RANKING MECHANICAL PULPS FOR THEIR POTENTIAL TO PHOTOYELLOW

Umesh P. Agarwal, USDA FS-Forest Products Laboratory, Madison, WI 53705
E-mail: uagarwal@.fs.fed.us

ABSTRACT

Recently found experimental evidence has provided strong support for an alternative photoyellowing mechanism that suggests that pulp-photoyellowing occurs due to direct photooxidation of hydroquinones (present in mechanical pulps) top-quinones. Because hydroquinones were found to be present in pulps, it may be possible to quantify them. Quantification of mechanical-pulp hydroquinones is important because it would provide information on a pulp's potential for photoyellowing. One of the ways to accomplish this is to use the method that successfully detected hydroquinones, namely the method of "oxygen sensitivity of laser-induced-fluorescence (LIF)". Preliminary findings of this work will be discussed in the presentation.

INTRODUCTION

Mechanical pulp photoyellowing remains scientifically not well understood although recently obtained direct Raman evidence [1], indicating presence of *p*-quinones, has provided important insights on to what causes brightness loss in such pulps. It is becoming increasingly clear that the mechanistic pathways that can lead to the formation of stilbenes and/or *o*-quinones are not important in mechanical pulp photoyellowing. For example, for the former case, no direct supporting evidence has been found [2]. Moreover, findings of the research specifically targeted to study the role of stilbenes in the light-induced brightness loss have been negative [3,4].

The issue of formation of *o*-quinones upon light exposure is more complex, but can be discussed on the basis of the critical evaluation of all relevant evidence. The strongest evidence negating the likelihood that *o*-quinones are produced upon photoyellowing was provided by the FT Raman spectroscopic analysis of photoyellowed pulps where no band belonging to *o*-quinone structure could be detected [1]. However, the new feature that was produced upon photoyellowing was found to be due top-quinones. The past evidence that has supported formation of *o*-quinones, namely ^{31}P NMR data, seems to be becoming controversial as new research is showing that, in pulp and lignin, it may not be possible to distinguish between phosphorylated *o*- and *p*- quinones [5, 6]. If indeed that is the case, then signals previously assigned to *o*-quinones might as well have been due to *p*-quinones. Irrespective of the final outcome of the ^{31}P NMR assignment-controversy, of the two techniques, Raman and phosphorous NMR, the former method requires no chemical treatment of the pulps. This aspect alone makes Raman results more trustworthy because the sample is not modified at all. Another question, from a mechanistic point of view, is what causes formation of *o*-quinones. Although a-carbonyls in lignin have been proposed as precursors of *o*-quinones, it is doubtful if the former group even exists in pulps. Not only is the direct evidence indicating presence of a-carbonyls lacking, studies of MWLs (which show that a-carbonyl groups are present in lignin) have suggested that carbonyl groups are likely to be produced as a consequence of milling [7]. In contrast, the proposed mechanism for the formation of *p*-quinones (reproduced in Fig. 1, [1]) indicates that these groups are produced as a result of direct photooxidation of hydroquinones – the groups that are present in wood, mechanical-pulp, and MWL.

In addition, Raman studies of bleached mechanical pulps [2] have provided further support to the conclusion that hydroquinone/*p*-quinone redox system is responsible for the brightness loss in photoyellowed mechanical pulps. It was found that both reductive and oxidative bleaching of non-photoyellowed TMP produced

Raman intensity decline in the region where *p*-quinones contributions are detected and that the decline was directly proportional to the increase in pulp brightness.

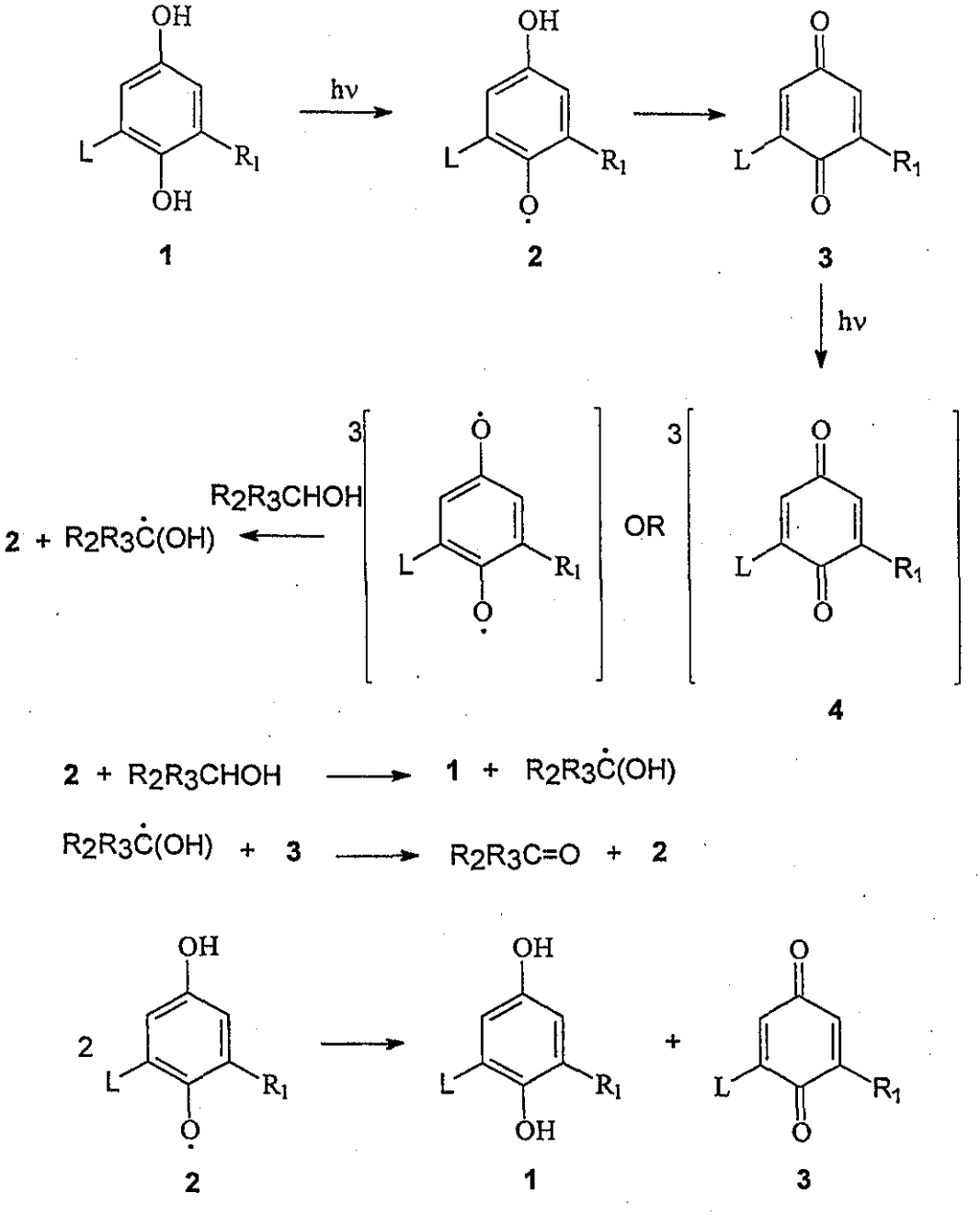

Figure 1. A mechanistic representation of what happens when mechanical pulps, containing hydroquinone groups (1), are exposed to light. Direct evidence in support of photoformation of *p*-quinone (3) and carbonyl (non-quinonoid) groups was obtained. Hydroquinones were detected indirectly by the method of oxygen quenching of laser-induced fluorescence [1].

The scheme in Fig. I suggests that light drives both the hydroquinone-to-quinone and quinone-to-hydroquinone reactions. A hydroquinone (1) is converted to a semiquinone radical (2), then to 3, a *p*-quinone. The *p*-quinone (3) absorbs light to produce a triplet state (4) or a diradical, which, in presence of an alcohol, produces 2 and a hydroxylR_2R_3 radical (H abstraction). In a subsequent step (Fig. 1), the hydroxyl radical reacts with a quinone to generate a keto group. The formation of the keto group is supported by the detection of the IR absorption band at 1727 cm^{-1} in photoyellowed thermomechanical pulps. The semiquinone radical (2), generated by the excited state quinone (4), reacts with another molecule of alcohol and regenerates hydroquinone (1). Lastly, it is possible that two semiquinone radicals (2) interact and disproportionate, by simultaneous reduction and oxidation, into a hydroquinone and a quinone. Nevertheless, pulp being a solid matrix with low hydroquinone concentration, the latter reaction is not likely to be encountered. Additional reactions of semiquinone and hydroxyl radicals, not shown here, are also possible, for example, grafting reactions.

Although detected indirectly, using the method of oxygen sensitivity of laser-induced-fluorescence (LIF), hydroquinones were found to be present in lignin, mechanical pulp, and wood [1]. This finding was based on the work carried out in the author's laboratory and arose from the fact that the LIF contribution of hydroquinones was quenchable by molecular oxygen. In lignin and lignin-containing non-photoexposed samples, hydroquinones were likely to be responsible for a significant part of the 514.5 nm-excited LIF signal [1].

In light of above results, it should be possible to quantify hydroquinones in a mechanical pulp. Additionally, assuming that most photoyellowing is caused by hydroquinones, it should also be possible to predict the photoyellowing rank of a pulp in a group of mechanical pulps. Although, in the past, the method of accelerated photoyellowing has been used to provide this information, the present method if successful may be more advantageous. The method is based on the assumption that any variation in the hydroquinone concentration (among pulps) will be reflected in the intensity of the LIF signal that is O_2 sensitive.

EXPERIMENTAL

Hydroquinone models as well as a number of pulp/paper samples are being studied. Different concentrations of a model are being used to find out if the concentration and the intensity of the oxygen quenchable LIF signal are linearly correlated. Pulp and paper samples, consisting of unbleached, bleached, hardwood, softwood, CTMP, SGW, and lignin-free pulps, are being used as well. These samples are also being photoaged, using an accelerated method, to determine a sample's relative photoyellowing rank. This will allow a comparison of the two ranking approaches.

A conventional Raman system (based on 5 14.5 nm laser excitation) is being used to obtained data on the O_2 sensitivity of the LIF for various samples. Steady state spectra in both O_2-only and O_2-fkee environments are being obtained. Further details on the Raman instrumentation have been provided in a previous publication [1].

RESULTS AND DISCUSSION

To provide an example of the results that are being obtained in the O_2-sensitivity-of-the-LIF work, Fig. 2 shows an LIF spectrum of methyl-hydroquinone and its sensitivity to molecular oxygen. Such curves have previously been obtained for wood, mechanical pulp, and lignin samples. To correlate O_2-sensitive LIF signal to the concentration of hydroquinones in the sample, the peak signal intensity of the normalized spectrum "d" in Fig. 2 would be subtracted from that of spectrum "c". This would produce that portion of the LIF signal that was sensitive to O_2. The oxygen sensitive signal is expected to be directly proportional to the concentration of the hydroquinones. Using various concentrations of hydroquinone model a calibration curve will be generated and used to estimate the concentration of a hydroquinones in non-photoyellowed mechanical pulps. The hydroquinone-concentration order is expected to resemble the photoyellowing order of the mechanical pulp – higher hydroquinone amount implying more likelihood of photoyellowing.

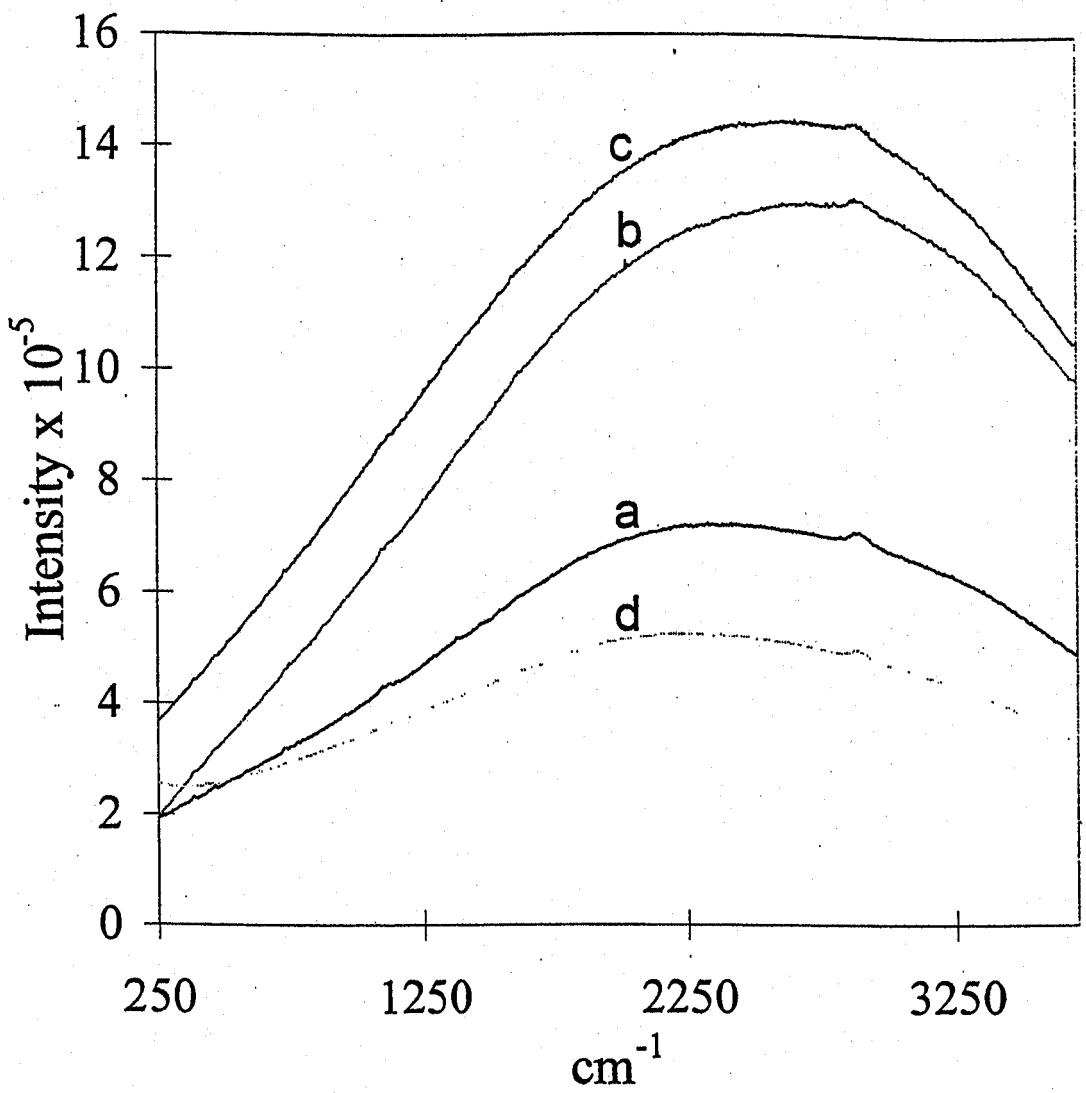

Figure 2. Laser-induced fluorescence (514.5 nm excited) of methyl-hydroquinone (MHQ) and its sensitivity to O_2; (a) spectrum of MHQ-containing filter paper in air, (b) spectrum when N_2 is flushed through the sample cell, (c) after 1 h of N_2 flushing, and (d) when N_2 flushing is stopped and O_2 flushing is started. Molecular oxygen clearly quenches the fluorescence of the hydroquinone.

REFERENCES

1. Agarwal, U.P., Assignment of the photoyellowing-related 1675 cm^{-1}Raman/IR band and its implications to the mechanism of the color reversion of mechanical pulps. J. Wood Chem. Tech. 18, 381(1998).
2. Agarwal, U.P. and Atalla, R.H., Using Raman spectroscopy to identify chromophores in lignin-lignocellulosics. In Lignin: Historical, Biological, and Materials Perspectives, Eds. W.G. Glasser, R.A. Northey, and T.P. Schultz; ACS Symp. Series # 742; ACS Washington DC; 1999; Chapter 11.
3. Ruffin, B., Castellan, A., Grelier, S., Nourmamode, A., Riela, S., and Trichet, V., Evaluation of the contribution of lignin stilbenes phenol units in the photoyellowing of peroxide-bleached lignin-rich pulps. J. Applied Poly. Sci. 69, 2517(1998).
4. Ruffin, B. and Castellan, A., Photoyellowing of peroxide-bleached lignin-rich pulps. Can. J. Chem. 78, 73(2000).
5. Zawadzki, M, Runge, T. and Ragauskas, A., Facile detection of ortho- and para-quinone structures in residual lignin by ^{31}P NMR spectroscopy. J. Pulp Paper Sci. 26, 102(2000).
6. Zhang, L. and Gellerstedt, G., Detection and determination of carbonyls and quinones by modern NMR techniques. Proc. 10th ISWPC, Vol. II, June 7-10, Yokohama, Japan, pp. 164
7. Chen, C. -L., Determination of carbonyl groups. In Methods in Lignin Chemistry, Eds. S.Y. Lin and C.W. Dence, Springer-Verlag, Berlin, 1992, pp. 446.

Agarwal, Umesh P. 2000. Ranking mechanical pulps for their potential to photoyellow. In: Sixth European workshop on lignocellulosics and pulp. Advances in lignocellulosics chemistry towards high quality processes and products: 2000 SEPTEMBER 03–06: Bordeaux. FR. Bordeaux. FR: Bordeaux Universite: 95–98.