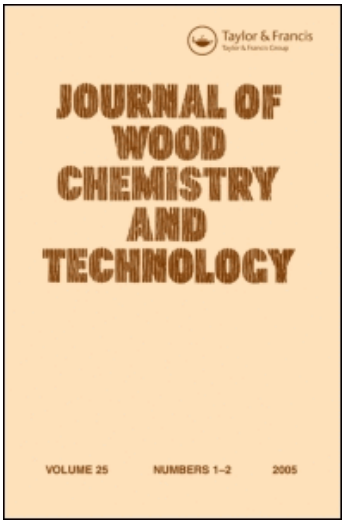


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Laser-Induced Fluoresence of Lignins with Excitation from 457 to 621 Nanometers

David M. Hanson[a]; Donna Cietek Wenzel[a]
[a] International Paper Company Corporate Research Center, Tuxedo, New York

To cite this Article Hanson, David M. and Wenzel, Donna Cietek(1991) 'Laser-Induced Fluoresence of Lignins with Excitation from 457 to 621 Nanometers', Journal of Wood Chemistry and Technology, 11: 1, 105 — 115
To link to this Article: DOI: 10.1080/02773819108050264
URL: http://dx.doi.org/10.1080/02773819108050264

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 11(1), 105-115 (1991)

LASER-INDUCED FLUORESENCE OF LIGNINS WITH EXCITATION FROM 457 TO 621 NANOMETERS

David M. Hanson[1] and Donna Cietek Wenzel
International Paper Company
Corporate Research Center
Tuxedo, New York 10987

ABSTRACT

Laser-induced fluorescence has been used to examine changes in lignin and black liquor during the course of kraft pulping. When excited with a laser at 457 and 488 nm, lignin samples isolated during the course of pulping, purified, and redissolved in alkali exhibited increasing fluorescent emission intensity. This may be explained by changes in lignin structure during pulping. At higher excitation wavelengths, differences between samples diminished. Black liquors showed decreasing fluorescent intensity with increasing pulping. We attribute this behavior to the increase in optical density of the liquors as cooking time proceeds. The optical density increases with cooking time because greater amounts of lignin and other materials dissolve from the wood and enter the black liquor.

INTRODUCTION

Traditional fluorescence using ultraviolet and xenon light sources has been proposed for measuring lignin concentration and studying the nature of lignin.[2-6] Research in our laboratory[7] demonstrated that fluoresence with excitation by a He-Ne laser (632.8 nm) could be measured. When analyzing lignins dissolved in tetrahydrofuran, lignin fluorescence increased during kraft and soda pulping.

In order to examine fluorescence of lignins dissolved in alkaline solutions and raw black liquors, we conducted a series of experiments at the MIT Regional Laser Center. The objectives of these studies were to:

1. Examine excitation at wavelengths from 457 to 621 nm.
2. Collect emission spectra.
3. Analyze lignins dissolved in alkaline solutions.
4. Analyze raw black liquor samples.

RESULTS AND DISCUSSION

Lignin Samples Dissolved in Alkali

Figure 1 shows the response in fluorescence with excitation at 488 nm for kraft lignins isolated from digestion liquors and then redissolved in alkali. The spectra were normalized to an equal concentration of lignin. The normalized spectra of the lignin excited at 488 nm show an increase in intensity through the course of pulping. This may be explained by changes in lignin structure during pulping. Minor changes in the detected signal between samples may be caused by tube-edge effects, focusing, and residual impurities in the prepared lignins.

Figures 2 and 3 show data from the same lignin solutions as in Figure 1, except with the excitation at 582 and 621 nm, respectively. The normalized spectra do not show a definite trend as with excitation at 488 nm, although there are some minor differences in the intensities. When noise is considered, the detected signals are similar throughout the course of the cook, since more sensitive photon count settings were necessary at these higher excitation wavelengths.

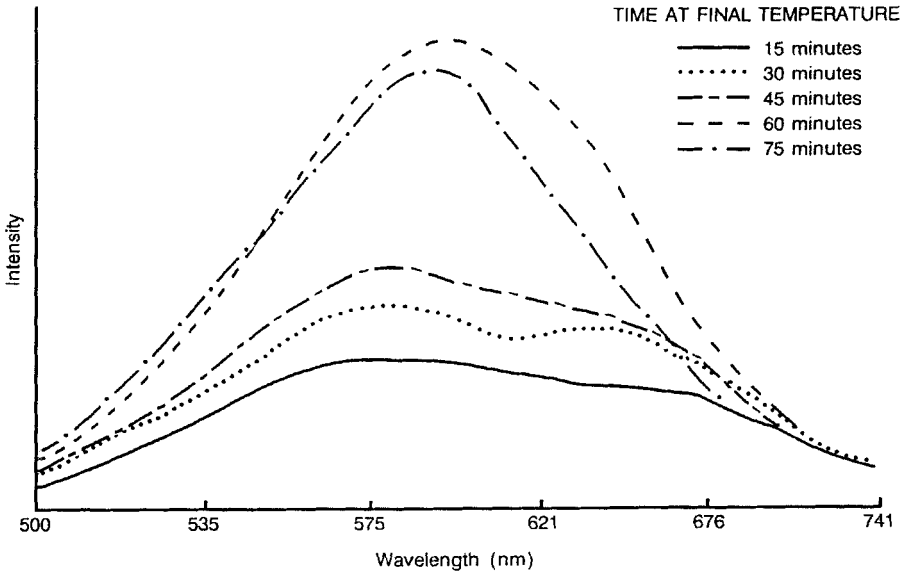


FIGURE 1. NORMALIZED (TO GRAMS/LITER) LASER-INDUCED FLUORESCENCE WITH EXCITATION AT 488 NM OF KRAFT LIGNINS ISOLATED AT DIFFERENT TIMES AFTER REACHING THE FINAL PULPING TEMPERATURE OF 170 DEGREES CENTIGRADE.

With excitation at 488, 582, and 621 nm, we also observed an increase in spectral compression as the excitation wavelength increased. The peak maxima of the spectra move closer to the excitation wavelength and cover a narrower range of wavelengths. We may have reached the end of the useful range of the photomultiplier tube where the detector sensitivity decreases.

In a previous study[7], lignins were dissolved in tetrahydrofuran and monitored for fluorescence using excitation at 632.8 nm. The fluorescence per unit concentration increased to a plateau value during pulping.

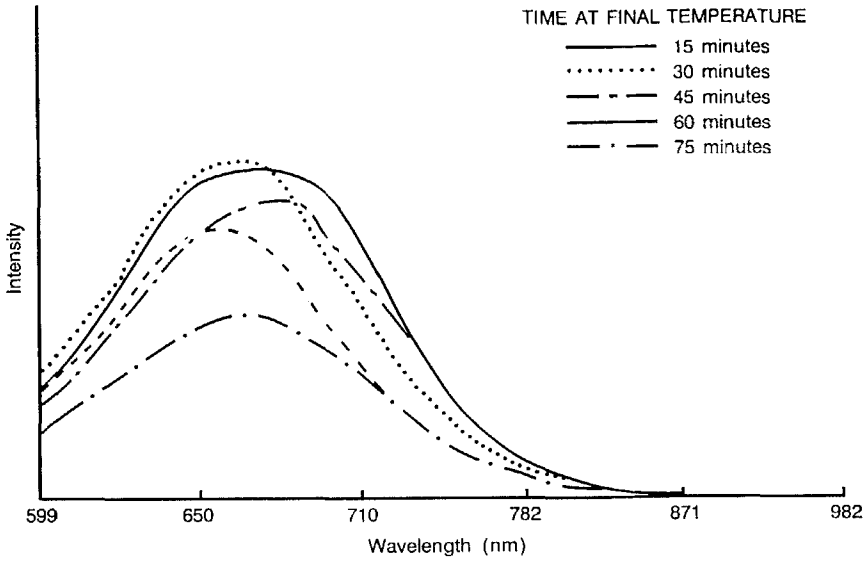


FIGURE 2. NORMALIZED (TO GRAMS/LITER) LASER-INDUCED FLUORESCENCE WITH EXCITATION AT 582 NM OF KRAFT LIGNINS ISOLATED AT DIFFERENT TIMES AFTER REACHING THE FINAL PULPING TEMPERATURE OF 170 DEGREES CENTIGRADE.

These lignins, being dissolved in tetrahydrofuran, were not ionized. The results in the current study were obtained on ionized lignins. We observed differences with excitation at lower wavelengths, but did not observe the differences when the excitation wavelengths approached 632.8 nm, the previously used wavelength. As with difference spectra in ultraviolet spectroscopy, we may be detecting different structures in the lignin depending on whether the lignin is ionized or non-ionized.

With the visible wavelength excitation, the flourescence of ionized versus non-ionized molecular species could be

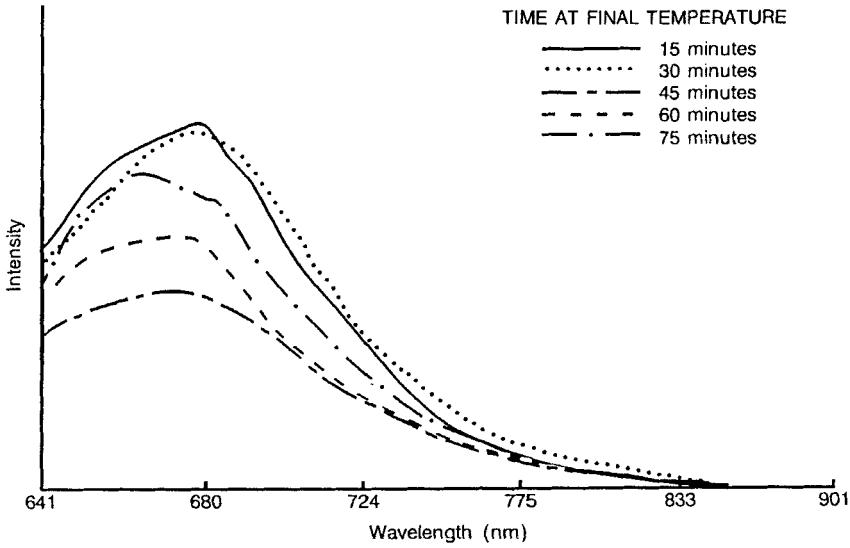


FIGURE 3. NORMALIZED (TO GRAMS/LITER) LASER-INDUCED FLUORESCENCE WITH EXCITATION AT 621 NM OF KRAFT LIGNINS ISOLATED AT DIFFERENT TIMES AFTER REACHING THE FINAL PULPING TEMPERATURE OF 170 DEGREES CENTIGRADE.

useful in examining lignin structural changes, such as extension of conjugation. This would require further fundamental research.

Table 1 gives the normalized (weight basis) intensity of the fluorescence at the peak maxima for softwood and hardwood lignins isolated at different times during kraft cooking. Intensity is reported in photon counts/second and account for differences in the sample concentration. With the excitation at 457 and 488 nm, there is an increase in the intensity during the course of pulping, except for the final sample. We have no explanation for this anomaly. With the excitation

TABLE 1.

Fluorescence at Different Excitation Wavelengths of Lignins. Isolated During Kraft Cooks of Softwoods and Hardwoods.

Wood Type	Time at Final Temperature (minutes)	Intensity[a] 457 nm	488 nm	514 nm	595 nm
Softwood	0	78	184	94	95
Softwood	23	137	189	101	95
Softwood	45	161	268	90	108
Softwood	68	174	279	92	112
Softwood	90	134	251	90	141
Hardwood	0	168	182	62	144
Hardwood	21	226	252	67	167
Hardwood	42	342	643	81	138
Hardwood	63	327	367	93	113
Hardwood	85	116	191	56	123

[a]photon counts/S

at 595 nm, the fluorescence was constant during the course of pulping, agreeing with our earlier findings using excitation at 582 and 621 nm.

Black Liquor Samples

Fluorescent intensities for softwood and hardwood black liquors excited at 457 nm are given in Table 2. The intensity readings are reported as photon counts per second. Similar results were obtained when we used excitations at 488 and 514 nm. The black liquors were collected at the same time samples for lignin isolation were taken. Comparisons between samples can be made within a series of excitation wavelengths but not between wavelengths, because of the large differences in the power of the laser at the three different settings. Also, as the optical density of the black liquor

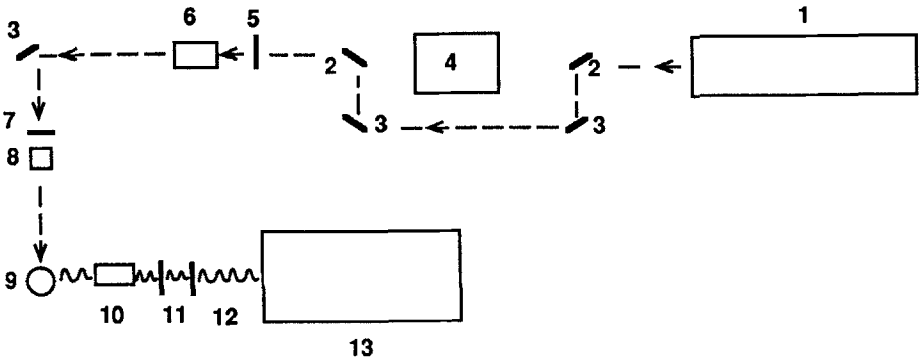
TABLE 2.

Relative Fluorescence of Black Liquors at 532 nm with Excitation at 457 nm.

Hardwood/ Softwood	Time at Final Temperature (minutes)	Fluorescence
Hardwood	0	1821
	21	931
	42	208
	63	138
	85	66
Hardwood	0	2072
	21	244
	42	88
	63	77
	85	82
Softwood	0	390
	23	242
	68	78
	90	67
Softwood	0	2403
	23	417
	45	156
	68	236
	90	74

increased, surface effects became more difficult to minimize using system optical adjustments.

In general, we observed a decrease in the intensity of fluorescence during the course of pulping. This decrease was found between cooks and was reproducible when reading the intensity within black liquors from a single cook. Although the absolute magnitude varied, decreasing intensity was found with the excitation at all of the wavelengths tested. This effect is probably caused by the increasing optical density of the liquors through the cook and the low fluorescent quantum yields.



1 Coherent Model 52 laser
2 Mirror for directing beam around dye laser
3 Mirror
4 Coherent Model 590 dye laser
5 Pin hole
6 Prism for removing unwanted light bands
7 Pin hole
8 Focus for laser
9 Fine focus and sample holder
10 Lens for spectrometer
11 Lens
12 Flat
13 Spectrometer and photomultiplier

FIGURE 4. DIAGRAM OF THE LASER OPTICAL SYSTEM USED AT THE MIT REGIONAL LASER CENTER - MIRRORS 2 AND 3 ARE REMOVED WHEN USING DYE LASER.

EXPERIMENTAL

A diagram of the system at the MIT Regional Laser Research Center is seen in Figure 4. The system contains a Coherent Model 52 argon ion laser, a Coherent Model 590 dye laser, a Spex dual grating monochrometer, a photon counter, and a Northstar Horizon-based control and adata-acquisition system. The remainder of the system consists of the necessary optics to direct and focus the light beam on the optical bench.

We obtained our samples from laboratory kraft cooks of hardwood and softwoods. The black liquor was divided: one portion was saved for the black liquor measurement and the other was carefully acidified to pH 2, forming a precipitate. This precipitate was washed and dried. The isolated lignin was then dissolved to a known concentration in 0.1N sodium hydroxide. The dissolved lignin and black liquor samples were placed in capillary tubes and the tubes were sealed with wax. Measurements of fluorescence were collected at 90 degrees to the incident beam.

The argon ion laser has lines at 457, 488, and 514 nm which are useful in measuring fluorescence. To extend the range and include longer wavelengths, we used the dye laser with Rhodamine 6G and all lines of the argon ion laser to excite the dye. With the dye laser, wavelengths up to 621 nm could be reached.

Collected data were normalized for concentration differences. We used the computer to change the scale of the spectra for plotting purposes. The system is normally run as a Raman Spectrometer and data are collected from the origin

in units of reciprocal centimeters, resulting in nonlinear namometer markings on the spectra.

CONCLUSIONS/RECOMMENDATIONS

Laser-induced fluorescence of kraft lignins dissolved in alkali showed increasing fluorescence in the early stages of pulping when exited at 457 and 488 nm. In the later stages of pulping fluorescence stabilized or decreased. Excitation at higher wavelengths did not show this trend. Previously, we had studied these same lignins dissolved in tetrahydrofuran and excited at 632.8 nm. These nonionized lignins gave increasing fluorescent intensity during the early stages of pulping with stabilization of the fluorescence at later stages.

The two methods complement each other in studying lignins. The method of dissolving lignin in alkali will be sensitive to formation or loss of phenolic hydroxyl groups in addition to the other changes that can occur to lignin during pulping. Dissolving the lignin in tetrahydrofuran should allow better examination of the changes in conjugation without the effect of ionization. Fundamental research into these methods will be needed to correlate lignin structure to measurement of fluorescence. Relationships between the extent of conjugation and fluorescent intensity could be examined.

ACKNOWLEDGEMENT

We would like to thank W. Fookes for preparing the lignin and black liquor samples; and Ms. P. Calderale for

preparation of the manuscript. Thanks also go to the staff at the MIT Regional Laser Center, particularly Robert Quinn, Dr. Ramschandra Desari, and Dr. John Thomas for their assistance with the Raman Spectrometer.

REFERENCES

1. Current Address:
Grays Harbor Paper Company
Hammermill Paper Company
Hoquiam, Washington 98550

2. Bublitz, W., TAPPI, 64, 73 (1981).

3. Bublitz, W. and Wade, D., Sven. Papperstidn., 18, 535 (1979).

4. Bublitz, W., TAPPI Pulping Conf., 73 (1978).

5. Lundquist, K., Josefsson, B. and Nyquist, G., Holzforschung, 32, 27 (1978).

6. Lundquist, K., Egyed, I., Josefsson, B. and Nyquist, G., Cellul. Chem. Technol., 15, 669 (1981).

7. Hanson, D. and Wenzel D., 1988. J. Wood Chem. Technol., 9, 189 (1989).