A.J. Appita Journal (2006), 59(6), 452-458.

[2] McDonough, T.J.; Kinetics and Modelling of Kraft Pulping. In *Alkaline Pulping*, Malcolm, E.W. and Grace, T.M., Editors Joint Textbook Committee of the Pulp and Paper Industry. **5**: (1989).