

# Fundamental insights into the oxidation of lignocellulosics obtained from singlet oxygen photochemistry

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Received 24 February 2004; received in revised form 31 May 2004; accepted 31 May 2004

Available online 23 July 2004

## Abstract

A photochemical approach for the delignification of lignocellulosics, specifically Southern kraft softwood pulp, was adopted to provide insight into the nature of the general oxidative chemistry leading to lignin removal and carbohydrate (cellulose) degradation. This is the first paper that primarily provides a systematic investigation of the singlet oxygen photochemistry of kraft pulp, in which Rose Bengal (RB) was employed as the photosensitizer to degrade lignin, and secondarily describes the resultant properties of the pulp. The oxidative chemistry was efficient until approximately 50% of the native lignin polymer remained, at which point the carbohydrate component was not exempt from depolymerization reactions. This study examined the influence of lignin chemical characteristics and a general metal-based radical inhibitor on the reactivity of singlet oxygen. In general, the oxidative chemistry obtained in this study from singlet oxygen was not unlike what has been observed in ground state oxygen reactions.

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**Keywords:** Singlet oxygen; Photodelignification; Lignocellulosics; Selectivity

## 1. Introduction

The aspect of harnessing photochemical oxidation reactions as opposed to traditional ground state or thermal chemical reactions for targeting lignin depolymerization reactions has received a considerable amount of attention within the last 10 years [1–5]. This attention derives in part from environmental regulations that seek to minimize the application of chlorine and chlorine-containing bleaching chemicals for the bleaching of kraft pulp. Additionally, photodelignification is a very novel and powerful approach to target lignin residues since the photochemical interactions leading to delignification can be selectively tuned by the appropriate choice of light energy. Photodelignification strategies rely principally on generating reactive species, such as hydroxyl radicals that can hydrolyze the generally unreactive ether bonds found between monomeric phenyl propanoid units in the three-dimensional structure of lignin. A fairly robust oxidant that has recently seen success for chemically degrading the lignin superstructure is singlet oxygen [6].

Marcocchia and his coworkers reported that irradiation of a slurry of kraft pulp with UV light in the presence of oxygen under very mild conditions reduced the lignin content of the pulp. It was found that this delignification was strongly dependent on the process conditions, such as the concentration of oxidant and substrate and the intensity and wavelength of the irradiating light [7]. It was known that the UV irradiation of ground state oxygen generated various reactive species. Singlet oxygen is among these species that can be generated via a stepwise photochemical process. In general, photochemical conversion processes that employ a photosensitizer for the transfer of excitation energy to the triplet ground state of oxygen are well established [8,9].

Singlet oxygen is an excited state of molecular oxygen with pronounced electrophilic character, hence reacting well with electron-rich groups such as olefinic or aromatic derivatives [6,10]. These electron rich groups tend to form an intermediate exciplex as a result of charge transfer reactions between the electron-rich substrate and the singlet oxygen. This exciplex is able to later form dioxetanes, hydroperoxides, or endoperoxides [11]. Shown in Fig. 1 is an example of the reactivity of singlet oxygen with a lignin-like monomeric unit that typically possesses aromatic character.

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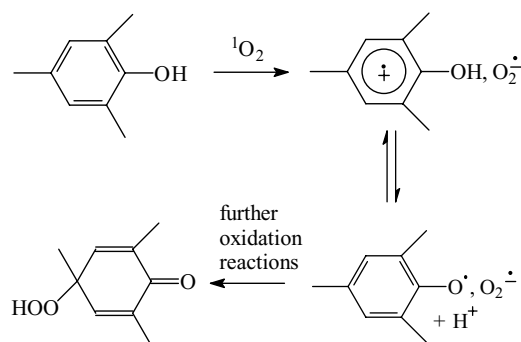


Fig. 1. Reaction mechanism that describes the singlet oxygen oxidation of lignin-like monomers. The highly oxidized aromatic units are susceptible to further oxidation, including an intramolecular superoxide Michael reaction (after deprotonation of the terminal hydroperoxyl group).

In our studies, we examined the influence of singlet oxygen on the delignification and carbohydrate chemistry of two types of kraft softwood pulp, one having an increased level of condensed phenolic structures versus a “control.” We were particularly interested in determining if there was an enhancement in the efficacy of delignification versus carbohydrate damage due to the highly electrophilic nature of singlet oxygen.

## 2. Experimental/materials and methods

### 2.1. Substrates and preparation for photolysis

All lignocellulosic substrates were commercially obtained from a sponsor of the Institute of Paper Science and Technology at the Georgia Institute of Technology. The substrates were derived from kraft pulping of loblolly pine (*P. taeda*) whose final product contained 4% by mass of residual lignin with the remainder being carbohydrates, principally cellulose. The approximate degree of the polymerization of the carbohydrate component was determined using the accepted cupriethylene diamine (CED) dissolution method that involves viscometry [12]. All work was done in deionized water that had a concentration of the pulp substrate at 1% mass/mass. Sufficient sodium hydroxide was added to this suspension to obtain a concentration up to 10% on a mass/mass basis to the substrate which gave a pH of approximately 11–12. We used a 0.5% mass/mass concentration of Rose Bengal (RB) relative to the substrate which was 17% relative to the amount of lignin in the starting sample (0.7 mmoles per 100 g of pulp sample) that had an optical density over 1 in the visible portion of the spectrum. The residual lignin used in these experiments was obtained via a literature acidolytic procedure in which the substrate is boiled in a dioxane/HCl solution for several hours to provide virtually intact lignin [13].

The suspension was placed in a jacketed dewar which was immersed in a water bath that was maintained at 45 °C for

the duration of the photolyses. A mechanical stirring rod was inserted into the suspension that prevented the dilute slurry to flocculate or to settle and ensured homogeneous exposure and temperature for the ensuing photolysis.

### 2.2. Substrate photolysis and measurements

A 400 W medium-pressure Hg Hanovia lamp was inserted into an ice water-cooled pyrex jacket (wavelength cutoff = 300 nm) which was then inserted into the dewar containing the pulp slurry. Once the irradiation began, the pulp slurry was stirring and reached a steady state temperature of 45 °C despite the temperature of the water bath since the lamp was so intense. The chemical properties of the substrate were measured over a period of five hours of irradiation. The lignin content was measured using the standard TAPPI test method, while the carbohydrate molecular weight was measured as described previously (see Section 2.1). In a separate set of experiments, the water was partially substituted by ethanol (up to 5%) by simple dilution to volume to maintain a 1% solid mass/total solid and water mass ratio. Finally, in a last set of experiments, the raw (extracted) residual lignin was reacted with singlet oxygen produced from the oxidation of hydrogen peroxide by sodium hypochlorite. This was done to avoid highly efficient direct photolysis reactions of the lignin since it would dissolve in a pH = 11 solution. In this set of experiments, the lignin was a precipitate in weakly alkaline (pH = 8), cold hydrogen peroxide (26%) solution. Sodium hypochlorite (30%) was added drop wise over a period of 15 min while each drop was allowed to stir completely. This generated an instantaneously high concentration of singlet oxygen at the surface similar to what occurred during rose bengal-sensitized singlet oxygen production in which incident radiation generated singlet oxygen since the system is not optically transparent. After 2 h of reaction, the lignin was isolated by filtration, washed with a cold, acidic (HCl, pH = 3) water, and freeze-thawed to provide a powder for NMR and UV-vis.

## 3. Results and discussion

### 3.1. Control experiments and depolymerization of lignin and carbohydrates

Control experiments were done to determine the contribution of individual variables to the photodelignification response of the substrate under study. Shown in Fig. 2 is the delignification response of the substrate as a function of the variables. It is not surprising that heat removes approximately 20% of the lignin available since leaching studies have shown this to be the case [14]. The spectral output of the lamp only causes an additional 14% delignification to occur. Again, this result is not surprising since the lignin is a chromophore that can undergo photooxidation reactions or can sensitize the production of singlet oxygen via a car-

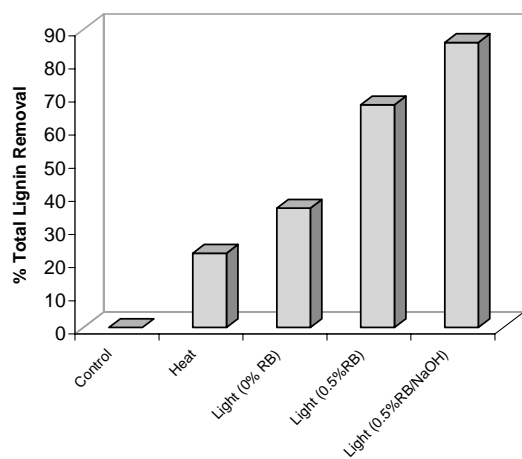


Fig. 2. The total delignification response of the pulp is shown as a function of specific variables after 22 h of the reaction. The “control” refers to the pulp in water at ambient temperature over the time frame of the experiment. The thermal reaction was conducted at 45 °C. Light was irradiated to pulp in various conditions.

bonyl  $\sigma \rightarrow \pi^*$  transition [15]. The addition of rose bengal induces a significant level of photodelignification despite the relatively neutral deionized water used for the experiments. The addition of base, however, expedites the removal of the lignin polymer since the oxidatively degraded phenolic groups on the lignin tend to dissociate in basic conditions. We heated or irradiated these substrates up to a maximum of 22 h in these sets of experiments to maximize the chemical changes induced in the lignin despite having base depletion after approximately 15 h of irradiation. We nevertheless obtained highly photobleached pulps after this time even with 14% lignin from the control remaining, suggestive of the high level of photobleaching attainable with singlet oxygen. We examined the effect of photolysis time on the extent of depolymerization of the substrates with and without oxygen sparging and magnesium sulfate. We noticed under ambient conditions that there was no significant change in the depolymerization of lignin with and without magnesium sulfate, but significant and reproducible changes were observed when oxygen is continuously supplied to the system. In Fig. 3, the

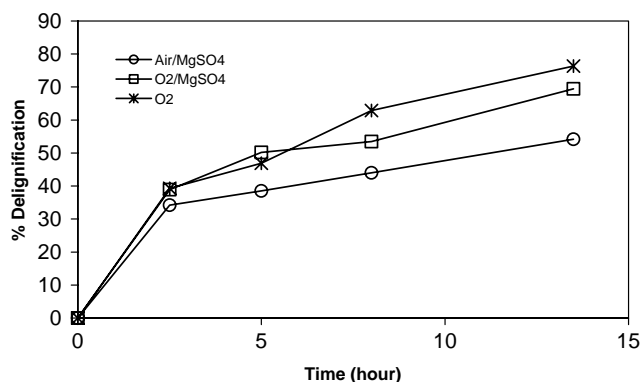


Fig. 3. The percentage delignification of the substrate with and without oxygen and magnesium sulfate as a function of photolysis.

depolymerization of lignin is shown as a function of both photolysis time and oxygen sparging. The inclusion of magnesium sulfate as a radical inhibitor by uptaking manganese has literature precedent [16]. Thus, we included as a probe of the level of oxygen radical character of the photodelignification process since its chemical interaction is predicated on intercepting transition metals that catalyze Fenton-type chemistry. As observed, the process of photodelignification appears to not only be mediated by a singlet oxygen electrophilic attack of the lignin moieties, but also by concomitant radical generation ensuing from this process given the ability of magnesium sulfate to reduce the level of delignification as demonstrated previously. The presence of radicals is therefore an intrinsic part of the delignification process, probably arising from side reactions involving peroxide heterolytic cleavage reactions after singlet oxygen electrophilic attack on the aromatic residues. Adding more oxygen by sparging appeared to enhance the photodelignification, perhaps owing to increased levels of singlet oxygen or due to oxygen's ability to participate in ground state radical reactions leading to delignification products.

The global change in the chromophoric content of the substrates was followed by monitoring the brightness of these samples as determined using a Technidyne Brightmeter based on a MgO standard normalized to 96 [17]. Shown in Fig. 4 are the results from analysis of those substrates. Clearly, the profiles of the brightness results correlate remarkably well with the delignification profiles shown in Fig. 3. Not surprisingly, the increases in brightness are therefore associated with the stepwise removal of the lignin polymer during the photolysis, which we confirmed by applying Kubelka–Munk analyses of the data that showed a strong correlation between the  $k/s$  (absorption/scattering coefficient where all sheets had the same scattering coefficient) and the lignin levels.

Finally, the changes in the carbohydrate, principally the cellulose, were analyzed to determine the selectivity of the photodelignification reaction. As discussed earlier, the reactivity of singlet oxygen is preferential for lignin; yet, the ensuing radicals generated will likely cause carbohydrate

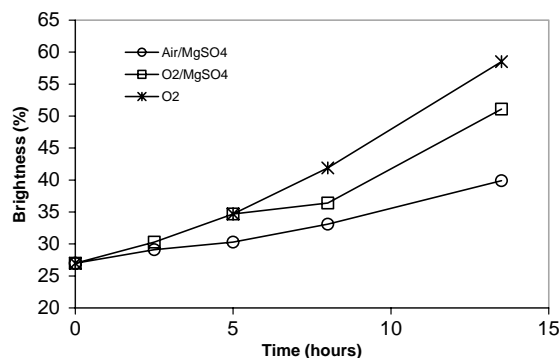


Fig. 4. The TAPPI brightnesses of the substrate with and without oxygen and magnesium sulfate as a function of photolysis.

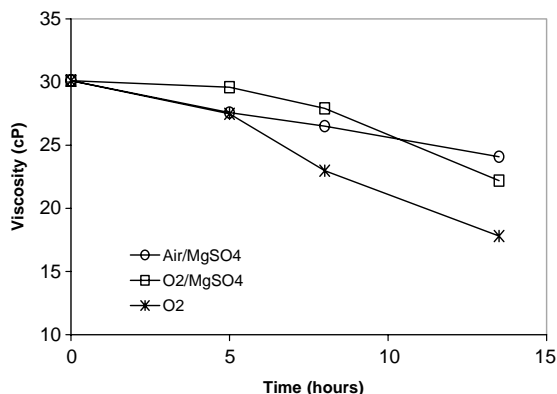


Fig. 5. The CED viscosities of the substrate with and without oxygen and magnesium sulfate as a function of photolysis.

degradation. Shown in Fig. 5 is a plot of the viscosity or integrity of the cellulose of the substrate against the irradiation time. In general, the ability of the magnesium sulfate addition to offset cellulose integrity loss is reduced with the application of oxygen. Without it, the propensity for degradation of the cellulose is very high. These results strongly suggest that despite the relatively high selectivity of singlet oxygen for lignin, radical generation is a phenomenon that likely follows singlet oxygen chemistry given the indiscriminate cellulose damage that is modulated by magnesium sulfate to a degree. Given the results to date, it was determined that the threshold for the failure of reaction selectivity is the 50% delignification level as shown in Fig. 6. The irradiation was performed over a sufficient time window (22 h) to allow for the generation of the selectivity curve. The curve is very similar in appearance to the oxygen delignification curves generated over the last 30 years [18]. Thus, it is safe to conclude that the radical chemistry in oxygen delignification is operating in the singlet oxygen system despite the more selective nature of singlet oxygen for lignin.

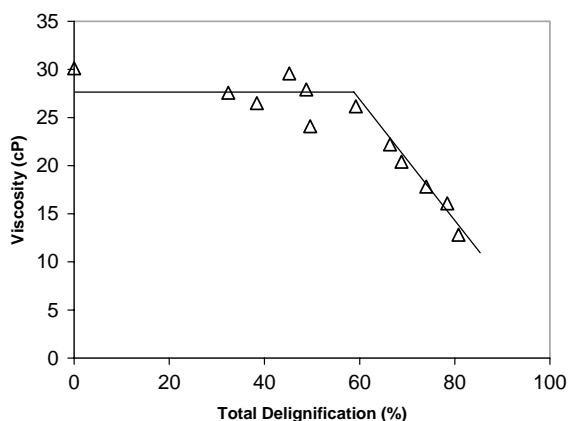


Fig. 6. A selectivity plot of the CED viscosity of the pulp samples as a function of delignification by application of singlet oxygen for 22 h.

### 3.2. Chemical reactivity of lignin with singlet oxygen

In order to further elucidate the chemistry occurring following singlet oxygen generation, we examined its effect on the residual lignin of the substrate which was obtained via a chemical extraction process from the substrate. The lignin was dissolved in a mildly basic hydrogen peroxide solution (20%) which was cooled in an ice bath. To this solution, a sodium hypochlorite solution (30%) was added dropwise very slowly over the course of several hours. The oxidation of the hydrogen peroxide ultimately leads to the chemical generation of singlet oxygen in yields comparable to the rose bengal photochemical method [19]. We were interested in simulating the chemical environment of the lignin in the pulp since the turbidity of the substrate mixture allowed for only surface reactions and it is complicated by lignin being chemically and physically entrained within the fiber substrates. Since exposure of the lignin in basic water would have been too efficient, it was necessary to develop a system that mimicked the photochemical conditions and could also be easily controlled. Thus, upon completion of the chemical reaction, we examined the chemical structure and absorbance of the lignin obtained. We performed a standard  $^{31}\text{P}$  NMR of the lignin as described in the literature and these results are displayed in Table 1 [20]. Not surprisingly, we observed a large, nearly 50% increase in the levels of the carboxylic acids in the lignin. This result is typical of what is observed in the reactions of ground state oxygen with pulp or lignin [21]. Certainly, this suggests that despite the initial electrophilic reactions of singlet oxygen with lignin, it is likely that ensuing oxidations follow some of the typical reactions associated with ground state oxygen reactions, such as ring additions by hydroperoxide and oxygen followed by ring openings to the muconic esters and acids [22].

However, unlike ground state oxygen reactions, the levels of condensed phenolics (i.e., conjugated lignin monomers at the C5 positions of the benzene moieties) were reduced during the singlet oxygen reactions. This may be a consequence of the high electrophilic reactivity of singlet oxygen and was tested by subjecting substrates enriched in condensed phenolics to singlet oxygen reactions. We also examined the absorbance of the lignin samples before and after the reaction. The results are shown in Fig. 7. As is readily apparent, the singlet oxygen-treated lignin sample has a reduced absorbance by over 20% throughout the near-UV and the visible portions of the spectrum. Again, this result is consistent

Table 1

A list of the amounts of each of the chemical groups in lignin for the control and singlet oxygen-treated lignin samples

Chemical group	Control lignin (mmol lignin/g substrate)	Oxidized lignin (mmol lignin/g substrate)
Aliphatic hydroxyls	1.38	1.15
Condensed phenolics	0.82	0.79
Guaiacyl phenolics	0.94	0.88
Carboxylic acids	0.28	0.43

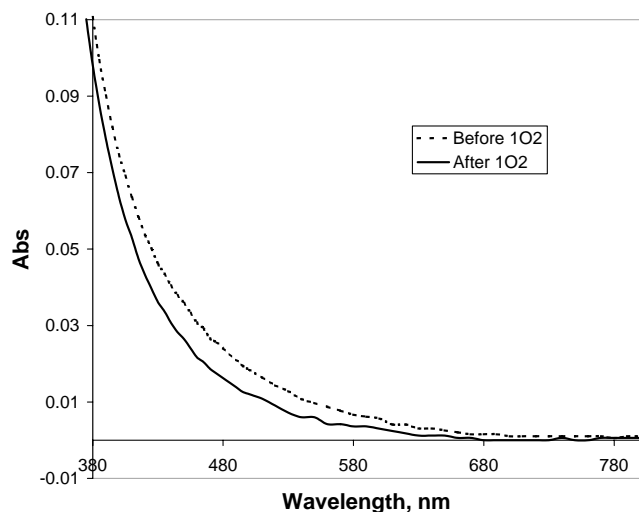


Fig. 7. UV-vis spectra of lignin dissolved in dioxane before and after singlet oxygen reaction.

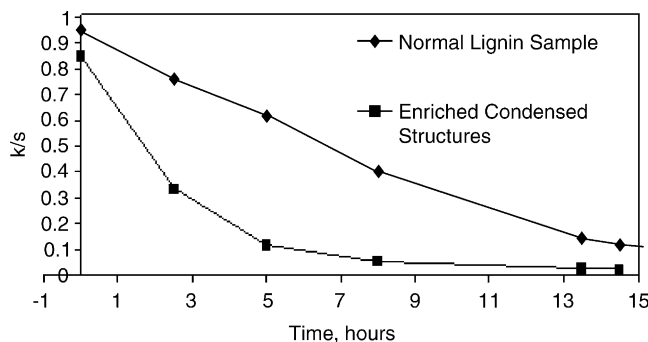


Fig. 8. A plot of the changes in  $k/s$ , the absorption/scattering coefficient ratio, vs. irradiation time for a normal substrate vs. a substrate enriched in condensed lignin units.

with a set of oxidation reactions that degrade the benzene chromophores that comprise the lignin structure.

Fig. 8 demonstrates the  $k/s$  results for the reaction of singlet oxygen with a substrate possessing a typical level of condensed phenolics and a substrate enriched by 20% in condensed phenolics. Both samples have approximately the same initial absorbance. However, it is apparent that the enriched condensed phenolic substrate has a higher kinetics of reaction than the control substrate. This result is consistent with a higher driving force for reaction since the enriched phenolic substrate would tend to react more efficiently with singlet oxygen leading to more oxidized product that would have reduced absorbance in the near UV.

#### 4. Conclusion

This study has investigated the reactivity of singlet oxygen with kraft softwood substrates with respect to the

chemistry of the lignin and the cellulose. It was determined that despite the relatively high selectivity of singlet oxygen for lignin aromatic units, the degradation of the cellulose nevertheless occurs after approximately 50% removal of the lignin. The most salient difference between this system and a typical ground state oxygen delignification system is the absence of condensed phenolic units in the lignin. In fact, it was discovered that both the condensed and noncondensed (guaiacyl) units react well with singlet oxygen.

#### Acknowledgements

We gratefully acknowledge the sponsors of the Institute of Paper Science and Technology Center at the Georgia Institute of Technology who have helped to make this work possible. We are also indebted to Professor C. Foote of UCLA whose insightful advice propelled this work.

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