Acid Prehydrolysis of Wood

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ABSTRACT

Acid pretreatment of wood provides significant energy savings during refining but reduces the brightness of the pulp. Acid treatments also extract carbohydrates from wood. Addition of an acid pretreatment process to a thermomechanical pulping process therefore offers an opportunity to reduce refining energy cost and provide a secondary product from a fermentation ethanol plant. A process being investigated by BioPulping International and the Forest Products Laboratory involves pretreatment with oxalic acid or diethyl oxalate and offers 25% or more reduction in specific refiner energy consumption, with a minor sacrifice in brightness. This treatment also results in extraction of approximately 6% of the wood mass. Similarly, research during the late 1970s on sulfonated chemimechanical pulping at low pH determined that bisulfite reduced specific refining energy, maintained brightness, and released carbohydrates. The similarity in behavior of these two pretreatments suggests a common mechanism that is the subject of this study. Our hypothesis is that both acids provide optimal conditions, either buffering at pH 2 or mildly reducing conditions, for pretreating wood. To test this hypothesis, a series of spruce and aspen veneer samples were pretreated with sodium bisulfate, sulfurous acid, and oxalic acid. These three acids can provide buffering near pH 2 and a range of redox potential. The wood chip brightness of the sodium bisulfate and oxalic acid experiments were similar but at a given yield sulfurous acid seems to preserve brightness better than does either bisulfate or oxalic acid. The redox activity does not seem to affect results.

INTRODUCTION

The concept of prehydrolyzing wood chips before conventional pulping is not new. In his book *Pulping Processes*, Rydholm lists 41 references for pretreating chips for kraft pulping using various acids, sulfite liquor, or autohydrolysis with hot water [1]. Generally, these papers were reporting research intended for the production of low-hemicellulose-content dissolving pulps. Several prehydrolysis patents were obtained by Richter in 1933 [2]. The idea of using the resulting hydrolyzate to produce ethanol is also not new. Companies producing prehydrolysis kraft dissolving pulps evaluated ethanol as a co-product to improve operating efficiency. Acid pretreatment for mechanical pulp grades is also not novel. Brecht and Kilpper heated grinder bolts up to 160°C for as long as 14 h prior to conventional stone grinding. Autohydrolysis under these conditions will produce a final pH around 4 and will hydrolyze most of the hemicellulose in the wood. The resulting brown pulps were obtained in 80–85% yield and gave a 20–30% reduction in grinding energy [3]. Similar studies were carried out by McGovern [4]. Several studies using mineral acid pretreatment have been carried out by McDonough and co-workers [5], and numerous papers report sulfurous acid cooking prior to refining both for chemi-thermomechanical pulps and semichemical pulp [6-8]. Nearly all these papers report lower brightness and a 20% or larger reduction in refining energy.

Interest in prehydrolysis treatments today is pursuing a different value metric, but the principles are the same. The resulting wood pulp must be suitable for paper or paperboard, which represents 80% or more of the ultimate process value. The filtrates produced need to maximize the yield of sugars and minimize compounds that inhibit growth and function of bacteria or yeast. In an extensive study of water, sulfurous acid, and sulfuric acid hydrolysis of aspen,

Mackie and others found little evidence for fermentation inhibitors with either sulfurous or sulfuric acid pretreatments [9]. In mechanical pulping, the 20% energy savings reported by Brecht and Kilpper is low relative to what is often observed with autohydrolysis and various acid pretreatments where energy reductions of 30–40% are reported [10].

The USDA Forest Service, Forest Products Laboratory, in Madison, Wisconsin, has been pursuing energy reduction in production of thermoechanical pulp (TMP) using fungal pretreatments for many years [11]. In this work it was discovered that fungi released surprisingly high levels of oxalic acid and that oxalic acid by itself provided many of the benefits observed with fungal treatments [12]. Research on pretreatments with oxalic acid and a related project using diethyl oxalate are part of a project managed by the AF&PA Value Prior to Pulping partner companies. The major advantages reported for prehydrolysis using oxalic acid or diethyl oxalate are reduced energy (35–55%) and improved strength [10]. These are not unique to oxalic acid and can be accomplished with mineral acids. Use of oxalic acid is also reported to reduce brightness loss relative to use of autohydrolysis and mineral acids [10,13]. Brightness loss is a concern for TMP because the common uses—newsprint, supercalendared (SC), and lightweight coated (LWC) paper—all have higher brightness requirements, and the ability to bleach the TMP back to the desired brightness is limited. The improved brightness retention using oxalic acid raises questions as to what is chemically unique about oxalic acid treatment and if the effect can be duplicated with other acids. Two hypotheses were proposed:

1. Hydrolysis of wood at pH 1 to 2 will not reduce brightness as much as other pretreatments. Oxalic acid is a difunctional acid with pKa values of 4.2 and 1.3. Bisulfate, oxalic, and sulfurous acids will provide a buffered treatment pH in the range of 1 to 2, higher than in a pretreatment using sulfuric acid and lower than is typically achieved with autohydrolysis or acetic acid [14].

2. Mild reducing conditions will preserve wood brightness during acid hydrolysis treatments. Table 1 shows the reduction potential for the three acids used in this study. Under the conditions of these experiments, oxalic acid is the most reducing, sulfurous acid is mildly reducing, and bisulfate is not redox active.

To avoid artifacts, brightness and yield changes were measured on the unrefined wood chips. Pulp produced in lab- and pilot-scale refiners is usually of low brightness relative to commercial operation. The low brightness may be due to rust contamination from discontinuously used steam pipes or oxygen entrainment at high temperatures because of batch processes. These represent uncontrolled effects that can be avoided by measuring optical changes on the wood chips without refining the chips to produce pulp.

EXPERIMENTAL

Several 25- by 25-cm sheets of never-dried commercial spruce and aspen veneers were obtained for the experiments. The veneer was cut into 2.5- by 2.5-cm wood chips and stored in a freezer until ready for processing. Prior to use, wood samples were thawed and saturated with water. Three wood chips were loaded into a PTFE-lined 50-ml pressure vessels. Sufficient water and chemical were added to provide the 16-to-1 liquor-to-wood ratio (18-to-1 for softwood) and the target chemical charge (Table 2). Chips were soaked in the treatment solution for 1 h and the pressure vessel was sealed, placed into a heating block set to the target temperature, and held at that temperature for times specified in Table 2. Treated chips were soaked multiple times with deionized water to remove dissolved sugars and oligomers and then air dried under restraint. Wood samples were sanded with 400-grit sandpaper to prepare them for reflectance testing. Reflectance measurements were performed using a Hitachi U-3010 UV-Visible spectrometer (Hitachi, Schaumburg, Illinois) equipped with a 150-mm integrating sphere and using a MgO standard.

Table 1. Properties of the acids

Acid	pKa_1	pKa_2	E°
Oxalic acid	1.27	4.27	–0.481
Sulfurous acid	1.89	7.20	0.158
Sulfuric acid	Not measurable	1.99	None

Table 2. Treatment conditions for each acid

	Acid molarity	Temperature (°C)	Time at temperature (min)
1	0.10	120	0
2	0.10	120	60
3	0.15	102	0
4	0.15	120	60
5	0.015	150	0
6	0.015	150	60
7	0.01	150	0
8	0.01	150	60
9	0.055	135	0

Brightness was calculated by integrating the product of reflectance and illuminant, optics, filters, and phototube response given in table 2 of TAPPI T-452 relative to the MgO standard. The value reported as brightness correlates well with Tappi and ISO brightness measurements made on several wood chips. Chips used in the hydrolysis experiments were too small for standard brightness measurements with available instruments designed for paper testing. Yields were determined from dissolved solids by neutralizing an aliquot of solution and drying. An effort was made in each case to adjust for the acid. Sulfurous acid was removed by nitrogen purging the sample and sulfuric acid by precipitating with barium. The yield for the oxalic acid experiments was corrected directly for the dissolved acid. Yields were checked against the lignin and sugar analysis of the residual wood and do not appear to have significant systematic errors due to different methods of adjusting for the acid.

RESULTS

The relationship between brightness and yield for sulfurous acid is significantly different ($p = 0.0091$) from that for the other two acids (Figure 1). The brightness relationships for oxalic acid and bisulfate do not appear to be significantly different ($p = 0.68$). The higher brightness obtained when using sulfurous acid is not due to delignification but may be due to sulfonation of lignin. Even higher brightness is usually reported for sulfonation conditions at higher pH [7,8]. The brightness improvement observed when treating wood with oxalic acid could also be due to complex formation with trace metals and the ability to dissolve and remove iron oxide and other high-valence transition metals.

A second observation is that sulfurous acid reduces yield 17% more than oxalic acid does ($p = 0.014$), and oxalic acid reduces yield 4% more than sodium bisulfate ($p = 0.002$) (Figure 2). The data in Figure 2 is a subset of the conditions tested and includes results with both aspen and spruce. The effectiveness of sulfurous acid could be due to the formation of lignosulfonates, which have a lower pKa value (0.5) [15] than that of sulfurous acid (2). The final pH of the reactions using sulfurous acid is nearly 0.5 units lower under mild treatment conditions and about 0.2 units lower under the moderate treatment conditions than those obtained with the other two acids.

Numerous kinetic models for hemicellulose and cellulose hydrolysis are described in the literature [16-19]. The simplest approaches assume an Arrhenius activation energy [10,16,19], and there have been reports that pulping H-factor functions to integrate time and temperature into a single relative rate value for the prehydrolysis. Reported activation energies vary from 96 kJ/mol (diethyl oxalate, oxalic acid prehydrolysis) [10] to 189 kJ/mol (waste paper with sulfuric acid) [17]. The H-factor method with an Arrhenius activation energy of 134 kJ/mol is in the same range, suggesting that H-factor is an acceptable first approximation of reaction rate. Because as a minimum each hemicellulose polymer, the amorphous cellulose, crystalline cellulose, and lignin all have different hydrolysis rates, activation energies, and kinetic relationships, this is a very simplified approach. H-factor does not provide a direct linear relationship with yield over the entire range of hydrolysis conditions tested in this work. It was also clear that higher chemical charges were increasing the rate of hydrolysis, and as shown in Figure 2, the rates also depended on the acid used.

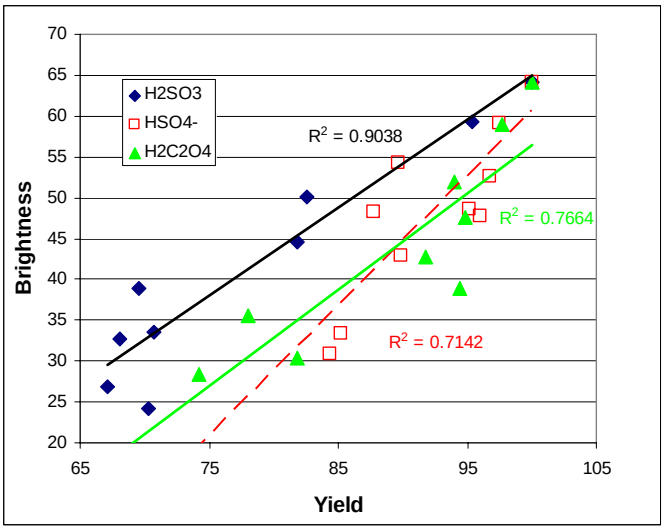

Figure 1. Brightness relative to treatment yield for aspen.

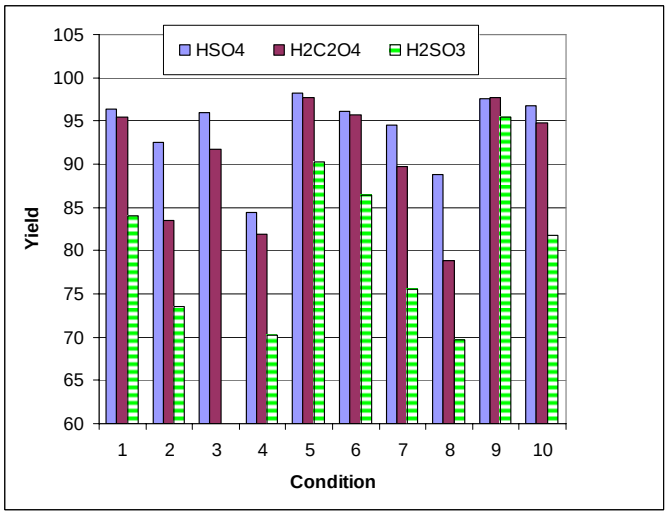

Figure 2. Chip yield after pretreatments using sulfurous acid, oxalic acid and sodium bisulfate.

Assuming a second-order reaction dependant on starting biomass and acid concentration, the following rate equation applies:

$$\frac{dm}{dt} = -k[\mathrm{H}^+][m] \tag{1}$$

where m is residual mass, t time, $[\mathrm{H}^+]$ acid concentration, and k the rate constant. As an acid-catalyzed reaction, $[\mathrm{H}^+]$ does not change during the reaction. Integrating the kinetic equation gives

$$\int_0^t \frac{dm}{m} = -[\mathrm{H}^+]\int_0^t k\,dt \tag{2}$$

$$\ln(m) - \ln(M_0) + C = -[\mathrm{H}^+]kt \quad (3)$$

where M_0 is mass at time zero. For the case of biomass hydrolysis, a graph of ln(yield) relative to reaction time is not a straight line. A major simplification is the assumption that most of the wood can be hydrolyzed. Most of the hemicellulose and some of the cellulose are easily hydrolyzed, but this represents less than 40% of the wood. Considering that some components of the wood are soluble in water or acid and not subject to the reaction constraints and that some components will not hydrolyze or hydrolyze only slowly under the reaction conditions, the starting wood can be considered to be composed of three components. Letting the soluble component be represented by *S*, hydrolyzable carbohydrate by m_0 and the non-hydrolyzable component by *r* (resistant), the starting biomass $T = S + r + m_0 = 1$. The biomass remaining (yield) after partial hydrolysis is $Y = r + m$. Solving yield for m/m_0 gives $m/m_0 = Y/m_0 - r/m_0$. Substituting m_0 for M_0 in Equation (3) and shifting to the exponential form gives

$$\ln(m) - \ln(m_0) + C = -[\mathrm{H}^+]kt \quad (4)^*$$

$$Cm/m_0 = e^{-[\mathrm{H}^+]kt} \quad (5)$$

$$\frac{Y}{m_0} - \frac{r}{m_0} = \frac{e^{-[\mathrm{H}^+]kt}}{C} \quad (6)$$

$$Y = \frac{m_0}{C}\left(e^{-[\mathrm{H}^+]kt}\right) + r \quad (7)$$

Plotting yield against the exponent of $[\mathrm{H}^+]kt$ should fit a linear equation with slope m_0/C and intercept *r*. At time zero, the exponential term equals 1. Yield is $m_0 + r$, making the constant 1. This plot is shown in Figure 3 for softwood, substituting H-factor for *kt* and molar acid charge for H^+. Linear regression values for both hardwood and softwood and the three acids are summarized in Table 3. Using H_2SO_3 as the acid appears to make more material available in the beginning of the treatment (soluble) and more available for hydrolysis. Substituting either hydrogen ion activity (pH) or the product of molar concentration and activity coefficient does not have any appreciable affect on the results. For a given severity factor (H-factor multiplied by acid concentrations), prehydrolysis with sulfurous acid dissolves about twice as much material as does either oxalic acid or sodium bisulfate.

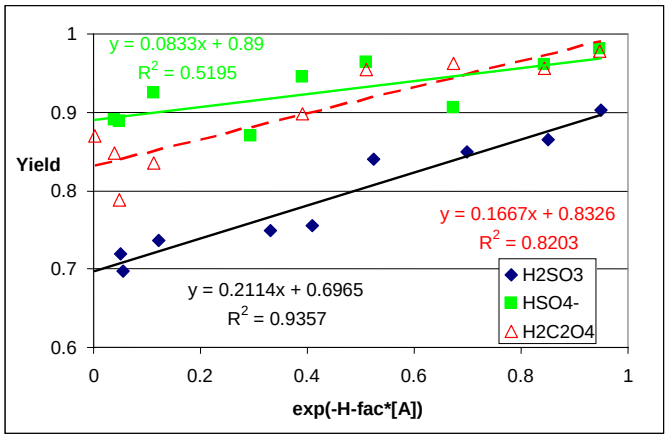

Figure 3. Yield relative to exp(–H – fact[*A*]) where [*A*] is molar concentration of the anion. Slope is the hydrolyzable carbohydrate and intercept is the recalcitrant carbohydrate.

* Note *C* is just a constant and the transition from Equation (4) to Equation (5) requires the value of *C* to change to e^C. This constant is not critical to the analysis.

Table 3. Carbohydrate accessibility as indicated by the kinetic plots[a]

	Hydrolyzable		Soluble	Resistant		R^2
$H_2C_2O_4$, HW	0.225	0.105	0	0.785	0.058	0.82
H_2SO_3, HW	0.255	0.102	0.093	0.652	0.054	0.86
HSO_4, HW	0.103	0.110	0.048	0.849	0.076	0.41
$H_2C_2O_4$, SW	0.167	0.070	0	0.892	0.037	0.82
H_2SO_3, SW	0.211	0.072	0.093	0.696	0.038	0.93
HSO_4, SW	0.083	0.049	0.03	0.89	0.027	0.52

[a] HW, hardwood; SW, softwood. Error is 95% confidence interval.

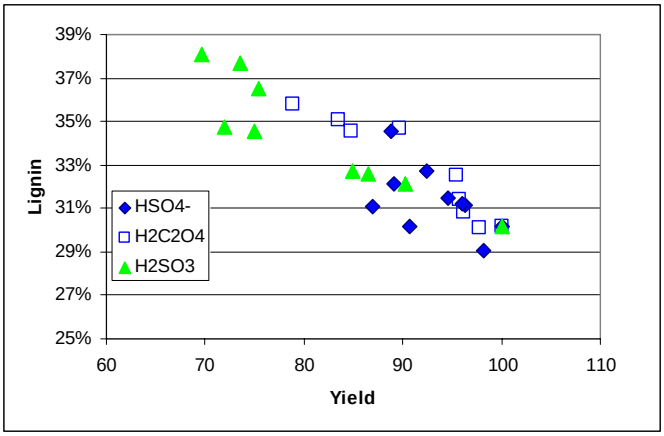

Figure 4. Residual lignin in the softwood prehydrolysis experiments.

Additional information on the efficacy of the acids is available from the composition of the wood remaining after treatment. Residual lignin is plotted against yield for the softwood experiments in Figure 4. Sulfurous acid does not appear to have a significantly different impact on delignification ($p = 0.106$) relative to the other two acids. In the spruce experiments, all prehydrolysis increased residual lignin concentration. With pretreatments of spruce, the acids are apparently less effective at dissolving lignin than carbohydrates, but this is not the case with aspen where the sulfurous acid does appear to increase lignin removal ($p = 0.0092$) and lignin contents are 2% to 4% lower than the trend observed for oxalic acid and sodium bisulfate. Differences in the behavior of hardwoods and softwoods during acid prehydrolysis have been noted by Richter [20] and Rydholm [1] and explained as an increased susceptibility of softwood lignin towards condensation reactions. According to both Richter and Rydholm, this tendency is reduced when the pretreatment is with sulfurous acid. Richter [20] shows minor delignification in hardwoods under all acid pretreatment conditions, and little or no delignification in softwoods, as confirmed in this research.

Glucose yield (at a given total yield) was not influenced by choice of acid when treating aspen ($p = 0.446$), but spruce (Figure 5) showed a 2% reduction in residual glucose when using sulfurous acid relative to oxalic acid. This is offset by a 2% increase in residual mannose content. Both differences are quite small and not statistically significant ($p = 0.416$). Although the glucose fraction of the remaining wood is clearly in the same range when using sodium bisulfate as acid (Figure 5) the range of yield data and the scatter in the data are such that a regression fit is not meaningful and it is not possible to reach a conclusion on glucose yield. Using sulfurous acid, Richter showed a 1% greater loss in yield and 4% greater loss in alpha cellulose with western hemlock, and 3% greater loss in yield and 2% greater loss in alpha cellulose when pretreating birch [20]. The comparison is to sulfuric acid treatment (as

opposed to sodium bisulfate), but otherwise conditions are similar. Unfortunately, Richter did not check for mannose.

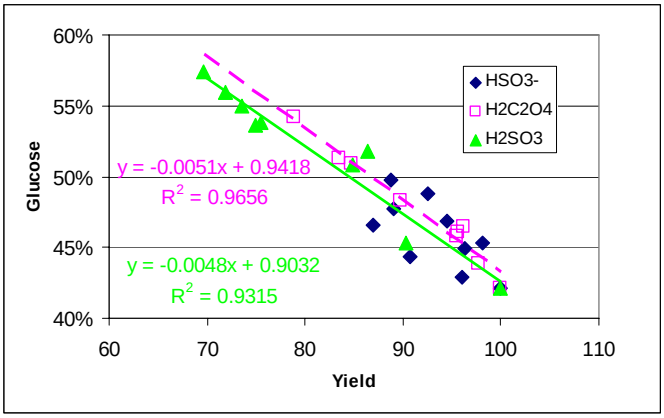

Figure 5. Residual glucose relative to total yield when treating spruce. The solid line is the linear regression fit to the sulfurous acid data, the dashed line is the regression fit to the oxalic acid data.

CONCLUSIONS

Pretreatment of wood chips prior to pulping is of interest to the paper industry as a way to add a valuable co-product and increase profitability of papermaking. One process of interest is pretreatment prior to thermomechanical pulp production because the acid pretreatment provides a substantial reduction in specific energy required to produce the pulp. A downside of acid pretreatment is a loss in brightness that is very difficult to recover with subsequent bleaching, which would increase bleaching costs. The research conducted here evaluated three acid treatments for impact on brightness. To avoid problems with brightness losses in pilot-scale refining, the research was carried out on wood veneer chips and the brightness measurements were made directly on the wood samples. Results show that at a given chip yield, treatment with sulfurous acid produces a brighter wood chip than does pretreatment with either oxalic acid or sodium bisulfate, which give about equal brightness losses. Although this suggests that the answer to the hypothesis that controlling pH in the range of 1–2 may be the critical issue in improved brightness outcomes with oxalic acid, this conclusion needs to be confirmed with a more general pH treatment study and follow-up work on other potential mechanisms, such as metal sequestration and possible oxidation processes in batch refining. The brightness advantage obtained when using sulfurous acid was observed with both aspen and spruce veneer chips. Sulfurous acid also gave more extensive hydrolysis (lower yields) at similar treatment severity than either of the other two acids.

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Oxalic Acid Pretreatments

- Oxalic acid is effective for pretreating wood chips for thermomechanical pulping.
  - Decreases specific refining energy by about 25%
  - Does not impact brightness significantly
  - Yield loss is 5-10%
- Diethyl oxalate (thought to hydrolyze to oxalic acid in use) gives similar benefits in refining.

Mineral acids

- Previous work with mineral acids gave the energy reduction but produced a severe loss in brightness.
  - Rueckert, IPST Masters independent study projects, with Dr. Tom McDonough.

pKa = 1.27

- This makes oxalic a moderately strong acid. Stronger than typical organic acids but not a strong acid that is dissociated under concentrated conditions.
- The pKa of 1.27 means that it will usually form a buffer solution when used to treat wood chips and provide a final pH between 1 and 2.

Other acids

- Other acids will also provide pH buffers between pH 1 and 2.
- H_2SO_3 – pka = 1.89 and 7.2
- HSO_4^- - pKa = 1.99

Reducing potential

- The major possible benefit of reducing potential is to control air oxidation reactions.
- The sulfite ion (SO_3^{2-}) in it's various forms is very mildly oxidizing relative to the standard hydrogen electrode, but very capable of reducing oxygen to form sulfate ions.

Therefore:

- If the higher brightness is due to the final pH between pH 1 and pH 2, both sulfurous acid and sodium bisulfate should provide similar brightness.
- If the higher brightness is due to oxalic acid scavenging oxygen, sodium bisulfate should give low brightness, but sulfurous acid will give higher brightness.
  - Efficiency should be reaction rate dependant and final brightness should be higher than when using bisulfate, but could be either higher or lower than when using oxalic acid.

Experimental

- Wood veneer was cut into squares about 1” by 1”
  - Both spruce and aspen.
- Sample treatment was to soak in acid for 1 hour then heat to temperature.
- L/W was 16 to 1 for aspen, 18-1 for spruce.
- Heating was in 50 ml teflon® lined pressure vessels.

Experimental

- Temperature varied from 120° to 150°
- Time at temperature varied from 0 minutes to 60 minutes.
- Acid concentration varied from 0.015 molar to 0.15 molar.

Analysis

- Filtrate was collected and tested for dissolved sugars and total carbohydrates (dissolved oligomers plus sugars)
- Veneer samples were restraint dried and checked for brightness using a UV-Vis spectrometer equipped with an integrating sphere.
- Veneer chips were tested for yield, lignin and remaining carbohydrates.

Analysis: yield

- Yield was determined from the oven dried treated veneer sample and solution concentration.
  - adjusted for behavior of the acid
  - Oxalate by adjusting for oxalate mass.
  - Sulfurous acid- evaporates
  - Bisulfate precipitated with barium.
- Yield data has been checked against sugar yields in the solutions and in the remaining wood and show no appreciable differences (error).

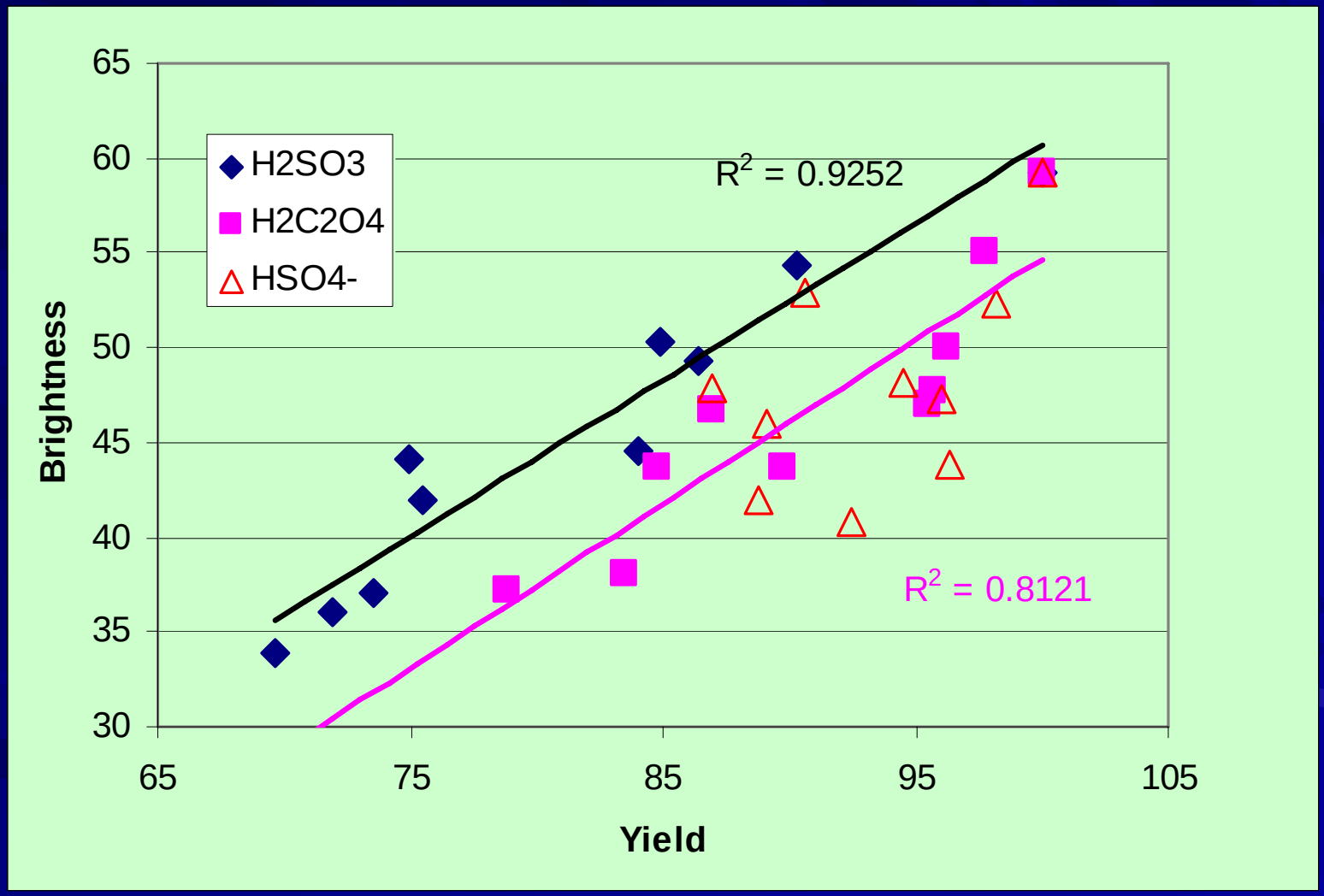
Analysis

- Final filtrate pH
- Hydrolysis rate was estimated as H-factor, calculated for the time and temperature provided by the pressure vessels and heating block.

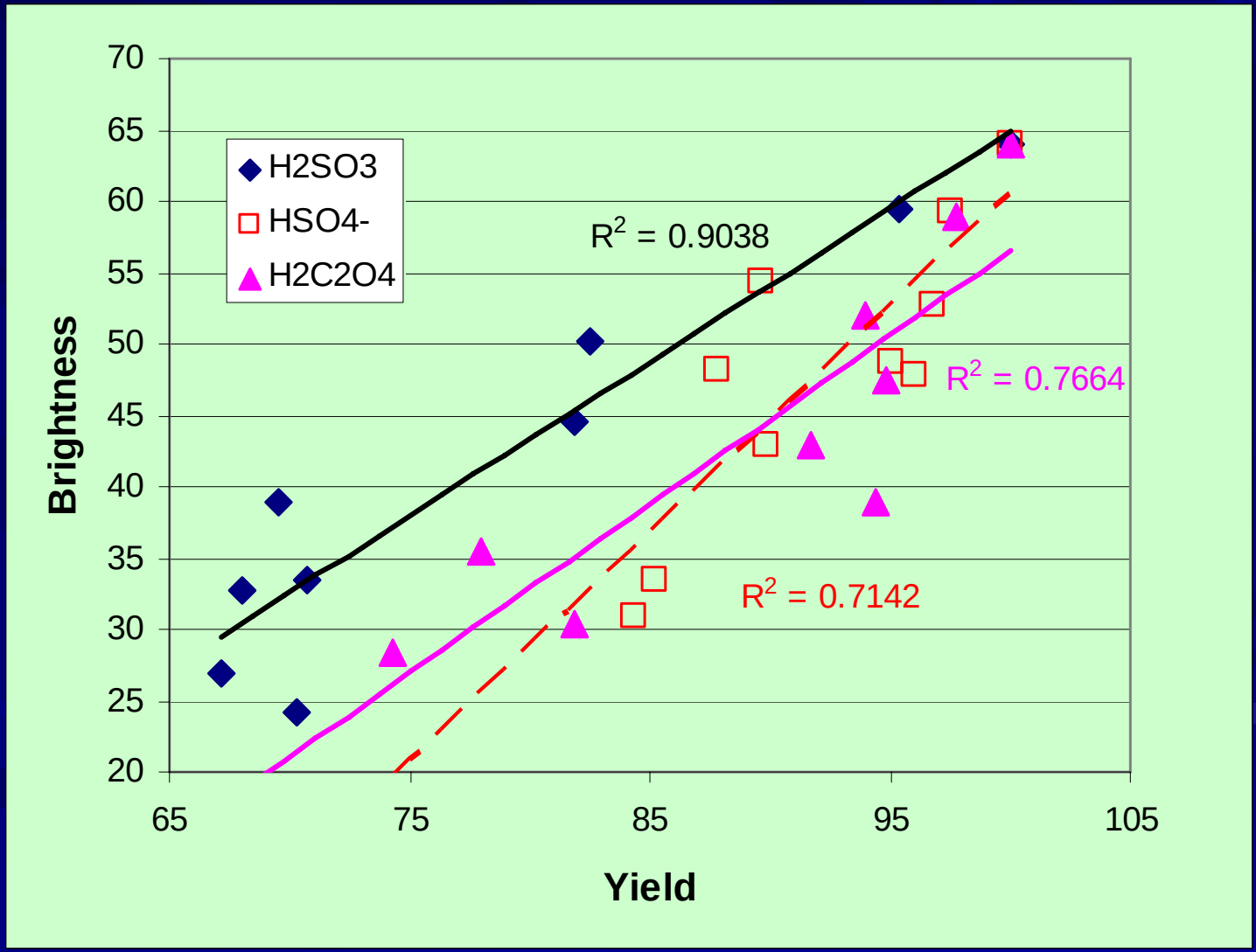
Results summary:

- Higher brightness at a given yield when using sulfurous acid.
- Lower yield at a given treatment condition when using sulfurous acid.
- Similar brightness and yield when using oxalic acid and sodium bisulfate.

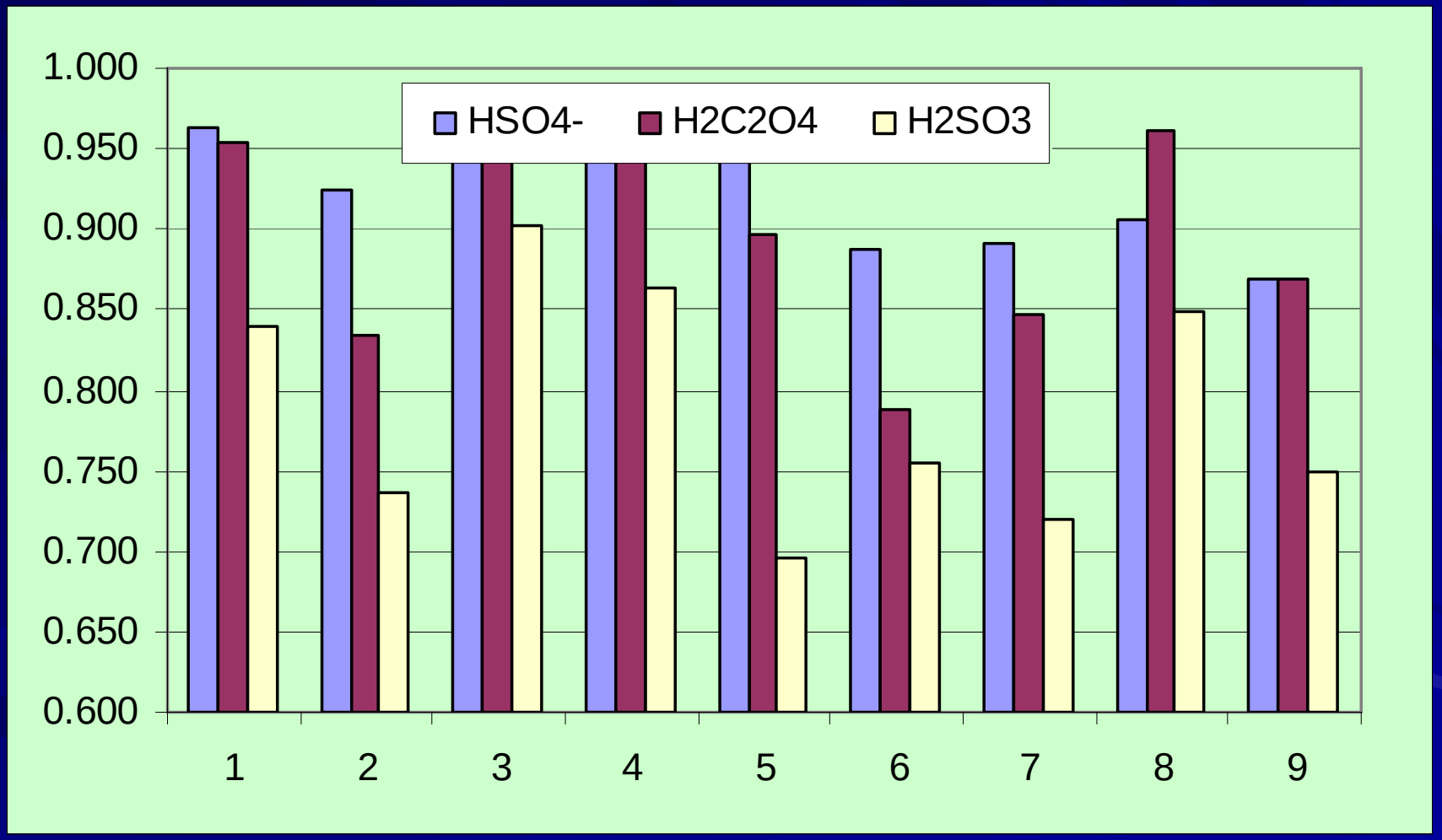
Veneer brightness: Softwood



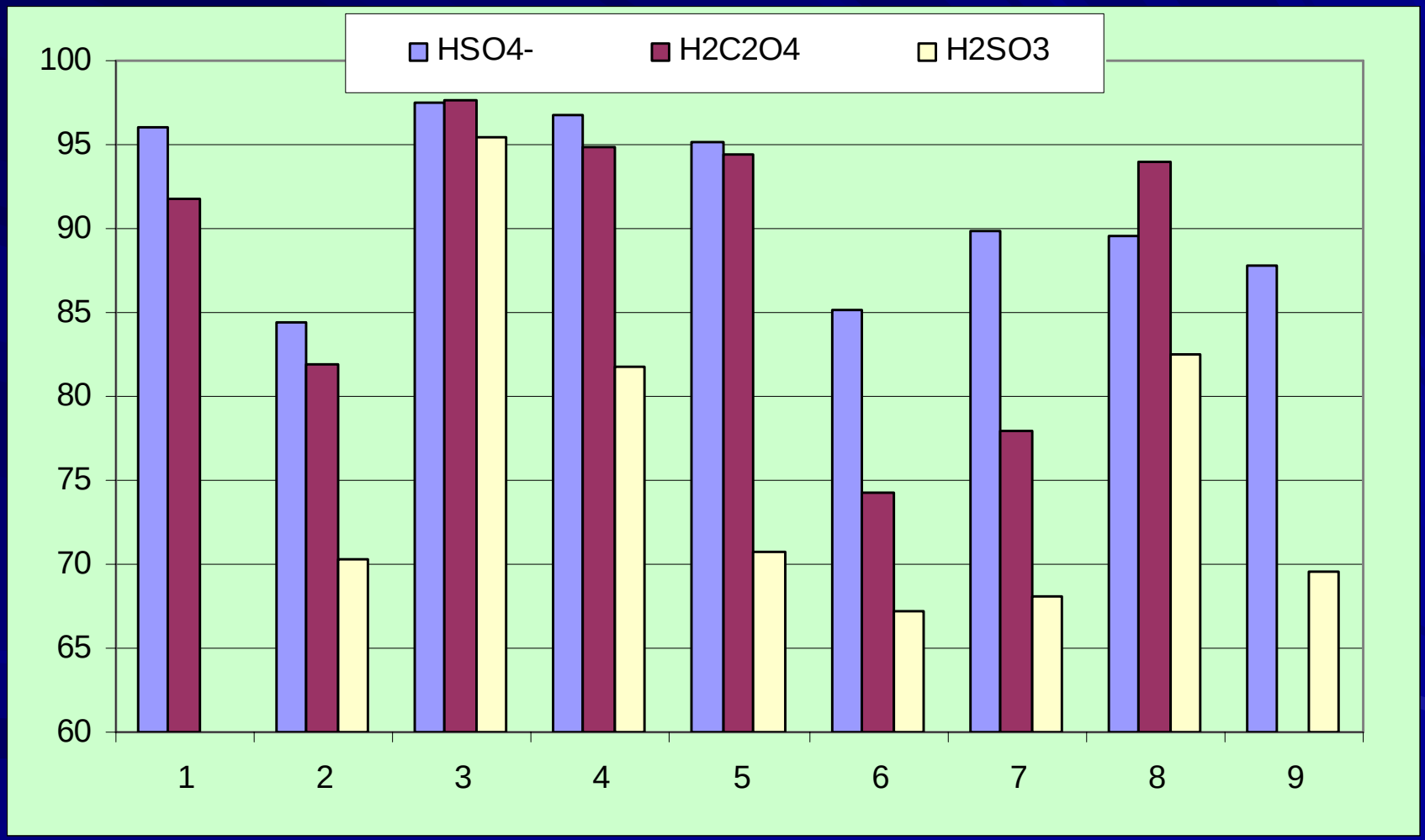
Veneer Brightness: Hardwood



Softwood Yield



Hardwood Yield



Severity - Kinetics

$$\frac{dm}{dt} = -k[\mathrm{H}^+][m]$$

$$\int_0^t \frac{dm}{m} = -[\mathrm{H}^+]\int_0^t k\,dt$$

Integrating and Rearranging

$$\ln(m) - \ln(m_0) + C = -[\mathrm{H}^+]kt$$

$$Cm/m_0 = e^{-[\mathrm{H}^+]kt}$$

What about yield?

- Three portions of the wood mass: soluble (*s*), hydrolyzable (m_0), and resistant (*r*).
- *m* in the kinetics is the remaining part of the hydrolyzable portion.
- Yield (Y) = *r* + *m* or m = Y - *r*

Substitute Y – *r* for *m* and rearrange

$$\frac{Y}{m_0} - \frac{r}{m_0} = \frac{e^{-[\mathrm{H}^+]kt}}{C}$$

$$Y = \frac{m_0}{C}\left(e^{-[\mathrm{H}^+]kt}\right) + r$$

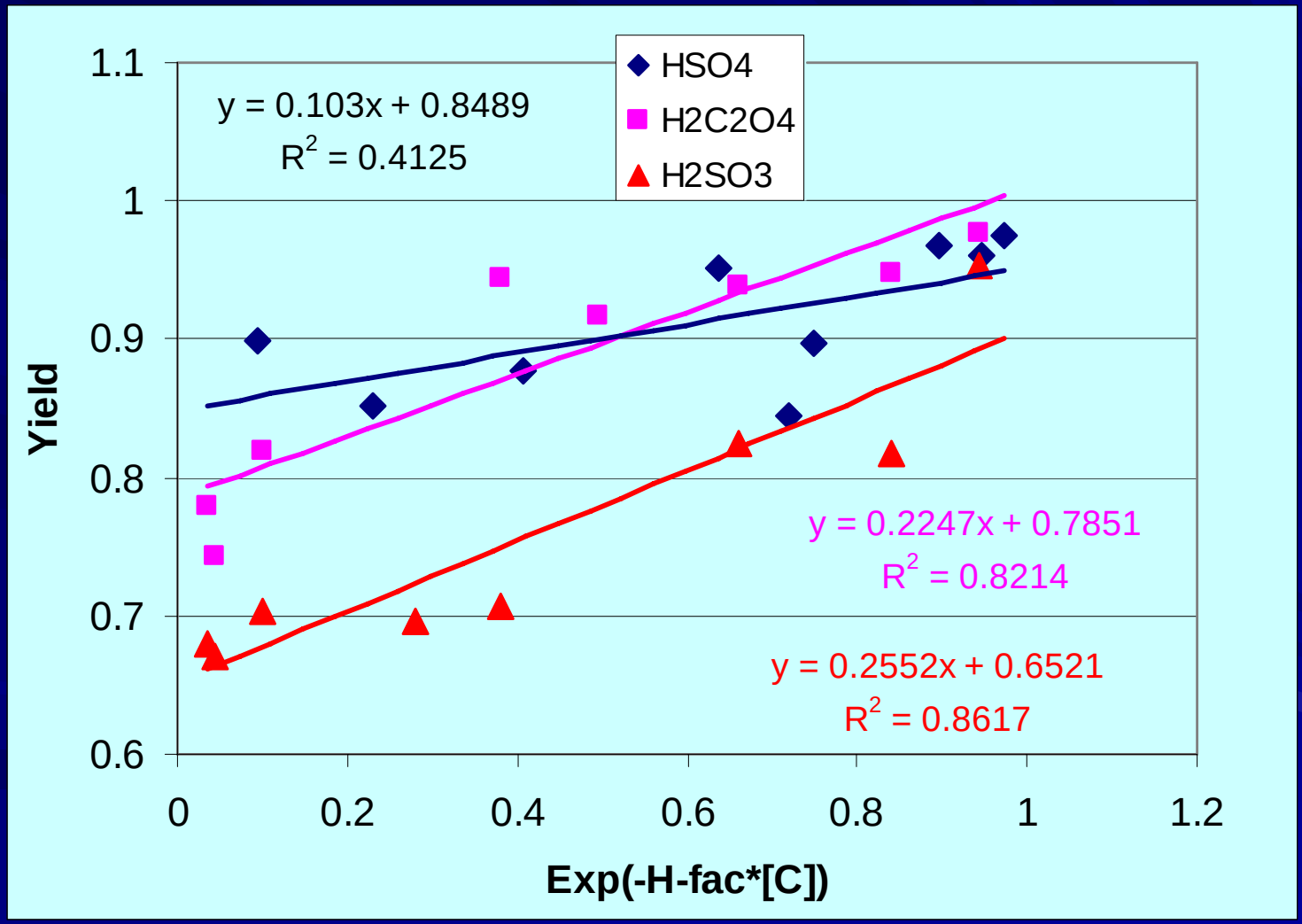
$$Y = \frac{m_0}{C}\left(e^{-[\mathrm{H}^+]kt}\right) + r$$

- Plot yield against $e^{(-H)kt}$ should give a straight line with intercept equal to the hydrolysis resistant portion of the wood and slope equal to the hydrolyzable portion and a constant.
- At time zero, Y = $r + m_0$ and C must = 1.
- And $1-r-m_0 = s$ allowing all three wood fractions to be determined.

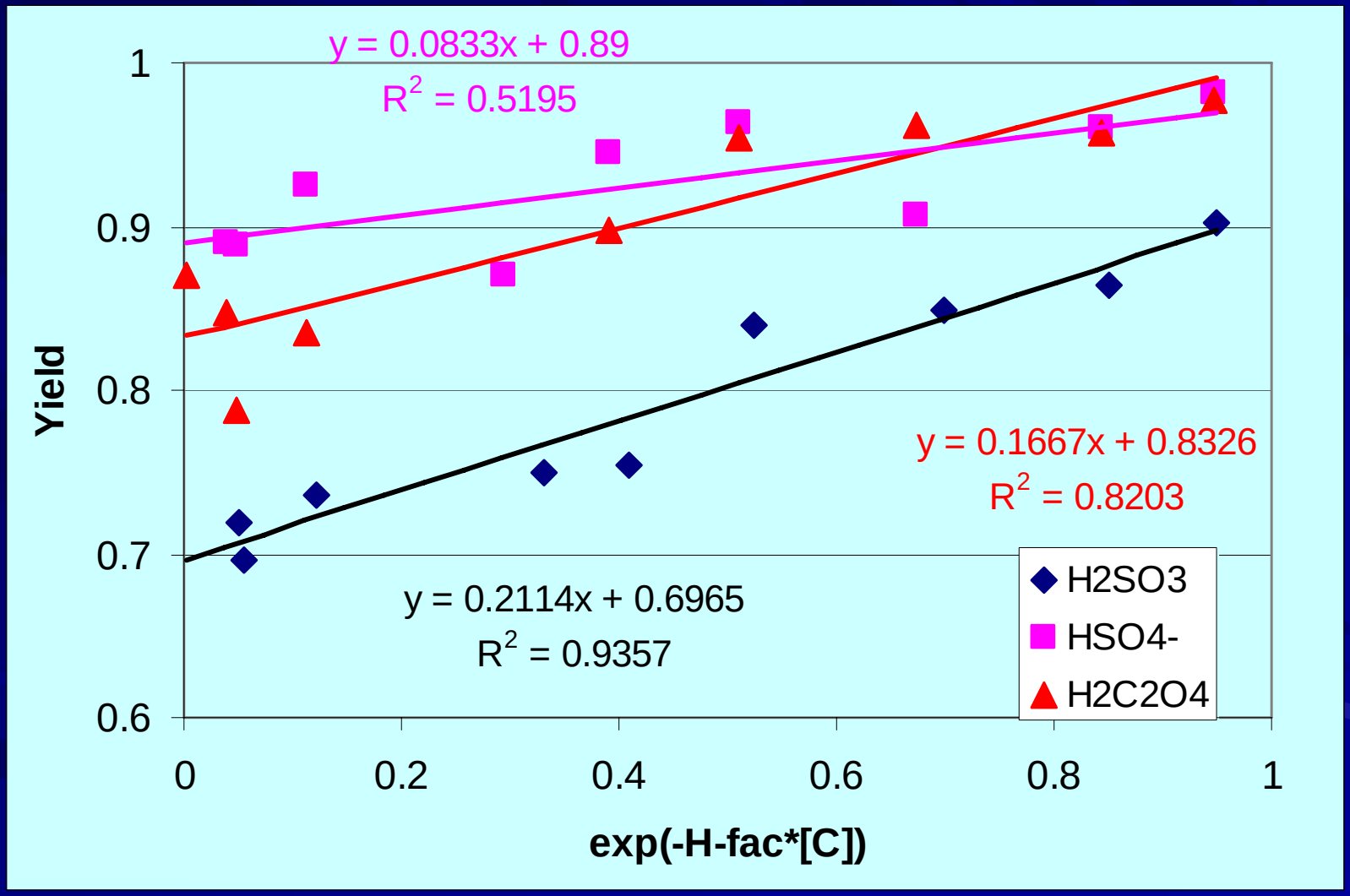
Treatment severity

- H-factor has been reported to be a reasonably accurate kinetic rate approximation for wood hydrolysis by Adriaan vanHeiningen
- Therefore, *kt* can be estimated as H-factor, and H^+ can is either the starting acid concentration or final pH.

Aspen


HSO4
H2C2O4
H2SO3
y = 0.103x + 0.8489
R2 = 0.4125
y = 0.2247x + 0.7851
R2 = 0.8214
y = 0.2552x + 0.6521
R2 = 0.8617
Yield
Exp(-H-fac*[C])
1.1
1
0.9
0.8
0.7
0.6
0
0.2
0.4
0.6
0.8
1
1.2

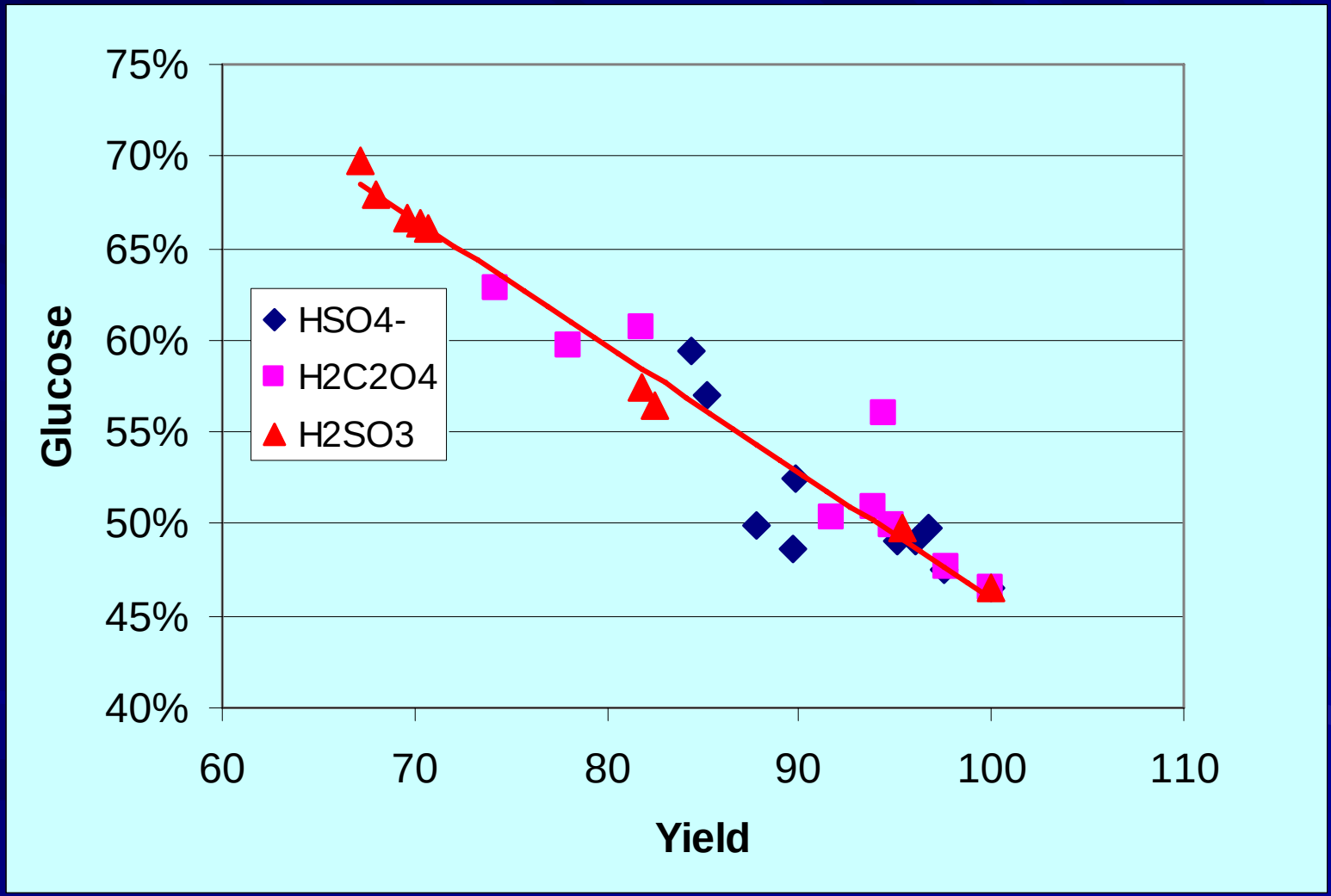
Spruce


y = 0.0833x + 0.89
R2 = 0.5195
y = 0.1667x + 0.8326
R2 = 0.8203
y = 0.2114x + 0.6965
R2 = 0.9357
H2SO3
HSO4-
H2C2O4
Yield
exp(-H-fac*[C])
1
0.9
0.8
0.7
0.6
0
0.2
0.4
0.6
0.8
1

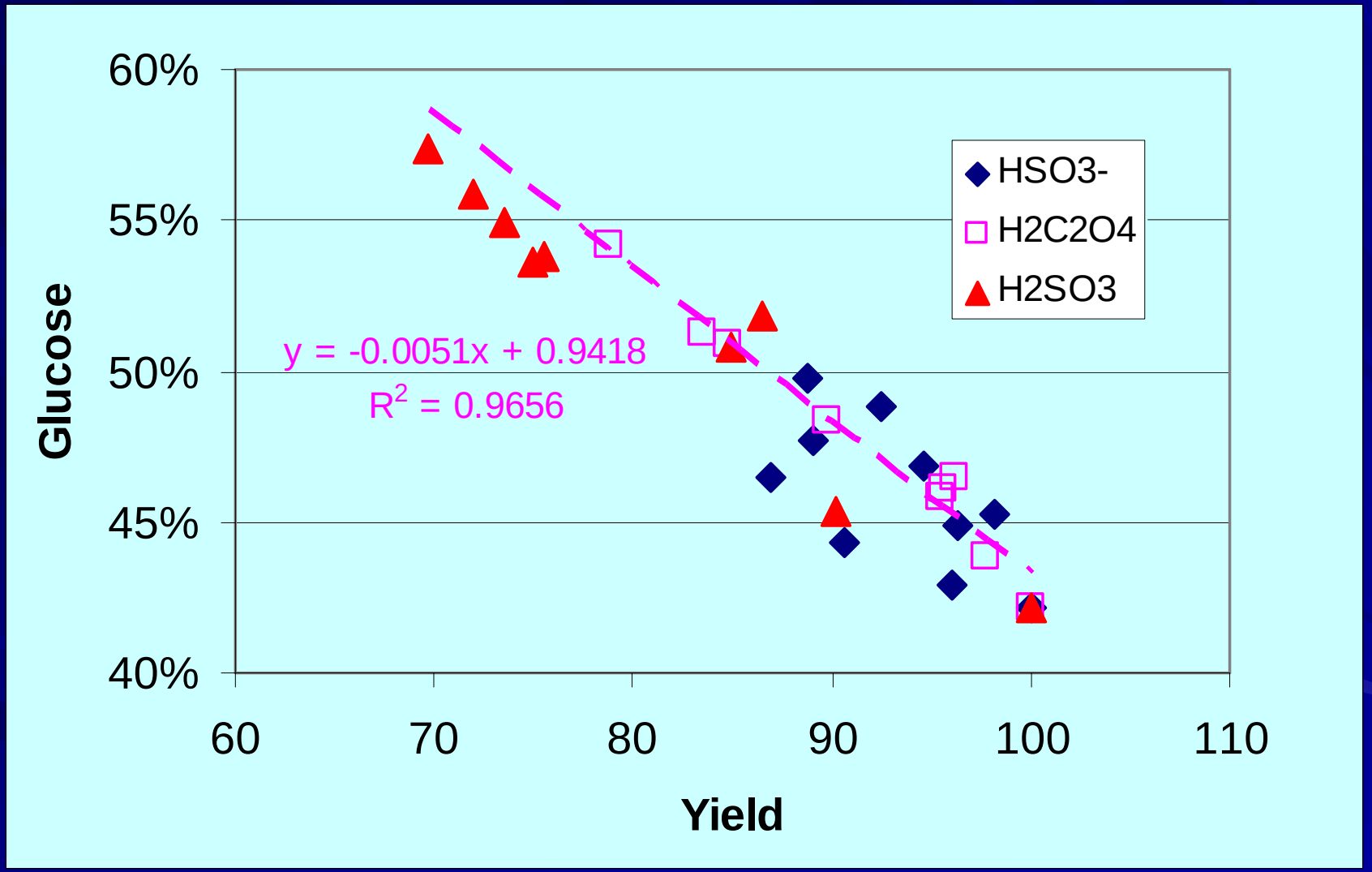
Results of the Regression

	m_0	r	s	R^2
HW $H_2C_2O_4$	0.225	0	0.785	0.85
HW H_2SO_3	0.255	0.093	0.652	0.86
HW HSO_4^-	0.103	0.048	0.849	0.41
SW $H_2C_2O_4$	0.167	0	0.892	0.82
SW H_2SO_3	0.211	0.093	0.696	0.93
SW HSO_4^-	0.083	0.03	0.89	0.52

% Glucose in Wood - HW



SW-remaining glucose in wood



Conclusions

- Tentative: pH control is primarily responsible for the higher brightness of oxalic acid treated wood.
  - Need to perform refiner studies and controls against acetic and sulfuric acids.
- Sulfurous acid has unique ability to hydrolyze wood relative to oxalic acid and sodium bisulfate.
- H-factor does provide a useful integration of hydrolysis rate and time.

Rudie, Alan; Reiner, Richard; Ross-Sutherland, Nancy; Kenealy, William. 2007. Acid prehydrolysis of wood. In: Proceedings of TAPPI engineering, pulping and environmental conference. 2007 October 21-23. Jacksonville, FL: Atlanta, GA: TAPPI press. 8p. Available online: http://wwwtappi.org