

Excitation Energy Transfer in Lignin: Fluorescence of Kraft Residual Lignin

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INTRODUCTION

The extent to which excitation energy transfer occurs in natural and residual lignin and the manner in which specific lignin functionalities participate in these processes is largely unknown, in part, due to the complexity of lignin. Although excitation energy transfer has not been directly studied in lignocellulosics, several researchers have observed indirect evidence of its occurrence. The steady-state fluorescence behaviour of isolated residual lignins from *Pinus taeda* kraft pulps cooked to final Klason lignin contents of 4 - 22% is presented. Several studies have examined the fluorescence of milled wood lignin, lignin model compounds, and pulping liquors, but kraft residual lignin has not been extensively characterized. This work discusses the fluorescence spectra of isolated lignin from different kraft pulps subjected to a variety of pulping conditions.

EXPERIMENTAL

Kraft Pulping

- Kraft pulps from *Pinus taeda* were cooked to final Klason lignin contents of 4 - 22% in an electrically-heated, rotating, multi-unit digester
- Condition A used high effective alkali (21.4%) and low sulfidity (23.2%)
- Condition B used low effective alkali (14.6%) and high sulfidity (56.8%)
- Constant residual lignin content pulps were cooked to ~4.0% Klason



Figure 2: Total luminescence plot for a representative residual lignin sample

Correlation with Process Variables and Lignin Functionalities

Correlation with Na₂S Charge

- Fluorescence intensity at 360 nm for lignins from pulps cooked to the same residual lignin content
- Strong correlation to initial Na₂S charge (Figure 3)
- A result of the amount of sulfur in the residual lignin and how or where it is incorporated into the lignin
- This was the only relationship identified between a pulping variable and residual lignin fluorescence

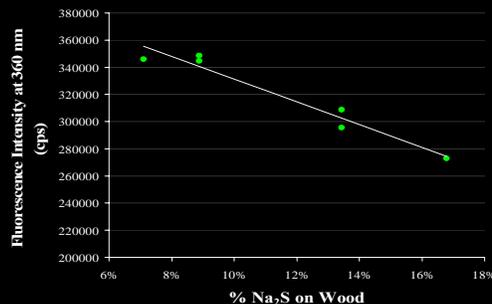


Figure 3: Fluorescence intensity at 360 nm (λ_{em} 310 nm) versus %Na₂S on wood during cooks to constant final residual lignin content ($R^2 = 0.95$)

Isolation of Residual Lignin

- Residual lignin was isolated by acid hydrolysis following methods common in the literature

Fluorescence Spectroscopy

- 12 mg/L lignin solutions were prepared using 14:1 (v/v) 2-methoxyethanol/deionized water as solvent
- Fluorescence spectra were collected with an ISS PC-1 steady-state fluorescence spectrophotometer
- Emission spectra used excitation at 310 nm and excitation spectra were collected using emission at 360 nm

Determination of Carbonyls

- KBr/lignin pellet samples were prepared for FTIR spectroscopy
- Carbonyl content was determined by integrating the area between 1840 cm^{-1} to 1550 cm^{-1}

RESULTS

Spectral Features

- The excitation maxima occurred at $\lambda_{ex} \approx 315$ nm with emission maxima at $\lambda_{em} \approx 360$ nm for all samples
- The Stokes shifts range from 3870 cm^{-1} to 4170 cm^{-1}
- The general shape of the spectra were the same regardless of pulping conditions
- Appears to be a ratiometric response in the excitation spectra with changes in the shoulders at 290 nm and 330 nm
- In the emission spectra, the shoulder at 380 nm changes significantly with different pulping conditions

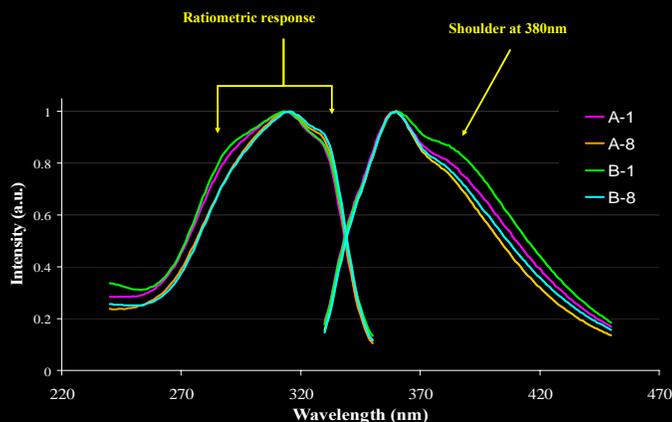


Figure 1: Normalized fluorescence spectra for A-1, A-8, B-1, and B-8 residual lignins (Sample designations 1 and 8 correspond to residual lignin contents of ~22% and 4%)

Implications to Energy Transfer

- The shape of the emission spectra is independent of excitation wavelength (Figure 2)
- This behaviour is unusual for complex mixtures of fluorophores
- All samples display same behaviour regardless of cooking time, temperature or chemical charge
- May indicate that the structure of kraft residual lignin retains sufficient connectivity and/or structure to facilitate energy transfer despite substantial delignification and chemical modification

Fluorescence/Carbonyl Relationship

- Ratiometric response in the excitation spectra correlated well with %CO determined by FTIR
- Condition A and Condition B have different responses to carbonyl content
- Condition B samples displayed higher sensitivity to carbonyl content

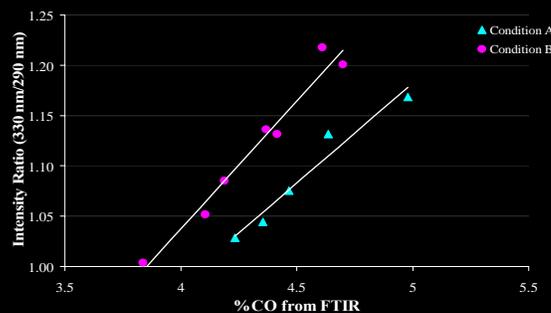


Figure 4: Ratio of fluorescence intensities (measured at 360 nm) at 330 nm and 290 nm versus percent carbonyls in lignin determined by FTIR ($R^2 = 0.96$ and 0.97 for Condition A and B respectively)

CONCLUSIONS

- The fluorescence properties of kraft residual lignin in solution are similar to that of other lignin samples in solution
- The dominant features of the spectra are independent of cooking conditions
- Carbonyl content and sodium sulfide charge did impact the fluorescence of the residual lignin
- The sodium sulfide process variable is important, not the final sulfur content; therefore the chemistry of the cook dictates where and/or how the sulfur is incorporated

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Ralming Yang and the IPST analytical department for preparing the KBr pellets and collecting the FTIR spectra. Portions of this work were used by C.I.T. and T.J.D. as partial fulfillment of the requirements for the Ph.D. degree at the Georgia Institute of Technology and Institute of Paper Science and Technology.