

MEASUREMENT AND CONTROL OF PEROXIDE BLEACHING INDICATORS

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ABSTRACT

The complicated chemical processes that occur during peroxide bleaching of pulp may be monitored by analysis of the dissolved substances in peroxide bleaching pressates with UV-visible spectroscopy. Sample preparation using filtration, pH adjustment and data manipulation assist in the extraction of information using UV absorbance spectroscopy. This information may be used to model peroxide residual, pulp brightness, wood species and other parameters that contribute to or describe the efficiency and quality of the pulp bleaching process. The use of multiple ratios of UV absorbance values is described and shown to provide superior information compared to partial least squares methods on the raw data. The efficiency of the bleaching process is optimized when the amount of peroxide compared to dissolved lignin is maximized and the amount of chromophores on the lignin is minimized.

INTRODUCTION

Bleaching Efficiency

Improving the efficiency of hydrogen peroxide bleaching of pulp is an unresolved pulp and paper measurement and control task. Peroxide bleaching efficiency may be measured in different ways, but the two broad categories of efficiency are process and chemical. Areas for improvement in efficiency are shown in Table 1. These changes in process and chemical efficiency are estimated to have a value of approximately 2-3% or about \$2M/year. These estimates depend upon market conditions and mill practices and are presented here to indicate the magnitude and components of the problem. The loss of revenue for off-spec pulp at a mill that is bottlenecked at the bleach plant is the market value of the pulp (\$600/ton); otherwise, the cost is the chemical cost.

Process Efficiency

Two primary areas of process efficiency that may be improved are the time it takes to change pulp grades and the ability to hold a set of bleaching conditions through the natural variation in chemical, pulp, production rates and water quality. The relative importance of improving one or the other depends on the mill. Mills with many pulp brightness grades obviously wish to minimize the time and the off-spec or switch-over pulp that is manufactured. Maintaining constant inputs and outputs during constant production is an issue particularly when the mill:

1. Has variable quality and brightness of wood chips from different sources
2. Has unstable water or water sources (river water)
3. Is bleaching to high brightness (chemical response is flat and can drift).

Chemical Efficiency

Numerous reactions, both favorable and unfavorable, may occur during the alkaline peroxide brightening of pulp. These reactions include peroxide induced brightening initiated by nucleophilic addition to carbonyls and other conjugated centers, alkaline yellowing and carbohydrate degradation reactions, peroxide degradation and radical reactions, and delignification. The complexity of these reactions and the potential interrelationships between inputs, outputs and chemical events is graphically illustrated in Figure 1. The many interrelated variables create a control problem with high dimensionality that is difficult to solve without information-rich

sensors. Despite the apparent complexity of the reactions, peroxide brightening is the method of choice for selective removal of color producing chromophores in mechanical pulps [1].

Brightness Efficiency

Peroxide brightening efficiency is normally understood to be the ratio of the brightness gain or b^* loss to the peroxide consumed during the brightening reaction. Many variables may be used to define brightening efficiency. Numerators may not only include the pulp optical properties but also the pulp yield, the amount of lignin removed and the amount of anionic trash formed. Although peroxide consumed is a logical choice for the denominator, as shown in Equation 1:

$$\text{Equation 1.0} \quad \text{Eff}_B = \frac{\Delta B_{ISO}}{\Delta H_2O_2}$$

one may also use peroxide charge, incremental peroxide charge, the charge of other process chemicals, (sodium hydroxide, sodium silicate) or the reaction time. In the mill situation the peroxide and other chemicals applied are important, but efficient use of applied chemical can lead to the application of lower chemical charges. When efficiency is measured as a function of the amount of peroxide consumed the relationship between efficiency and brightness can be very flat as shown in Figure 2. This figure shows that for high brightness pulp, near the top of pH and peroxide optimization curves, the efficiency of the process can vary by a factor of ~2.5 within just 1 brightness point.

Another way to look at efficiency is to evaluate the brightness change as a function of chemical modification of the pulp.

Delignification Efficiency is the efficiency of the bleaching process with respect to loss of lignin, Equation 2 where lignin removal is caused by the UV absorbance at 280 nm. This parameter is in recognition that small amounts of lignin must be removed as part of an efficient bleaching process, and that large amounts of lignin loss occur during inefficient peroxide bleaching.

$$\text{Equation 2.0} \quad \text{Eff}_B = \frac{\Delta B_{ISO}}{\Delta ABS_{UV280}}$$

In all cases the decrease in the brightness response with higher pH corresponds to a loss of delignification efficiency. This is partly due to decomposition of peroxide and partly due to an increase in unproductive delignification. We have gone to some lengths to understand the role of lignin removal during peroxide bleaching of mechanical pulps. Under mild conditions, the amount of lignin removed is more or less linear with brightness, but near the brightness ceiling or at the top of a pH, temperature, or peroxide bleaching curve there are increasing amounts of lignin removed without a corresponding improvement in brightness. The role and interrelationship between brightness, lignin removal, peroxide residual and delignification efficiency is graphically illustrated from lab results in Figure 3.

PEROXIDE BLEACHING INDICATORS

The results above show that small variations in brightness can correspond to substantial changes in process inputs (peroxide or alkali charge) as significant loss of efficiency. Changes related to the amount of peroxide, the amount of lignin and the color of the lignin all provide indicators of the progress and efficiency of the reaction. The formation of products during the brightening reactions is exquisitely sensitive to peroxide brightening conditions [3] and the monitoring of these products facilitates the selection of conditions required for optimal brightening of mechanical pulps.

Information in the UV Spectrum

Dissolved in the peroxide bleaching pressates is an array of wood-derived substances mixed with process chemicals and reaction products. Many of these substances may be detected by UV-visible spectroscopy. Figure 4 provides examples of UV absorbance spectra of softwood pressate at two pH values obtained on line at the Millar Western Forest Products Pulp Mill in Whitecourt, Alberta. We have found that there is additional information available when measuring the UV absorbance at two pH values as in the pH difference spectra first developed for lignin analysis by Aulin-Erdtman [2].

The information in the UV spectrum of the pressates provides:

- The amount of peroxide
 - A direct measure of peroxide ion concentration
- The amount of lignin removed
 - Related to delignification efficiency
- Chromophore groups on dissolved lignin
 - A good measure of chromophore destruction
- Ionization of lignin (phenolic ionization at pH~10, hydroquinones at pH~9, a-carbonyl structures at pH ~7, aromatic acids at pH~4)

This information may be extracted from different regions in the UV-visible spectrum. For example measurements at single wavelengths could be used to provide a measure of:

- Peroxide Anion Concentration A_{230} nm, pH 12
- Yellowness and Colour A_{320} - A_{600} nm
- Delignification A_{280} nm

In practice however, the UV measurements at any particular wavelength do not represent any single component and in general they do not correspond to any single property. Instead the information is covariate and ill-defined statistically because the variation at different wavelengths is similar.

UV Ratios Matrix

We have used ratios of UV absorbance values as a means for extraction of information from the spectra of process waters [4]. Multiple regression techniques use a data matrix in which the *i* index is the index for the sample and the *j* index is the index for the wavelength (in this case). The absorbance values from pulp and paper process waters at different wavelengths are nearly always covariant and extraction of the information can be problematic. The use of partial least squares can alleviate this problem, but this method still depends on a linear combination of variables. Properties that are non-linear with the independent variables may be modeled with functions or ratios of variables.

$$\mathbf{A} = \begin{bmatrix} A_{1,1} & \cdots & A_{1,j} & \cdots & A_{1,p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ A_{i,1} & \cdots & A_{i,j} & \cdots & A_{i,p} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ A_{n,1} & \cdots & A_{n,j} & \cdots & A_{n,p} \end{bmatrix}$$

Using a set of ratios the data matrix **A** is transformed into a new data matrix that may be called the ratio matrix **R**. This matrix is based upon a predetermined set of wavelengths for the numerators and denominators of the ratios. The *i* index is the index for the sample and the *j* index is the index for the wavelength of the numerators, the *k* index is the index for the set of wavelengths corresponding to the set of denominators that match the *j* indexed absorbance (or conversely emission) values for each sample. The ratio data matrix may be generally written as:

$$\mathbf{R} = \begin{bmatrix} \frac{A_{1,1}}{A_{\lambda a_1}} & \cdots & \frac{A_{1,j}}{A_{\lambda k_1}} & \cdots & \frac{A_{1,p}}{A_{\lambda q_1}} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \frac{A_{i,1}}{A_{\lambda a_i}} & \cdots & \frac{A_{i,j}}{A_{\lambda k_i}} & \cdots & \frac{A_{i,p}}{A_{\lambda q_i}} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \frac{A_{n,1}}{A_{\lambda a_n}} & \cdots & \frac{A_{n,j}}{A_{\lambda k_n}} & \cdots & \frac{A_{n,p}}{A_{\lambda q_n}} \end{bmatrix}$$

One way to characterize the amount of information in a data set is to determine the principle components. Principle components and analysis are a method of combining information from different variables into the minimum number of new linearly dependent variables that account for the variation in the data. A data set that has more principle components has more systematic variation that may be characterized and used to describe the source of the data. In Figure 5 the number of principle components is plotted against the systematic variation accounted for from the mill data using UV absorbance values, UV ratios and both ratios and absorbance values. The lower curve, and the greater number of principle components shown for the analysis with the ratios and UV absorbance values, shows the information content of the ratios is not redundant.

Apparatus and Methods

A prototype system was built for mill trials using National instruments LabVIEW software on an industrial computer. The computer was interfaced with two Ocean Optics S2000 miniature spectrophotometers, an AIS deuterium-tungsten light source and the sampling and dilution module. The sampling and dilution module had membrane filters with a Fluid Metering Corp. ratio dilution pump for metering the filtered sample with 0.1 M NaOH and phosphate buffers. These filters worked reliably over several months. The apparatus is sketched in Figure 6. Peroxide concentrations were measured following standard CPPA Test Method J.16P. Advanced Measurements of Calgary, Alberta programmed the LabVIEW software.

Composite Functions

We have used the UV values for modeling of peroxide concentration, softwood-hardwood ratios and ultimate brightness. Although based on chemical principles the models developed using multiple regression are to some degree process dependent. Ultimately they must be adaptive and updated over time. Shown in Figure 7 is the calibration of peroxide levels using four parameters derived from UV absorbance values and ratios.

CONCLUSIONS

The components dissolved during peroxide bleaching reflect the progress of the bleaching reaction. Detection of these products using UV-visible spectroscopy provides an information-rich foundation upon which an adaptive measurement and control system can be built.

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