

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

# Photochemical reactions of lignin: Opportunities for valorisation

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2022

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## Abstract

Lignin is the second most abundant biopolymer after cellulose and is the largest bio-based source of aromatic compounds. However, its heterogeneous and recalcitrant structure makes it difficult to depolymerise for use in renewable chemicals production. Photochemical reactions can be performed at mild conditions and can achieve efficient reaction pathways without the use of additional reagents. The potential efficiency gains in terms of energy and use of materials have led to renewed interest in photochemistry research, as we seek to improve the environmental sustainability of industry.

Concepts for valorisation of lignin through heterogeneous and homogeneous photocatalysis are currently being investigated. Although this photocatalyst research has shown some encouraging results, the synthesis, separation, and recycling of catalysts would add significant costs to a process. If it were possible to induce direct photochemical reactions with ultraviolet light, the difficulties associated with catalysis could be avoided, and it would bring a photochemical lignin valorisation concept closer to feasibility.

This thesis deals with the topic of how ultraviolet light can induce changes in lignin. The contents in Paper I describe our early work, which demonstrated that UV light causes changes to functional groups in lignin and that UV light can be used to extract lignin from sawdust. In our more recent experiments, we use 280 nm light from UV-LEDs using a homemade 3D printed photoreactor, the details of which are covered in Paper II. The results presented here also include a comparison between acetonitrile and aqueous NaOH as solvents for the photoreactions. The evaluation of whether benzophenone can be used as a photosensitiser to increase the reaction rate or yield toward desired products in reactions of Kraft lignin and 2-(benzyloxy)phenol, a model compound used to represent an ether bond between two phenolic rings, is covered in Paper III. We also needed to assess whether our conclusions are robust against changes in lignin concentration and light intensity, and an analysis of this is included in the results and discussion. Lignin has also been observed to act as a photocatalyst. The beginning of an investigation into this phenomenon is covered in this thesis using the photooxidation of methanol to formate as an example.  $^1\text{H}$  NMR is the primary analysis technique used in this work. Results based on GC-MS and diffusion NMR are included to demonstrate their intended use in future work. The analysis across all areas focuses on using the analysis methods to estimate reaction rates and selectivity toward certain products, and aims to understand the connections between these results and the details of the reactions.

The results gathered so far have laid the groundwork for understanding the complex relationships between the properties of lignin, reaction conditions, and changes which occur upon irradiation with UV light. The end of the thesis discusses future plans for increasing our understanding of these photoreactions.

**Keywords:** *Lignin, Photochemistry, NMR, Kraft, Photolysis, Biomass*



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## List of publications

This thesis is based on the following appended papers:

### **I. ‘Lignin and extractives first’ conversion of lignocellulosic residual streams using UV light from LEDs**

Jonna Hynynen, **Alexander Riddell**, Abdenour Achour, Zoltan Takacs, Mats Wallin, Jim Parkås, Diana Bernin

Green Chemistry, 23 (2021), 8251-8259,  
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### **II. A 3D printed photoreactor for investigating variable reaction geometry, wavelength, and fluid flow**

**Alexander Riddell**, Patric Kvist, Diana Bernin

Review of Scientific Instruments, 93 (2022), 084103,  
DOI: <https://doi.org/10.1063/5.0087107>

### **III. Photosensitised reactions of lignin and related model compounds**

**Alexander Riddell**, Jonna Hynynen, Abdenour Achour, Gunnar Westman, Jim Parkås, Diana Bernin

Manuscript

## **Publications not included in this thesis**

### **I. Effluents and residues from industrial sites for carbon dioxide capture: a review**

Francisco M. Baena-Moreno, Emmanouela Leventaki, **Alexander Riddell**, Joanna Wojtasz-Mucha, Diana Bernin

Environmental Chemistry Letters, (2022),  
DOI: <https://doi.org/10.1007/s10311-022-01513-x>

### **II. Levulinic acid-based “green” solvents for lignocellulose fractionation: On the superior extraction yield and selectivity towards lignin**

Elodie Melro, Alexander Riddell, Diana Bernin, Ana Rosa da Costa, Artur J. M. Valente, Filipe E. Antunes, Anabela Romano, Magnus Norgren, and Bruno Medronho

Manuscript





## **Contribution report**

- I. I wrote some sections of the manuscript, contributed to editing, and performed and analysed actinometry experiments, contributed to responses to reviewers.
- II. I wrote the manuscript, performed the experiments, and contributed to the design of the photoreactor.
- III. I drafted the manuscript, contributed to the data analysis, performed photoreactions, GC-MS experiments and UV-vis experiments.



## List of abbreviations

UV-Vis	ultraviolet-visible spectroscopy
n	non-bonding orbital
$\pi$	pi bonding orbital
$\pi^*$	pi antibonding orbital
UV	ultraviolet
S <sub>0</sub>	singlet ground state
S <sub>1</sub>	first singlet excited state
T <sub>1</sub>	first triplet excited state
NMR	nuclear magnetic resonance spectroscopy
ROS	reactive oxygen species
ACN	acetonitrile
2BP	2-benzyloxyphenol
<sup>1</sup> Δ <sub>g</sub>	singlet oxygen
LED	light emitting diode
FTIR	Fourier transform infrared
$\varphi$	quantum efficiency
$\lambda$	wavelength
HSQC	Heteronuclear single quantum coherence spectroscopy
GC-MS	gas chromatography – mass spectrometry
4BP	4-benzyloxyphenol
AOP	advanced oxidation process



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## 1. Introduction

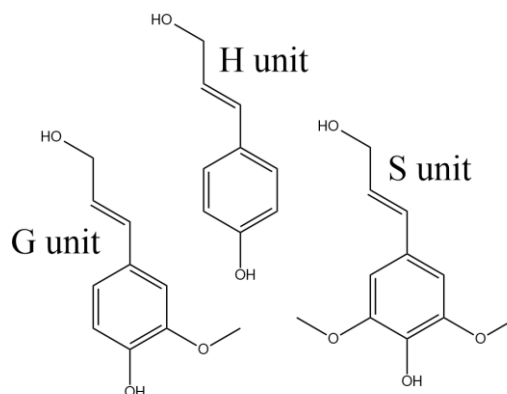
Lignin presents an important opportunity for the production of renewable chemicals. Lignin is the most abundant natural source of aromatic compounds and it is the second most abundant component in biomass, making up around 30% of dry wood mass<sup>1</sup>. This potential is widely recognised in the field of bio-based chemicals. However, most technical lignin, which is the lignin separated from cellulose in industrial processes, is burned for process heat. Other applications for lignin include bio-based resins, adhesives, or composites<sup>1</sup>, but lignin is not often converted into chemicals on an industrial scale.

The forestry and pulp and paper industries make up a significant portion of the economy of the European Union, and employ approximately 1.6 million people<sup>2</sup>. Researchers are evaluating how biomass can be better utilized to produce higher value products. These changes could be part of a shift toward a “bio-based economy”. This project focuses the utilisation of the lignin found in residual streams including woodchips, bark, and black liquor.

The field of photochemistry has been rejuvenated in recent years due to its potential to address several goals of “green chemistry”, including low temperature and low pressure reactions, efficient reaction pathways, and limiting the use of additional chemical reagents. Photochemical reactions of lignin has been investigated for degradation of lignin in wastewater treatment, and for production of chemicals using various classes of photocatalyst<sup>3</sup>. This project focuses on photochemical reactions of lignin without a photocatalyst so that costs associated with obtaining and separating catalyst particles can be avoided. We are investigating the use of ultraviolet light to induce photolysis, the potential advantages of which will be described in throughout this thesis.

### 1.1. Lignin Structure and Properties

Lignin is made up of H, G, and S subunits, shown in scheme 1.

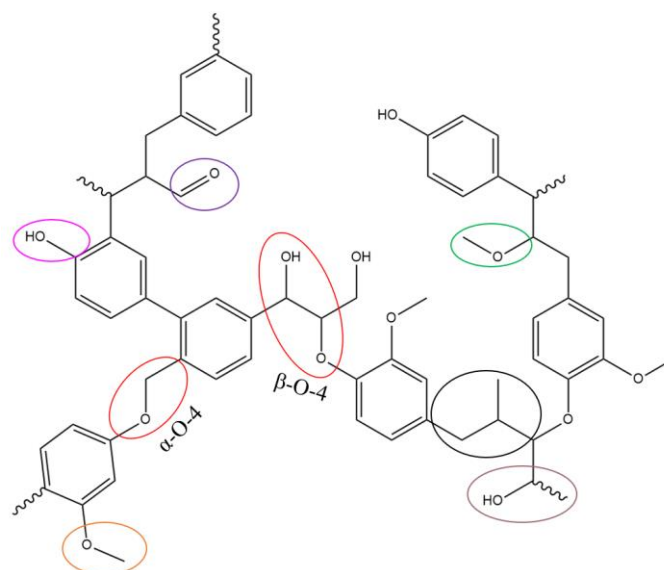


Scheme 1. The three aromatic monomer units from which lignin polymerises; coniferyl alcohol (G unit), p-coumaryl alcohol (H unit), and sinapyl alcohol (S unit)

The ratio of the three subunits in scheme 1 differs depending on the biomass source. The three units are differentiated by the number of methoxy groups on the aromatic ring. Softwood lignin in its natural state has almost all G units, which have one methoxy group. Due to its conjugated  $\pi$  systems, the lignin structure contains chromophores which give it a high absorptivity in the ultraviolet and visible spectrum. One part of the lignin structure which particularly interests researchers is the  $\beta$ -O-4 linkage, labelled in scheme 2. The study of these linkages is important because finding methods to selectively cleave the bonds between units would enable the conversion of lignin into its most desirable product, aromatic monomers.

## 1.2. Challenges Summary

The conversion of lignin into smaller chemicals is difficult because of two properties of lignin. One being its chemical recalcitrance, the other being its heterogeneity. Scheme 2 shows an example of a lignin structure.



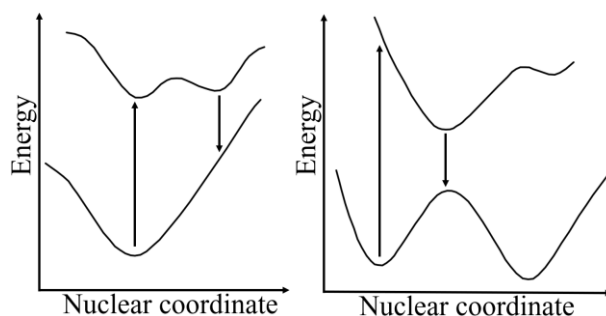
Scheme 2. Key functional groups in lignin. The functional groups are circled as follows; (purple) Aldehyde region, (brown) Aliphatic hydroxyl, (pink) Phenolic region, (green) Alkyl methoxy region, (orange) Aromatic methoxy region, (black) Aliphatic region.  $\beta$ -O-4 and  $\alpha$ -O-4 linkages are labelled and circled in red.

Lignin lacks steric regularity because it is synthesised in nature through the combination of radicals from dehydrogenated coniferyl, sinapyl, and coumaryl alcohols<sup>4</sup>. The chemical structure, amounts of functional groups, and molecular weight distribution in lignin vary depending on many factors including the species of the biomass source and the process used to obtain lignin from the original biomass. Selectivity in traditional thermal and catalytic reactions is difficult to achieve due to the molecules reacting in relatively uncontrolled ways at high temperatures, since the molecules can overcome several activation barriers. Heterogeneous catalytic systems also have the problem of catalyst deactivation via coking<sup>5</sup>.

## 1.3. How could Photochemistry help?

The use of photochemistry in lignin reactions is interesting for several reasons. Photochemical reactors can operate near ambient temperature and pressure, possibly enabling more selective reactions and reducing the energy requirements of the reactor. The use of light as a reagent would be useful if used in place of another chemical reagent because this can reduce chemical costs, simplify downstream separation, and it is sustainable since it can generate less waste. Photocatalytic reactions have already been investigated for the application of removing lignin from wastewater via “advanced oxidation processes”<sup>6</sup>. The aims of this project differ from wastewater treatment since the concentration of lignin in the reaction is far higher than those in wastewater since the aim is to convert lignin into valuable chemicals. The goal is to selectively depolymerise lignin, rather than to eliminate it. Approaches to depolymerise lignin with photocatalytic processes are also being investigated<sup>3</sup>. We argue that photolysis (photochemical bond dissociation) of lignin could be a useful depolymerisation method, in addition to the established uses of reactive oxygen species.





Scheme 3. Two theoretical scenarios for photochemical reactions

A schematic demonstrating two generalised possibilities for a photoreaction are shown in scheme 3. It can be seen from both plots that the energy profiles in the ground state and in the excited state are different. Efficient photoreaction pathways can exist for situations like the plot on the right. In this case, there is a relatively large activation barrier “hill” between the two “valleys”, so this molecule would require a large activation energy to react. However, in the excited state, the nuclear coordinates adjust to achieve an energy minimum. In this case, it turns out that the energy minimum in the excited state has a nuclear coordinate which is at the top of the activation barrier in the ground state, allowing the activation barrier to be “bypassed”. The photon needed to bring the molecule into the excited state contains more energy than the activation barrier of the ground state reaction. However, this approach could be efficient because ideally, the photons are being absorbed specifically by the target chromophore. For a thermal reaction to take place, the entire reactor would need to be heated so that some of the target molecules have enough energy to overcome the activation barrier according to a Boltzmann distribution. This can cause the problem of undesired side-reactions and requires more energy to operate the reactor at an elevated temperature/pressure. The left plot describes a situation where photoexcitation would not be an efficient approach because the nuclear coordinates will return to their original position once the molecule relaxes into the ground state.

#### 1.4. Photoreactor Design Details

Looking at lignin in solution, one can see that it has colour ranging from yellow to dark brown, depending on its concentration. Maintaining relatively homogeneous light intensity throughout the reaction volume is a challenge for photochemical reactor engineering. Light attenuation will be lower for lower concentration solutions of the absorbing species, but then the lower concentration would mean that dilute products would need to be separated from a larger volume of solvent. Therefore, for strongly absorbing species, it is advisable to use narrow reaction channels which allow for a high surface area to volume ratio and where the entire reaction volume can be irradiated near the “walls” of the reactor. A “microreactor” is a reactor which has at least one dimension less than one millimetre<sup>7</sup>. Flow microreactors are being researched extensively for photochemical reactions due to these advantages. The microreactor approach has the disadvantage of high costs for scaling up the reactor. Flow microreactors can be scaled through “numbering up”, which is the practice of running multiple channels simultaneously. Additive manufacturing techniques could be very useful in reducing the cost of reactors with parallel microchannels with geometries customised for the irradiation intensity, mixing, and temperature control requirements of a photochemical system. Due to the high reactor and operational costs, this approach is of most interest in pharmaceuticals and other high value chemicals. For the purposes of lignin conversion, it would eventually be necessary to understand how lignin concentration effects the kinetics and selectivity of its reactions so that the appropriate dimensions of a reactor can be evaluated (see section 3.7).

## 1.5. Absorbance, Energy States, and Electron Spins

Photochemical reactions begin when a photon is absorbed by a molecule, causing a transition of an electron to a higher energy level. Photons with sufficient energy to cause an electronic transition are in the ultraviolet and visible spectrum. Figure 1 shows the absorbance spectrum of lignin in acetonitrile.

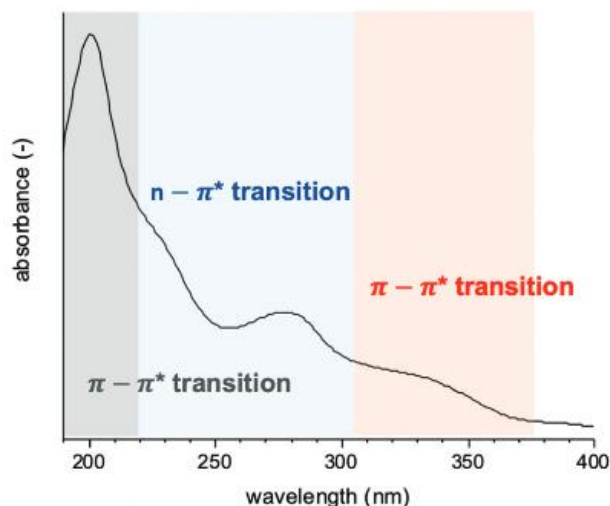


Figure 1. UV-vis absorbance spectrum of lignin in acetonitrile with regions shaded according to type of electronic transition. Copied with permission from Hynynen et al.<sup>8</sup>

In the ultraviolet and visible region,  $n$  to  $\pi^*$  and  $\pi$  to  $\pi^*$  are the two transitions which occur. “ $n$ ” stands for “nonbonding” and “ $\pi$ ” and “ $\pi^*$ ” are the pi bonding and pi antibonding orbitals respectively. Benzophenone, a photosensitizer later presented in this work, exhibits an  $n$  to  $\pi^*$  transition. When benzophenone absorbs a UV photon, a nonbonding electron from its oxygen atom is promoted to the  $\pi^*$  antibonding orbital. Since the ground state energy level is left with one electron, it behaves like an electrophilic radical and can abstract hydrogen from another molecule, while the excited electron can be donated. The orbital which an electron is excited from can have consequences for charge transfer and the behaviour of bonds in the excited state<sup>9</sup>, but these phenomena in lignin are not understood enough to be included in this thesis.



Scheme 4. (Left) Simplified Jablonski diagram with ( $S_0$ ) ground singlet, ( $S_1$ ) excited singlet, and ( $T_1$ ) excited triplet electronic energy levels and the transitions between them; (1) absorption, (2) fluorescence, (3) intersystem crossing, and (4) phosphorescence. (Right) Diagram showing how electronic spin and energy level determine ( $S_0$ ) ground state singlet states, ( $S_1$ ) excited singlet states, and ( $T_1$ ) excited triplet states.

Once a photon is absorbed, several photophysical processes can occur. The Jablonski diagram in Scheme 4 (left) summarises these possibilities. The rates at which these processes occur have major ramifications for the reactivity of the molecule in the excited state because it will determine the type of resulting excited state and its lifetime<sup>9</sup>. Scheme 4 (right) shows the difference between singlet and triplet states in terms of energy levels and electron spins.

The relaxation of triplet states occurs orders of magnitude slower than for singlet states, so the longer lifetime of these states often lead to higher reactivity. Another potentially important factor for lignin would be the location of the excited electron within the lignin molecule. The process of “energy transfer” can occur, meaning that the excited electron can transfer energy to other orbitals. This phenomenon has been measured in lignin using fluorescence spectroscopy<sup>10</sup>. For photochemical systems in general, cleavage of bonds, rotation of bonds, and photoisomerization can also occur due to photoexcitation<sup>9</sup>. Bonds in an excited state can also participate in the donation of an electron from the excited energy level, and acceptance of an electron into the hole left in the ground state. It is possible for an electronically excited molecule to act as an electron donor and acceptor at the same time, like in semiconductor photocatalysis. It also may be the case that photons cause reactions with other molecules in solution and a subsequent reactions with lignin. There is a broad range of possible transformations that could occur involving an irradiated solution of lignin molecules. The main questions are which photochemical events occur, which are desirable, and how can reaction conditions be changed to maximise the transformations of interest.

### **1.6. Wavelength Effects**

The effects of the incident wavelength on lignin reaction behaviour are still not well understood and will depend on several factors. One is the relationship between wavelength and absorbance, which can be easily measured with UV-Vis. When an electron is excited, its energy can go to one of many vibrational energy levels which fit within an electronic energy level. At this point it is unclear whether vibrational energy levels affect reactions in lignin. The electrons which are excited, and the orbitals they are excited to potentially makes a difference to which electron remains excited once energy transfer has been accounted for (this is studied with fluorescence spectroscopy)<sup>9</sup>. Since energy must be transferred “down” energy levels, the initial energy level, and thus wavelength, could affect this path. Energy transfer studies on photoexcited lignin molecules have shown a significant difference between excitation and emission wavelengths, suggesting that energy transfer is common within lignin molecules<sup>10</sup>. Upon excitation, energy states higher than  $S_1$  rapidly relax to  $S_1$  (Kasha’s rule) and typically do not have time to do anything other than relax to  $S_1$ . This explains why although there is a range of wavelengths which can excite a molecule, most organic molecules have wavelength-independent photochemistry<sup>9</sup>.

### **1.7. Solvent Effects**

The solubility of lignin is a complex topic because of the many ways which lignin samples can vary in terms of their molecular weight distributions and functional groups. In aqueous solutions, increased pH affects lignin solubility due to deprotonation of certain functional groups leading to coulombic repulsion between molecules<sup>11</sup>. For photochemistry, it is important to consider the absorptivity of the solvent to minimize light attenuation. Another factor is the generation of reactive oxygen species, which can be affected by the water and oxygen content of the solvent. Additionally, the effect that solvent has on NMR analysis is considered to avoid solvent peaks overlapping with peaks of interest.

### **1.8. Energy Transfer**

Energy transfer is likely to be an important phenomenon in lignin photoreactions, considering the findings of Albinsson et al., where spruce lignin exhibited a fluorescence spectra with a peak at 360 nm for an excitation wavelength range of 240 to 320 nm<sup>10</sup>. This work suggests that energy transfer is occurring from lignin chromophores to acceptors elsewhere on the lignin molecule. This will likely have consequences for photo reactivity of lignin, since it will determine the part of the lignin molecule which spends the most time in an excited state.

Energy transfer occurs in three ways; trivial energy transfer, exchange energy transfer (Dexter), and dipole-dipole interactions<sup>9</sup>. Trivial transfer, in which a photon is emitted by a donor and absorbed

by an acceptor, is unlikely to be the mechanism behind lignin energy transfer due to its low efficiency. Exchange energy transfer is a more likely explanation. Exchange energy transfer requires contact between orbitals, and usually involves an excited state being transferred down in energy. In lignin, the emission spectrum is significantly lower energy than the excitation spectrum, suggesting energy transfer to excited states with less energy<sup>10</sup>. Since the chromophores in lignin are contained within one molecule, chromophores are in close proximity to each other, aiding exchange energy transfer. Dipole-dipole energy transfer a complex, non-radiative energy transfer mechanism which need not be understood for this thesis. However, it should be noted that this process requires an overlap in the emission spectra of the donor and absorption spectrum of the receiving chromophore, and that the efficiency of this mechanism is inversely proportional to the sixth power of distance<sup>9</sup>. Based on these criteria, dipole-dipole energy transfer is unlikely to occur to a significant extent in lignin because of the limited overlap between absorption and fluorescence spectra.

Unlike in ground-state organic chemistry, molecules which are electronically excited become better electron donors and better electron acceptors<sup>9</sup>, since the hole in the ground state can accept electrons, and the excited electron can be donated. This allows excited lignin to act as a photocatalyst (see section 3.8).

### **1.9. Photocatalysis**

When attempting to understand lignin photolysis, it should be useful to consider which mechanisms are involved in photocatalytic reactions. In these systems, electrons in semiconducting particles (typically TiO<sub>2</sub>) are excited from the valence band to the conduction band. The excited electron acts as a reductant, and the hole in the valence band acts as an oxidant<sup>4</sup>. This leads to the generation of several reactive oxygen species (ROS) including the hydroxyl (OH•) and superoxide (O<sub>2</sub>•-) radicals. These ROS oxidize organic molecules in solution. The oxidation potentials of the ROS differ from each other and therefore, products formed from the oxidation of organic compounds can differ depending on the concentration of ROS<sup>4</sup>.

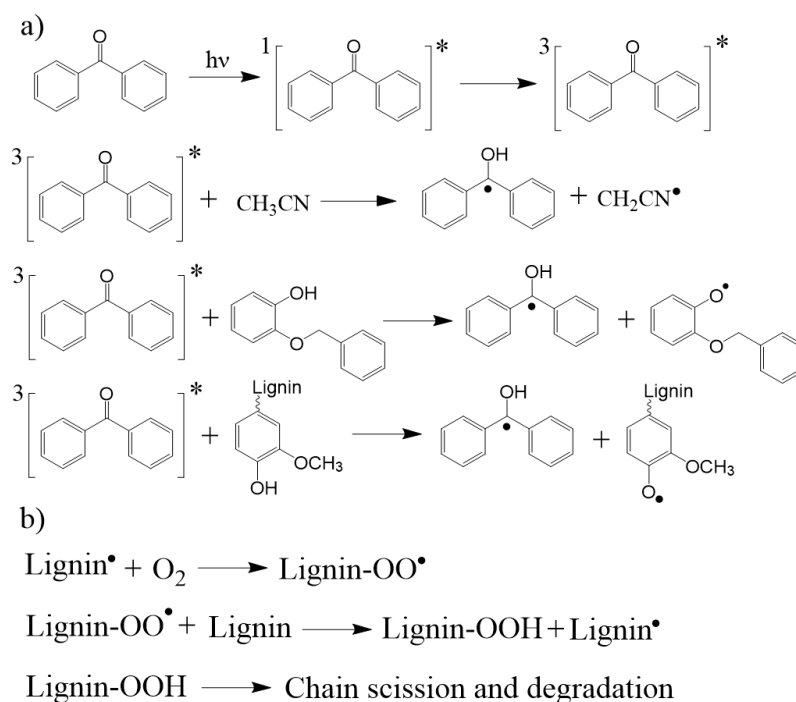
Homogeneous photocatalysts have not often been used in lignin conversion research, mainly due to the difficulty of separating the catalyst from the products after the reaction<sup>3</sup>. The potential advantage of homogeneous catalysis would be high selectivity of breaking C-C and C-O-C bonds through customised selection of metal ion and organic ligands. To our best knowledge, there are no studies on the conversion of technical lignin's with homogeneous photocatalysts, only lignin model compounds. These results could be relevant when compared with pure photolysis of lignin model compounds or compared with benzophenone photosensitised reactions of model compounds. A notable approach which has been combined with homogeneous photocatalysis is the two-step oxidation/reduction strategy by Stephenson et al.<sup>12</sup> The main idea is that the bond dissociation energy of the  $\beta$ -O-4 linkage decreases when benzylic alcohols are oxidized to ketones, leading to more efficient and selective fragmentation of the lignin model compounds studied. Whether we eventually try a two-step process or not, these findings are relevant in demonstrating the importance of adjacent functional groups in the breaking of a key linkage in lignin.

### **1.10. Photosensitisation**

Despite the advantages of performing reactions without catalysts or reagents using UV light, photolytic reactions often have poor yields and quantum efficiencies. This is partly due to short excited state lifetimes<sup>13</sup>. Triplet states are of particular interest when investigating the reactivity of lignin because triplet states (denoted T<sub>1</sub> for the first triplet state above the ground state) can have much longer lifetimes than excited singlet states (S<sub>1</sub>) due to the electrons in the T<sub>1</sub> state having the same spin in the ground (S<sub>0</sub>) and T<sub>1</sub> energy levels. This means relaxation to the ground state is a "forbidden transition" and the electron must undergo delayed fluorescence to return to the ground state<sup>9</sup>.

Photosensitisers like benzophenone (the focus of Paper III) can increase the population of T<sub>1</sub> excited states through energy transfer<sup>13,14</sup>. When benzophenone absorbs a UV photon, a nonbonding electron from oxygen is promoted to the π\* antibonding orbital (an n,π\* transition). Since the ground state energy level is left with one electron, it behaves like an electrophilic radical and can abstract hydrogen from another molecule. The electron in the antibonding orbital acts as a nucleophile<sup>9</sup>. Benzophenone has a very high quantum yield for triplet states. Intersystem crossing occurs very quickly (~10 ps), so triplet states are the most relevant in benzophenone photochemistry<sup>9</sup>. Benzophenone has a relatively long triplet lifetime in acetonitrile (ACN), the solvent used in this investigation, and has been observed to abstract hydrogen from acetonitrile<sup>15</sup>. In theory, aromatic ketones are very efficient sensitizers for hydrogen transfer<sup>16</sup> and might directly abstract hydrogen from lignin or its model compounds. Scheme 5 shows how benzophenone could abstract hydrogen from acetonitrile, lignin, and 2-(benzyloxy)phenol (a compound used to model an ether bond in lignin). The extent that benzophenone would extract hydrogen directly from these substrates is unknown and may in this case be uncommon due to the relative amount of acetonitrile being much greater (solutions of only 1 g/L).

The hydrogen abstraction approach has achieved a 10% yield of aromatic monomers from Dioxanesolv poplar lignin when hydrogen is abstracted from the CαH–OH group on a ZnIn<sub>2</sub>S<sub>4</sub> heterogeneous catalyst surface<sup>17</sup>. The persulfate radical (SO<sub>4</sub><sup>•-</sup>) can be used for hydrogen abstraction and the pre-oxidation of model compounds for the β-O-4 lignin linkage<sup>18</sup>. C<sub>β</sub>-H abstraction was found by Wang et al. to be the rate-determining step for C-C bond cleavage adjacent to ketones during their catalytic (not photochemical) depolymerisation of lignin<sup>19</sup>. Chain scission can occur where molecular oxygen reacts with a radicals on a polymer which were created from hydrogen abstraction by a photosensitiser<sup>20,21</sup>. A generalized version of this process is shown in scheme 5. Although it is difficult to assess the relevance of scheme 5 to our work, the importance of hydrogen abstraction in adjacent research areas motivates the investigation of benzophenone in lignin photochemistry.



Scheme 5. a) Possibilities for hydrogen abstraction from (2nd row) acetonitrile, (3rd row) a 2BP molecule, and (4th row) a lignin aromatic unit. b) Possible initiation of a chain scission mechanism involving lignin following hydrogen abstraction. Based on a diagram from Taylor et al<sup>20</sup>.

The role of reactive oxygen species (ROS) is of great importance for lignin photochemistry. In heterogeneous photocatalysis, molecules can be oxidised by the hydroxyl ( $\text{OH}\cdot$ ) and superoxide ( $\text{O}_2\cdot^-$ ) radicals which are formed from the holes and photoinduced electrons on the catalyst surface. Other types of ROS include singlet oxygen ( $^1\Delta_g$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The  $^1\Delta_g$  state is located about 96 kJ/mol above the ground state, and has a weak emission at 1270 nm<sup>9</sup>. It is typically formed via energy transfer from other molecules, including photosensitisers. Although benzophenone is not particularly efficient for the purpose, singlet oxygen can be produced through energy transfer from triplet benzophenone<sup>22</sup>. Due to their electrophilic nature, singlet oxygen reacts with electron-rich groups, including the aromatic structures in lignin<sup>23</sup>.  $\text{H}_2\text{O}_2$  participates in many types of thermal and photochemical reactions, and is often applied in wastewater treatment for oxidation of organic compounds, including lignin<sup>24-27</sup>. Reactive oxygen species can differ in their oxidation potentials, electronic states, and electrophilic/nucleophilic character. Products formed from the oxidation of organic compounds can differ depending on the concentration of ROS<sup>4</sup>.

Neumann et al. performed a series of experiments using flash photolysis and continuous illumination techniques with addition of quenchers, filters, and quinones to understand lignin photooxidation<sup>28,29</sup>. Neumann makes note of the quinoid structures which have been observed in lignin photooxidation studies and cites phenoxy radicals forming from hydrogen abstraction of phenols by molecular oxygen as their postulated origin. This was cited as the “main initial step” in the photodegradation of lignin. In the case of reactions with benzophenone, the excited triplet benzophenone could take the role of abstracting phenolic hydrogen. Neumann et al. found that although singlet oxygen does not participate in the initiation of degradation, it does participate in the formation of final products.

A photosensitiser approach which relies on a generation of many triplet states could face difficulties due to triplet-triplet annihilation<sup>9</sup>. Introducing carbocation radicals on lignin could lead to the problem of repolymerisation of lignin radical intermediates<sup>30</sup>.

### 1.11. Building of a 3D Printed Photoreactor with UV-LEDs

The photoreaction experiments we want to perform have a large set of requirements. We need to be able to adjust the geometry of the reactor for different situations including the use of an in-situ Fourier transform infrared (FTIR) probe, add air and nitrogen gas, and test for the effects of different reaction volume geometries. To achieve this, we designed a 3D printed set of rails and light modules which can be moved backward and forward, as shown in figure 2. This new photoreactor also works to ensure consistency in experiments. While performing photoreactions with a quartz beaker and a set of LEDs shining from one direction during the experiments for Paper I, we wondered if small fluctuations in the distance between the beaker and the light source would cause error in the results. The ability to use the rail system to fix the light sources and reactant container in place eliminated this concern.

Each of the LED “light modules” contains fans, which are required due to the heat dissipation of the high-power UV LEDs. The fans are attached to the light sources so that the position of the LEDs does not affect their ability to be cooled. These light modules can be modified and replaced relatively easy with LEDs of different wavelength. An example of one of these light modules is shown in figure 3. The use of LEDs is beneficial due to their narrow emission spectra, allowing for well-controlled wavelength-dependence reactions, or reactions using a combination of different wavelengths. The “batch” setup uses a quartz beaker and magnetic stirrer, while the “flow” setup uses a coil of UV-transparent fluoropolymer tubing and pump system (figure 2). Each time a modification to the reaction setup is made, ferrioxalate actinometry can be performed to estimate the incident light intensity specific to the experimental conditions. More detailed description of the reactor is given in Paper II.

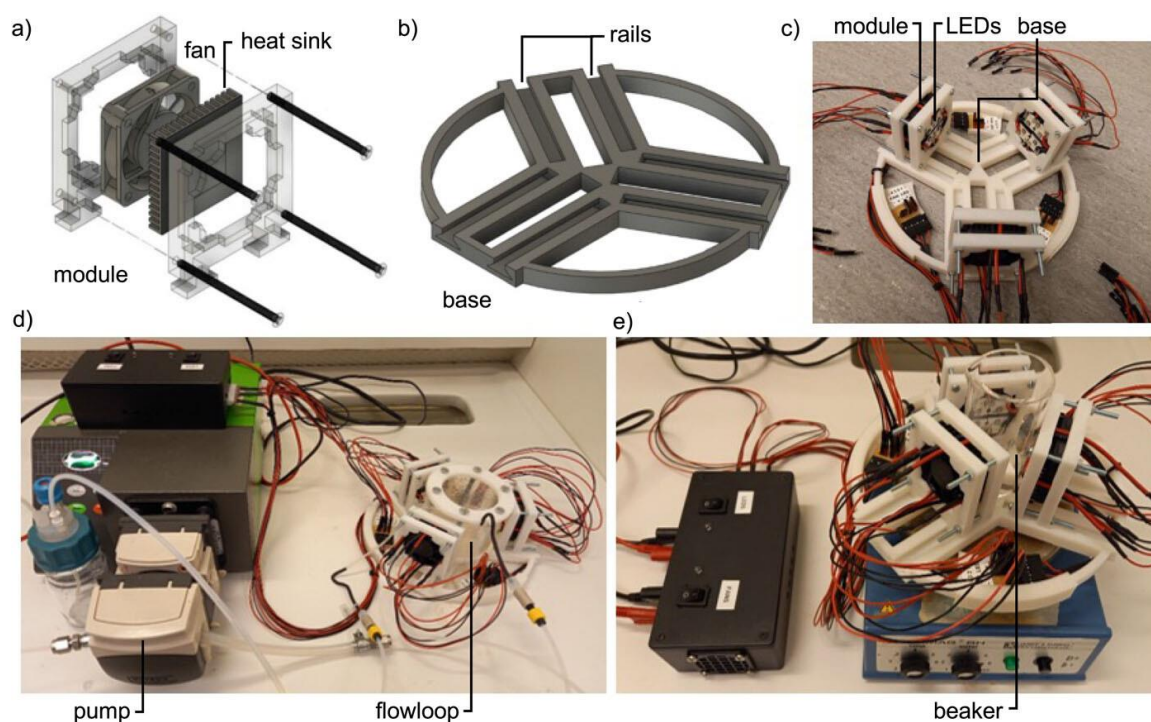


Figure 2. Images (a) of an LED module, (b) the reactor base with 3D printed rails, (c) LED modules positioned in the adjustable base, (d) and (e) the reactor setup in “flow” and “batch” setups respectively.

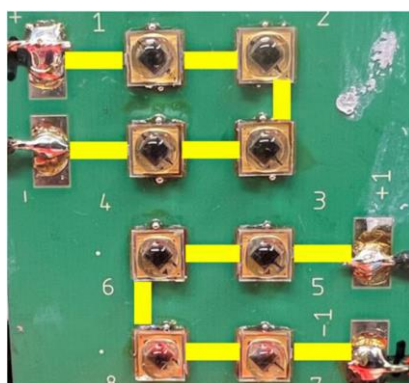


Figure 3. Image of a customised circuit board with eight LEDs mounted with heat-conducting paste. The yellow highlighted portions show the shape of the circuits.

### 1.12. Outlines and Objectives

To determine which transformations of lignin are desirable and quantify them, we need to define the information being evaluated. The information we focus on in this thesis are functional group densities and formation of small molecule products. In the future, we will include more information about molecular weight distribution. Although the most useful result of this work would be the production of valuable, small molecules from lignin, it could also be valuable to understand how the molecular weight and functionalisation of lignin can be altered through photolysis since this modified lignin could be further processed with other methods. It is also important to understand how, and how efficiently, photons are being “used” in the system. For example, does bond cleavage occur in areas at the ends of the lignin structure, resulting in small molecules products, or is cleavage occurring deeper into the structure, resulting in a lowering of the molecular weight. It may also be the case that radial-radical recombination occurs between lignin molecules, resulting in new carbon-carbon bonds creating larger lignin molecules<sup>30</sup>. Tracking changes in functional groups is important

because it gives clues about what reactions are happening. The analytical methods used to track these three categories of changes are described in the experimental section.



## 2. Experimental

### 2.1. Reactor Apparatus

The reactor used in this project was made within our group. LEDs are preferred as a light source due to their narrow emission bands. So far, we have used 265 nm and 280 nm light. The reactor can operate in a “flow reactor” mode in which the solvent is pumped through a spiral of UV-transparent fluoropolymer tubing. Continuous flow reactors have become a major interest in photochemical synthesis research, since they address several issues including light attenuation, mass transport, and temperature gradients<sup>7</sup>. We can also operate the reactor in a “batch” mode where reactions are performed in a beaker. The reactor can accommodate many different arrangements due to the adjustability of the LEDs. In the future, we will attempt to monitor photoreactions in-situ with Fourier transform infrared spectroscopy (FTIR).

### 2.2. Ferrioxalate Actinometry

Chemical actinometry is the practice of measuring changes of a well-defined photochemical system (the actinometer) to measure the radiant flux of a light source. Estimating incident flux from the power of a light source can be highly inaccurate because it neglects photons which are lost due to reflections, absorption by the reactor vessel, etc. This project has used ferrioxalate actinometry because it is one of the easiest and most common forms of actinometry. First the actinometer solution is prepared using the procedure from Murov<sup>31</sup>. This actinometer solution is prepared under red light to prevent the reaction from occurring prematurely. The actinometer solution is irradiated from 10-60 seconds in the reactor the same way as the reaction being studied, with the same volume, same reactor setup, and the same light intensity. The absorbance of the actinometer solution at 510 nm is measured with UV-vis and compared between the non-irradiated and irradiated samples. Using tabulated quantum yield values from Murov<sup>31</sup>, the reactor light intensity can be calculated. Although still better than using flux from the light source, we suspect that our actinometry measurements still have error of roughly 30% based on our own repeated measurements.

### 2.3. Quantum Yield and Quantum Efficiency

Quantum yield and quantum efficiency are important measures which are both frequently used in applications where photons cause a change in something. Quantum yield is defined as the number of events which occur per photon absorbed.

$$\Phi(\lambda) = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

We have so far not used quantum yield because due to the complex mixture in our reactions, we do not know how many photons are absorbed by each species. Quantum efficiency, the number of events per incident photon, is used in our work because the number of incident photons is measurable through actinometry.

$$\text{QE}(\lambda) = \frac{\text{number of events}}{\text{number of incident photons}}$$

### 2.4. Analysis of Reaction

When working with lignin, there are several variations in procedure that have been made with the intention of obtaining the most consistent results possible. First, lignin is taken in powder form and dissolved into the solvent of choice. It is important that adequate time is given for the mixture to reach equilibrium, because different parts of the lignin sample can solubilise at different rates. The solutions are then centrifuged to remove most of the large, solid particles from the mixture. Samples are withdrawn from the reactor throughout the duration of the reaction.

## 2.5. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is often used for measuring functional group concentrations, and sometimes molecular weights. Three types of NMR have mainly been used thus far in our analysis;  $^1\text{H}$  NMR, 2D NMR, and diffusion NMR.  $^1\text{H}$  NMR is used most often and is used to identify and quantify hydrogen containing functional groups in dissolved molecules. The major peaks for lignin dissolved in acetonitrile can be seen in figure 4.

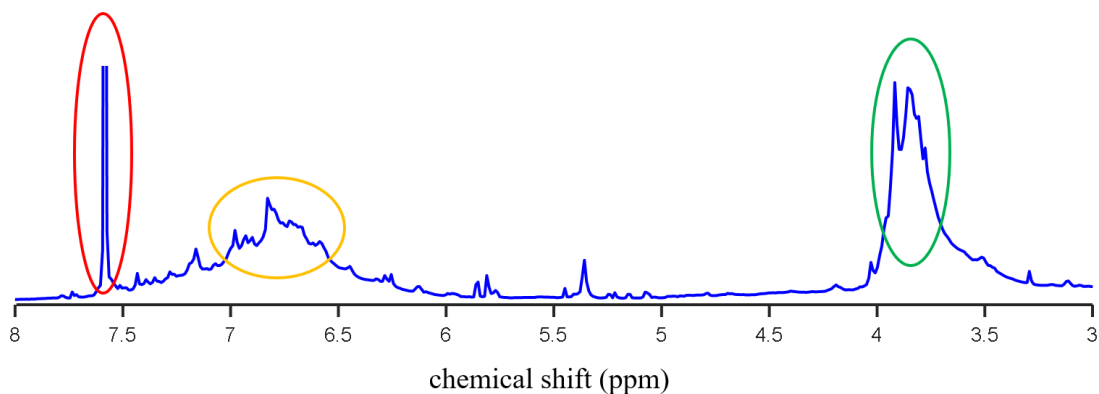


Figure 4. A typical  $^1\text{H}$  NMR spectrum for lignin dissolved in acetonitrile. The functional groups are circled as follows; (red) deuterated chloroform (used for NMR measurement), (orange) aromatic region, and (green) aromatic methoxy region.

Heteronuclear 2D NMR uses two axes with chemical shifts for two NMR active nuclei, often  $^1\text{H}$  and  $^{13}\text{C}$ . Use of two dimensions allows for better separation of peaks and functional groups to be differentiated in cases where the chemical shifts on one spectrum are overlapping. Heteronuclear single quantum coherence spectroscopy (HSQC) is one of these techniques, which we have used to confirm functional group identification.

Diffusion NMR is used to obtain an estimate of the molecular weight distribution of molecules in solution by estimating the diffusion coefficient for protons (possible across a range of chemical shift values). Diffusion NMR operates on the principle that nuclei which diffuse faster will cause a faster decline of signal. First, the magnetization is excited with a radio pulse at  $90^\circ$ . Then the magnetization is dispersed with a magnetic field gradient pulse of variable strength. Then a radiofrequency pulse inverts the magnetization so that it has a value negative to that following the dispersion. Finally, a second gradient pulse is used to refocus the signal. This results in the protons having varying signal intensities during the refocusing pulse. The relationship between these intensities and the strength of the magnetic field gradient can be used to obtain signal decays, which are then converted to diffusion coefficients<sup>32</sup>.

## 2.6. Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS is used in this project for the identification of molecular products following the reaction. Centrifuge filters are used to remove molecules with a molecular weight above 3 kDa. The samples injected are either kept in acetonitrile, or derivatized following the procedure of Allegretti et al<sup>33</sup>. From the retention time of the peaks and the mass spectrum of each peak (including the molecular ion), some suggestions can be made about the contents of the sample. However, matching mass spectra with examples from the MS libraries has proven difficult, leading to generalizations rather than definitive identifications of molecules.

## 2.7. UV-Vis Spectroscopy (UV-Vis)

UV-Vis is of basic importance to the project since the absorption spectra of lignin is important to understand possible relationships between wavelength and reaction rate. UV-Vis is also used for

quantification of incident light flux with Ferrioxalate actinometry. The UV-vis device is Lamda 365 from Perkin Elmer.

### **2.8. Lignin Fractionation**

Since samples of lignin are very heterogeneous both in terms of functional groups and molecular weight, it can be difficult to understand how different components of the lignin will be affected differently in a reaction. Therefore, many methods exist to separate a sample of lignin into different “fractions” by separating lignin molecules according to their solubility in various solvents. Analysing the properties of the different fractions of lignin, then observing the reactivity differences between the fractions can give clues about how lignin properties relate to its reaction behaviour. In this work, a fractionation method similar approach to the one described by Cui et al. was used<sup>34</sup>. Several other lignin fractionation methods are available<sup>35,36</sup>.

### **2.9. Lignin Model Substances**

Model substances are another tool which can be used to deal with the heterogeneity of lignin. Lignin model substances allow for specific linkages and functional groups to be studied in isolation. Examples of model substances could be 2-benzyloxyphenol (2BP) and 4-benzyloxyphenol (4BP). These were chosen due to them having ether bonds connecting two phenolic rings. The model substances are useful for beginning a reaction with simplified reactants, so it is easier to determine where new products are coming from.



### 3. Results and Discussion

#### 3.1. Beginning Work

The results in Paper I confirmed that irradiation of lignin and model compounds 2-benzyloxyphenol (2BP) and 4-benzyloxyphenol (4BP) with 265 nm and 280 nm light led to chemical changes. For example, a time series of a UV-vis spectrum for lignin showed that absorbance peaks were decaying over a 72 h reaction time, proving that chromophores in the lignin structure were being degraded. Additionally, both  $^1\text{H}$  NMR and 2D NMR spectra showed the appearance of new peaks, which demonstrated that new products form from the photoreaction. The question of whether lignin photoreactions are wavelength dependent was introduced in Paper I, with inconclusive results. This question can be revisited again in the future after we obtain more information about the photophysical properties of lignin, which will govern whether or not its photoreactions can be wavelength dependent<sup>9</sup>. Another part of this paper which has been left aside for now is the potential for UV light to aid in the process of lignin extraction from biomass. Paper I concluded that a “lignin and extractives first” approach, in which lignin is considered as an important component of biomass and valorised from the beginning of the biomass extraction process, could be compatible with the use of photochemical methods. The methodology developed for analysing lignin in Paper I has been carried over to our current investigation including an optimized photoreactor (see section 3.2).

To understand lignin photolysis, we have focused on measuring functional groups and appearance of small molecule products. Changes in these categories can be measured relative to total incident light to have a rough understanding of quantum efficiency of each change. Additionally, there are several factors which could affect the reaction including incident light wavelength, incident light intensity, species concentration, lignin fraction, choice of solvent, and presence of photosensitiser.

Several categories of experiments have been performed for different purposes, which can be combined in this section to obtain a broader picture. Reactions of Kraft lignin in acetonitrile were run to compare the products and reaction rates between benzophenone-sensitised and non-sensitised solutions. Reactions of lignin model compound 2-benzyloxyphenol (2BP) were performed with and without benzophenone photosensitiser to understand the effects of hydrogen abstraction. The 2BP experiments also serve the purpose of observing the cleavage of an important ether bond linking the two aromatic monomers as demonstrated in Paper I. Reactions of Kraft lignin were run in aqueous solutions of NaOH to determine the influence of lignin concentration and incident light intensity of the rate of formation of various molecules and functional groups.

#### 3.2. Testing of 3D printed Photoreactor

After building our new photoreactor, it was necessary to perform test reactions to check for the expected behaviour and ensure that future experimental results could be trusted. We performed ferrioxalate actinometry and sets of reactions of 2BP in acetonitrile.

Table 1. Ferrioxalate actinometry results for various photoreactor setups

Reactor	Setup	Wavelength (nm)	Total current (A)	Intensity ( $\times 10^{-5}$ mol photons $\text{l}^{-1} \text{s}^{-1}$ )
12 LEDs	Flow	280	5	3.1
12 LEDs	Batch	265	5	2
12 LEDs	Batch	280	5	2.1
24 LEDs	Flow	280	3	9.5
24 LEDs	Batch	280	3	8.3

The intensity values shown in table 1 can be used to calculate quantum efficiencies of photochemical processes. An updated photoreactor which uses 24 LEDs can reach intensities over three times higher than our original reactor design. Figure 5 shows the results of our experiments used to compare the “batch” and “flow” reactor setups.

The results in figure 5 indicate that the three reactor setups led to roughly equivalent reaction results. The question of whether this would occur for other systems is highly complex and outside the scope of this section. These results gave us some assurance that we can replicate and monitor reactions in several different setups.

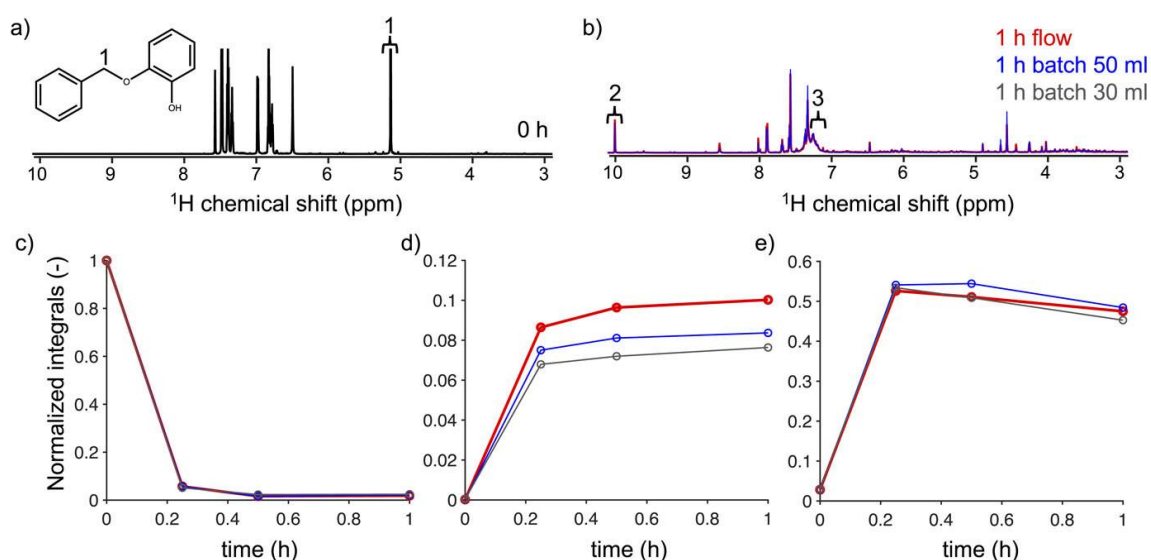


Figure 5. Photochemical reactions of 1 g/L 2BP using the 24 LED batch and flow setups. <sup>1</sup>H NMR spectra at (a) 0 h and (b) 1 h are shown, along with labelled peaks for (1) ether, (2) aldehyde, and (3) a selected aromatic peak. (c), (d), and (e) show the normalised integrals over time for peaks 1, 2, and 3 respectively.

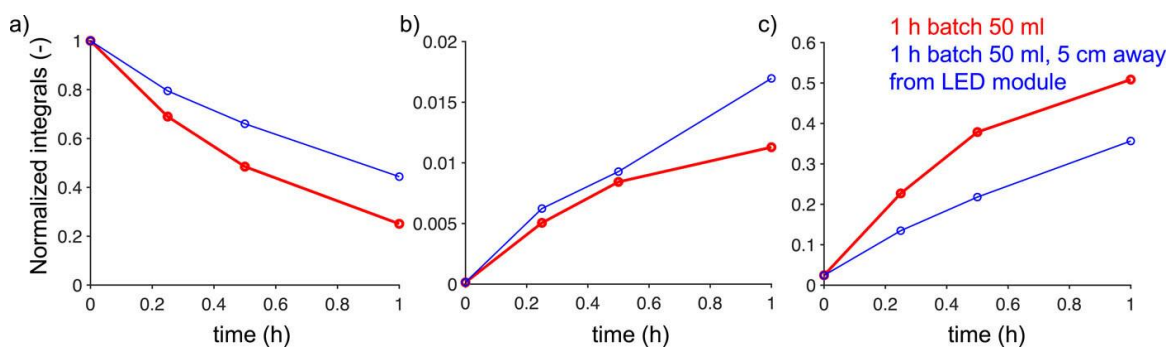


Figure 6. Photochemical reactions of 10 g/L 2BP in acetonitrile using the 24 LED photoreactor. The normalised integrals shown correspond to the (a) ether, (b) aldehyde, and (c) aromatic groups labelled in Figure 5.

The results of figure 6 were completely expected since moving the light modules further away significantly reduced the incident light intensity in the reaction volume, which reduced the reaction rate. The results were used in Paper II as a proof of concept that our methods of monitoring the photoreactions gave us results which are consistent with basic photochemistry concepts. With the experiments performed in this section, we gained assurance that our new reactor design, which is useful for many experimental scenarios, is also reliable enough to use.

### 3.3. Influence of Benzophenone: Sensitised and Non-sensitised Reactions in Acetonitrile

The impact of benzophenone on photochemical reactions on 2-(benzyloxy)phenol (2BP) and Kraft lignin was evaluated by comparing reactions with and without photosensitiser. 2BP is useful because it allows us to evaluate an “ $\alpha$ -O-4” (aryl-ether) bond between two aromatic rings with a single species, making it easier to track conversion and the formation of products. Softwood lignin was chosen because of its importance in Swedish pulp and paper manufacturing<sup>2</sup>. Differences between benzophenone-sensitised and non-photosensitised photoreactions could lead to a better understanding of the mechanisms which are important to lignin depolymerisation.

### 3.4. Lignin Reactions in Acetonitrile, with and without benzophenone

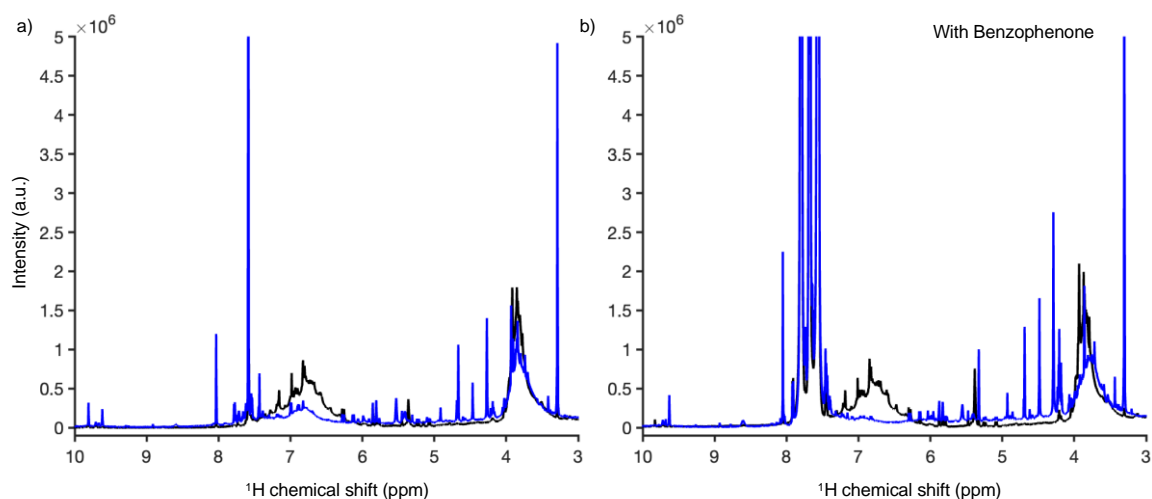


Figure 7. Comparison of lignin reactions in acetonitrile (left) without and (right) with benzophenone.

Figure 7 shows the <sup>1</sup>H NMR spectra of photoreactions with and without benzophenone. The benzophenone peaks appear on the right plot as the high intensity clusters between 7.4 and 8 ppm. Unfortunately, these peaks cover all other peaks in this region, which excludes them from the analysis. The broad peaks for aromatic compounds between 6 and 7.5 ppm decrease quicker in the reaction containing benzophenone. Although not yet confirmed, increase in reaction rate may have been caused by electrophilic attacks from singlet oxygen, or another reactive oxygen species. Photosensitisers have been observed in other cases to increase the concentration of singlet oxygen through energy transfer<sup>22,26,37,38</sup>. The formic acid peak is found slightly to the left of 8 ppm. Formic acid may react with lignin, considering that depolymerization, delignification, and hydrodeoxygenation, reactions of lignin and formic acid have been reported<sup>39-41</sup>, the results in table 6 for alkaline solutions, where the ratio of formic acid to methanol rate decreases over time may suggest that formic acid is reacting, but this is not proof. A peak for aldehyde can be seen in both plots around a chemical shift of 9.6<sup>24,42</sup>. Aldehyde and aromatic acid production could be affected by H<sub>2</sub>O<sub>2</sub>, which can react with these compounds<sup>24</sup>.

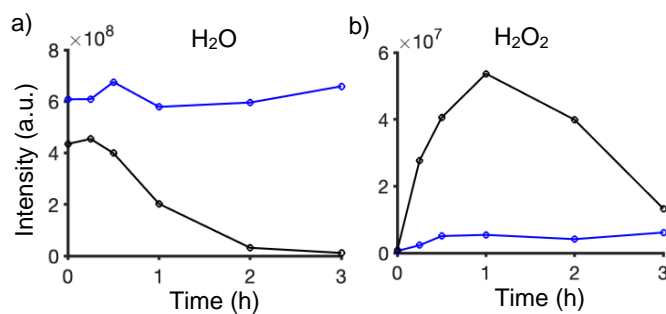


Figure 8.  $^1\text{H}$  NMR intensity vs time plots for (left) water and (right)  $\text{H}_2\text{O}_2$ , for the reactions (black) with benzophenone and (blue) without benzophenone.

It is possible that the increased conversion of  $\text{H}_2\text{O}$  to  $\text{H}_2\text{O}_2$  shown in figure 8 was caused by benzophenone because triplet photosensitisers like benzophenone have been observed to sensitise singlet oxygen formation<sup>43</sup>, which could react with  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{O}_2$ . UV light splits  $\text{H}_2\text{O}_2$  into two hydroxyl radicals, explaining why the concentration of  $\text{H}_2\text{O}_2$  decreases again after increasing to its maximum. The hydroxyl radicals have been reported in the research of advanced oxidation processes (AOPs) to oxidise lignin's aromatic structures into carboxylic acids<sup>27,44</sup>. The decrease of the methoxy peak in proportion to its own concentration is in agreement with the suggestion by Yao et al., suggesting that the decrease in methoxy groups is the result of direct UV photodegradation, and not reactions with reactive oxygen species<sup>45</sup>.

### 3.5. Reactions of 2BP in acetonitrile, with and without benzophenone

2BP solutions were prepared by mixing 30 mg of 2BP into 30 mL acetonitrile. For the photosensitised samples, 30 mg of benzophenone was also added. The reactions were performed in the “flow” reactor described in Riddell et al.<sup>46</sup> at an incident light intensity of  $3 \times 10^{-5}$  mol photons/(L\*s) of 280 nm photons for a period of 3 h. Figure 9 is a visualisation of how concentrations of compounds were monitored over the course of the reaction. Aliquots of approximately 1 mL were removed from the solution at reaction times of 0, 15 min, 30 min, 1 h, 2 h, and 3 h.

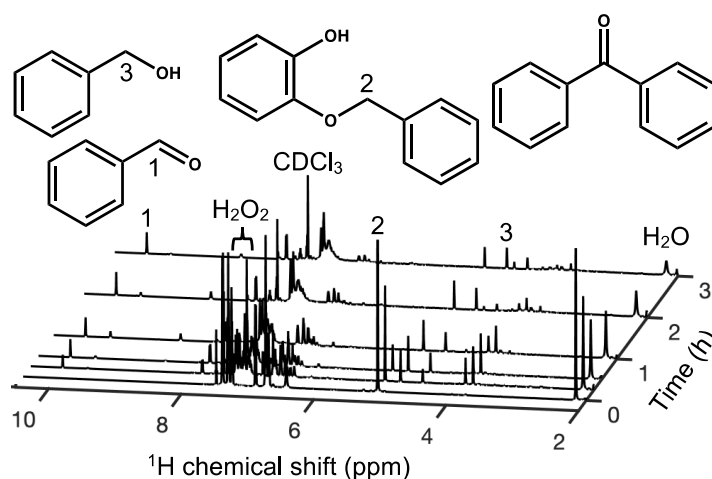


Figure 9. Molecular structures of important molecules (top left) benzyl alcohol, (bottom left) benzaldehyde, (middle) 2BP, (right) benzophenone. Example of  $^1\text{H}$  NMR time series is shown featuring (1) aldehyde, (2) ether, and (3) alcohol peaks.

In figure 9, one can see that the concentration of 2BP is decreasing, based on the peak for the ether bond, while the benzyl alcohol and aldehyde peaks are increasing, indicating the formation of



benzyl alcohol and benzaldehyde. Concentration profiles of 2BP and benzaldehyde are displayed in figure 10.

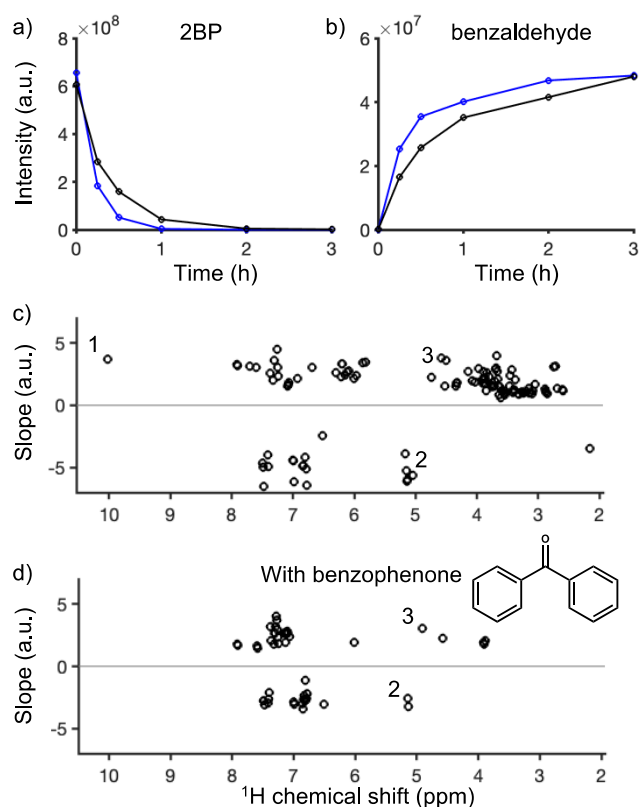


Figure 10.  $^1\text{H}$  NMR integrals of peaks highlighted in figure 9 corresponding to 2BP (a) and benzaldehyde (b) with irradiation time for reactions with the addition of benzophenone (black) and without (blue). The slope (open circles) of a linear fit of the change in intensities of a bin (width 0.01 ppm) divided by the change in time versus the average intensity as a function of  $^1\text{H}$  chemical shift without the addition of benzophenone (c) and with (d). The molecular structure of benzophenone is shown in (d).

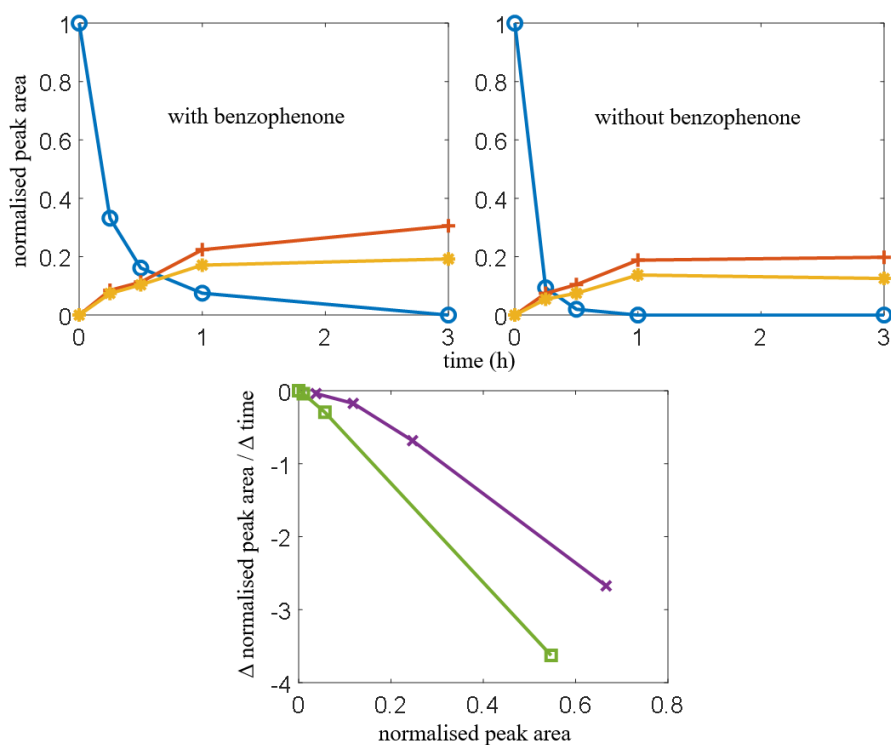


Figure 11. Top: Comparison of concentration over time for (blue) 2BP, (orange) benzaldehyde, and (yellow) benzyl alcohol. Each GC peak area is normalised by dividing by the peak of 2BP at 0 h. Bottom: rate of change versus concentration for reactions (purple) with benzophenone and (green) without benzophenone.

### 3.6. Acetonitrile and NaOH reactions comparison

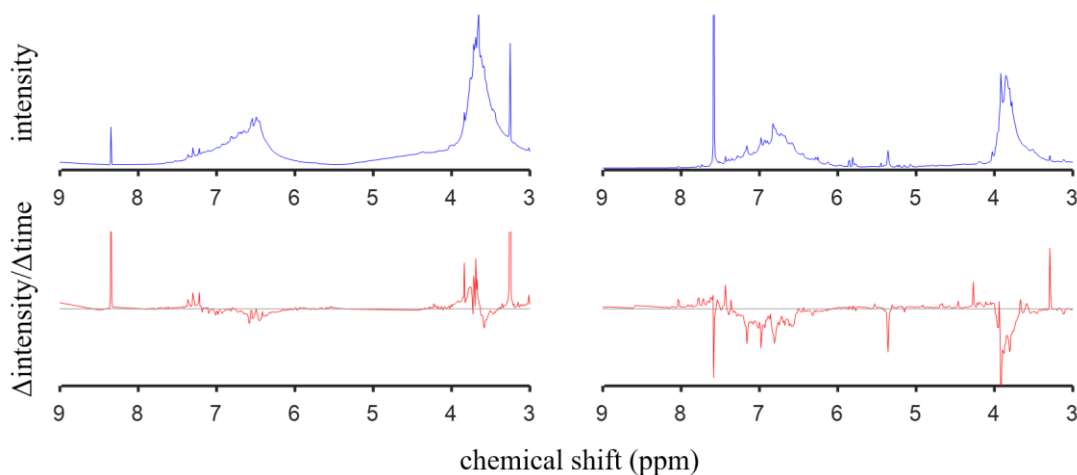


Figure 12. Comparison of lignin reaction in (left) aqueous NaOH and (right) acetonitrile. Vertical axes are not to scale. Water peak (usually between about 4.5 and 5.5) has been removed from the left plots for ease of reading. The (top) plots show the initial <sup>1</sup>H NMR spectra at 0 h. The (bottom) plots show the change in intensity between 0 h and 1 h with a grey line positioned at zero (no change).

From figure 12, one can see that more peaks are visible in the aromatic region before 6 and 8 ppm and between 5 and 6 ppm for lignin in acetonitrile (right). This is most likely related to the phenolic hydroxyl groups of lignin being visible in acetonitrile and having a chemical shift in this region. These reactions in these two solvents were performed with different light intensities (different sets

of experiments), so the rates cannot be quantitatively compared. The plots in red, which display changes in signal between 0 h and 1 h (not to scale) show different peaks growing and shrinking in both solvents. However, it is clear that the reactions in aqueous NaOH solutions have a lower quantum yield, since the reactions in NaOH are slower than in acetonitrile under higher light intensity. The reason for this is not yet known, but it will be important in the future.

### 3.7. NaOH Reactions: Evaluation of Concentration and Light Intensity Effects

Much of the analysis of lignin reactions depends on measuring changes in functional groups concentrations monitored by  $^1\text{H}$  NMR. Understanding relationships between lignin functional groups could be important in understanding the photochemistry of lignin. However, complications are introduced if one considers the range of experimental conditions which are not directly related to lignin properties but may nonetheless influence experimental results (ex. concentration of lignin, incident light intensity, distribution of light intensity, and heat/mass transfer). This is problematic because if reaction conditions are not varied, it becomes difficult to determine which conclusions have broad applicability. However, it is not practically possible to perform every series of experiments under multiple sets of reaction conditions. In situations like this, it can be practical to perform sets of experiments to identify the parameters which require the most focus<sup>47</sup>, thereby reducing complexity for experiments in the long term. Light intensity distribution and heat/mass transfer have been partly addressed through the use of a flow photoreactor with thin channels<sup>16</sup>. Initial lignin concentration and incident light intensity were two extrinsic variables which needed to be evaluated through experimentation.

Table 2. list of experiments analysed in this section

Reaction symbol in plots	Lignin mixture concentration g/L	Incident light intensity Mol photons/(L*s)	Current (A)
blue circle	1	$2.5 \times 10^{-5}$	4
orange cross	1	$3.7 \times 10^{-5}$	6
yellow asterisk	5	$2.5 \times 10^{-5}$	4
purple "x"	3	$3.1 \times 10^{-5}$	5
green square	3	$3.1 \times 10^{-5}$	5
cyan diamond	7.5	$6.2 \times 10^{-5}$	10
red triangle	10	$7.5 \times 10^{-5}$	12

Aqueous NaOH solutions were chosen as solvent for three reasons. The first was that the high solubility of lignin in basic solutions allowed a broader range of lignin concentrations to be tested with confidence that most of the lignin in solution was dissolved. The second reason was to enable comparisons between reactions in aqueous NaOH and in acetonitrile. The third reason is that black liquor is mainly a mixture of dissolved lignin in aqueous, alkaline solution, so the pulp and paper industry is interested in uses of lignin in this form. High pH has the effect of ionising phenol groups, which has been reported to increase the rate of degradation of lignin model compounds via singlet oxygen<sup>38</sup>.

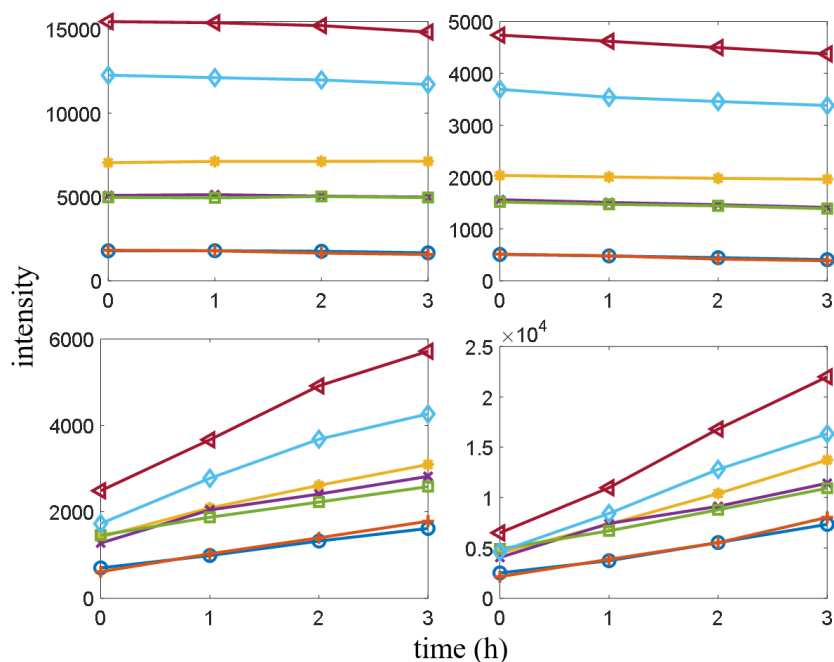


Figure 13. Plots of NMR intensity vs time for four key peaks; (top left) aromatic methoxy, (top right) aromatic, (bottom left) formic acid, and (bottom right) methanol. Refer to table 2 for symbols.

Table 2 uses the phrase “lignin mixture concentration” to mean the concentration of lignin powder added to the solvent. “The incident light intensity” measurements are estimates based on ferrioxalate actinometry. “current” refers to the electrical current of the photoreactor, which is proportional to the light intensity. “current” is used later in this section as a shorthand way of referring to the reactions. Figure 13 shows the intensities of 4 important  $^1\text{H}$  NMR peaks over the 3 h reaction time.

Table 3. Solution behaviour

Lignin powder added (g)	Aromatic methoxy ratio	Aromatics ratio	Formic acid ratio	Methanol ratio
1.0	1.00	1.00	1.00	1.00
1.0	1.02	1.01	0.87	0.86
5.0	3.93	3.99	2.02	1.78
3.0	2.84	3.07	1.82	1.61
3.0	2.78	2.99	2.08	1.95
7.5	6.84	7.25	2.46	1.85
10	8.63	9.31	3.54	2.58

One important detail in these results is that if one takes the ratio of initial intensities of any of these peaks, this is quite far from the ratios of lignin powder dissolved for the reaction, meaning the lignin in the mixtures used in the reactions was not completely dissolved. The solubility of lignin in alkaline solutions is of course a complex question that depends, among other things, on the molecular weight distribution and the density of phenolics in the macromolecule<sup>11</sup>. The ratios of peak intensities are shown in table 3.

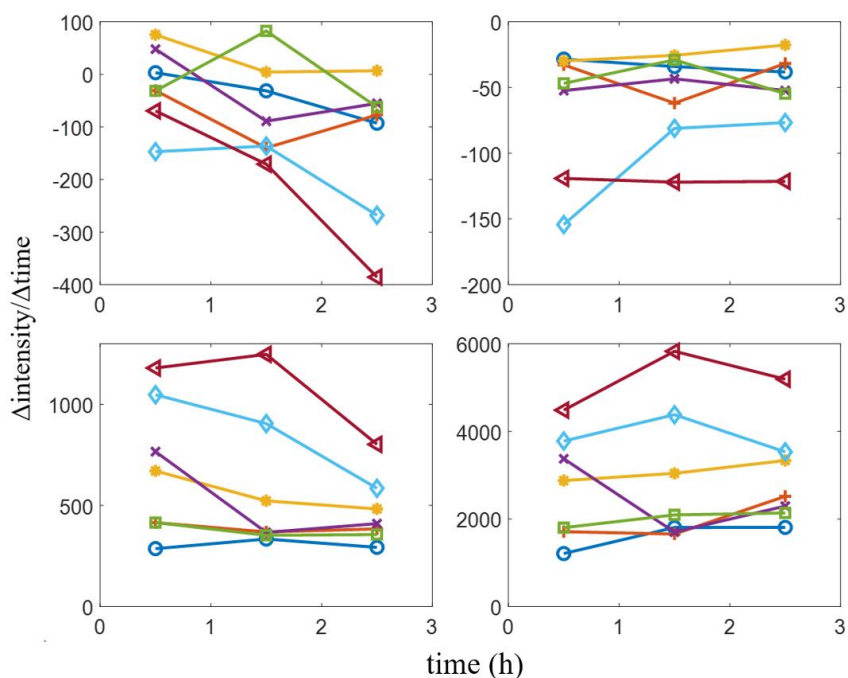


Figure 14. Estimated rates of change of (top left) aromatic methoxy, (top right) aromatics, (bottom left) formic acid, and (bottom right) methanol peaks. Three time points are plotted for the average change in peak intensity between the four times measured with  $^1\text{H}$  NMR. Refer to table 2 for symbols.

In our analysis, we assume that a peak intensity in  $^1\text{H}$  NMR is roughly proportional to the amount of a functional group which is dissolved in the solution. Table 3 demonstrates the difficulty which comes from the fact that functional groups appear in solution in different ratios from the amount of lignin added to the mixture. For example, if a lignin sample were to be 100% dissolved, one would expect all peak intensities for a 10g/L sample to be in a 10:1 ratio with a 1g/L sample. However, the aromatic groups are in a 9.31:1 ratio, and the formic acid is in a 3.54:1 ratio. The complexity of relationships between lignin solubility and reaction behaviour is an ongoing topic in lignin research<sup>48</sup>. When estimating reaction rates with  $^1\text{H}$  NMR, consideration should be given to this in cases where molecules could be dissolving or precipitating over the course of the reaction, and thus, be excluded from the analysis. Figure 14 shows the rates of change of the intensities of the same peaks over time. This is done to evaluate the effect of light intensity on reaction rates.

Additional information which can be taken from the plots in Figure 14 is the very small changes in the aromatic methoxy and aromatic groups compared with the increase in formic acid and methanol. This will later be compared with the acetonitrile reactions. It is also clear that there is some relationship between light intensity and reaction rate, since the reactions with the highest two light intensities are consistently at the top or bottom of each plot. However, this relationship is not as clear as expected.

Tables 4 and 5 show the “quantum efficiencies” of the increase of formic acid and methanol peak intensities. Each entry in the table is a change in peak intensity between two points in time divided by the light intensity for the experiment (estimated with ferrioxalate actinometry). These tables were used as an attempt to discern a relationship between light intensity, lignin concentration, and “quantum efficiency” of the formations of the two major products. “g/L” and “Amperes” are used in the tables as shorthand to denote the experiments, but the units used the analysis are units of  $^1\text{H}$  NMR peak intensity for concentration and moles of photons/(L\*s) for light intensity.

Table 4:  $\Delta$ formic acid / intensity ( $\times 10^7$ )

	1g/L, 4A	1g/L, 6A	5g/L, 4A	3g/L, 5A	3g/L, 5A	7.5g/L, 10A	10g/L, 12A
0-1 h	1.15	1.12	2.68	2.47	1.34	1.69	1.57
1-2 h	1.34	1.00	2.09	1.18	1.14	1.46	1.66
2-3 h	1.17	1.04	1.93	1.32	1.15	0.94	1.07

Table 5:  $\Delta$ methanol / intensity ( $\times 10^8$ )

	1g/L, 4A	1g/L, 6A	5g/L, 4A	3g/L, 5A	3g/L, 5A	7.5g/L, 10A	10g/L, 12A
0-1 h	0.48	0.46	1.15	1.09	0.58	0.61	0.60
1-2 h	0.72	0.45	1.22	0.55	0.68	0.71	0.78
2-3 h	0.72	0.68	1.33	0.74	0.69	0.57	0.69

There appears to be no strong relationship between lignin concentration and quantum efficiency or light intensity and quantum efficiency for either formic acid or methanol. As of now, no statement can be made explaining this. However, the determination of quantum efficiency for desired reactions is of great importance for the energy efficiency of a photochemical process, and will therefore continue to be a topic of interest. Table 6 shows ratios of rates of change of formic acid and methanol measured by  $^1\text{H}$  NMR.

Unlike with the quantum efficiency tables, there is some consistency of the  $\Delta$ formic acid /  $\Delta$ methanol ratios across the seven reactions. This means that although it is still difficult to explain formation rates for these two peaks, the relative growth rate between these two peaks appears to be independent of both lignin concentration and light intensity at 280 nm. As the reaction proceeds, more methanol is being produced relative to formic acid. This may not be true for all circumstances, and the effects of reaction conditions on “selectivity” will continue to be monitored along with reaction rates and quantum efficiency.

Table 6:  $\Delta$ formic acid /  $\Delta$ methanol

	1g/L, 4A	1g/L, 6A	5g/L, 4A	3g/L, 5A	3g/L, 5A	7.5g/L, 10A	10g/L, 12A
0-1 h	0.24	0.24	0.23	0.23	0.23	0.28	0.26
1-2 h	0.19	0.22	0.17	0.22	0.17	0.21	0.21
2-3 h	0.16	0.15	0.14	0.18	0.17	0.17	0.15

### 3.8. $\text{H}_2\text{O}_2$ and Formate Production: Lignin as a Photocatalyst

As mentioned before, lignin has many chromophores that have excitation energies over a wide range of wavelengths, can participate in energy transfer within the molecule<sup>10</sup>, and can likely participate in energy transfer or electron transfer with other molecules. Lignin has been observed by Miglbauer et al. to be destructively photo oxidised to produce  $\text{H}_2\text{O}_2$ , and lignin can photochemically oxidise low-oxidation species<sup>49</sup>. Although we have carried out only a preliminary investigation, we were curious if lignin could be substituted for homogeneous photocatalysts in other systems, such as the photooxidation of methanol to formate. We attempted to use lignin to replicate results in which Wang et al. produced  $\text{H}_2\text{O}_2$  and formate from an alkaline mixture of KOH and methanol with a production rate of  $188 \text{ mmol h}^{-1} \text{ g}^{-1}$  via an electron transfer mechanism using organic polymer dots<sup>50</sup>. After confirming that lignin is responsible for methanol oxidation against

a control, we undertook an experimental design of nine 1 hr experiments, varying methanol concentration, lignin concentration, and NaOH concentration, to see how much formate could be produced. The results are summarised in table 7.

Table 7: Oxidation of methanol to formate

% vol MeOH	Lignin conc. (g/L)	NaOH conc. (g/L)	Formate production rate (mmol h <sup>-1</sup> g <sup>-1</sup> )
40	5	100	0.37
20	3	67	0.45
40	1	100	1.12
10	5	33	0.25
40	1	33	0.55
40	5	33	0.20
10	1	33	1.06
10	1	100	1.69
10	5	100	0.38

The clear trend from table 7 is that the most efficient formate production on a “per gram lignin” basis happened for the 4 samples which used the lowest amount of lignin. Although the production rates are far below the 188 mmol h<sup>-1</sup> g<sup>-1</sup> result recorded by Wang et al., it is clear that lignin does increase the rate of methanol oxidation. The reaction also proceeded under sunlight and enclosed in a glass vial, suggesting that excitations by wavelengths of 300 nm or higher (based on glass transmittance) can drive the reaction. Further experiments in this area could be attempted again after we gain a better understanding for the factors which govern lignin’s excited state lifetimes and electron transfer properties.

### 3.9. Diffusion NMR

Diffusion NMR will be a useful tool to monitor changes in the molecular weight distribution of lignin. An example (collected by our co-authors from unpublished paper II) in which extractions of lignin were performed with levulinic acid at three sets of conditions is shown in figure 15. The hydrodynamic radii distribution and molecular weight distribution were estimated from measurements of the diffusion coefficients obtained by diffusion NMR. These results agreed nicely with size exclusion measurements performed by our co-authors (data not shown).

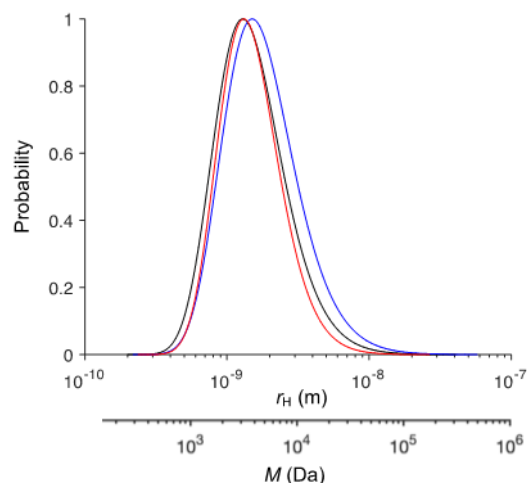


Figure 15. Hydrodynamic radii distribution ( $r_H$ ) for recovered lignin following levulinic acid extraction at (black) 200 °C for 6 h, (red) 140 °C for 2 h with 0.1 M HCl, and (blue) 160 °C for 2 h with 0.01 M H<sub>2</sub>SO<sub>4</sub> dissolved in DMF. The molecular weight scale has been established from a linear correlation of the data from Rönnöls et al.<sup>51</sup>

The distributions in figure 15 show that the molecular weight distribution for the blue curve is shifted towards higher molecular weights, and the red curve shows the narrowest distribution. Although diffusion NMR has not been used extensively so far, its ability to estimate molecular weight distributions will aid us in answering questions about how efficiently lignin is broken down by UV light. It could also lead to insights about how the molecular weight distribution of the initial lignin sample affects other results, such as the formation of small molecule products.



#### 4. Conclusions

Groundwork has been laid to investigate a problem which involves many variables related to both reaction conditions (ex. solvent, pH, reactor geometry, mixing, light intensity, presence of photosensitisers) and lignin properties (ex. molecular weight distribution and functional group density). A photoreactor has been built which satisfies current and future needs, including reactor size flexibility, the ability to change light sources, and the possibility of several reaction setups including stirring or flow. Test reactions on this reactor have demonstrated the expected behaviour with consistency, an important requirement for quantitative work. Reactions of 2BP in acetonitrile have shown that UV light at 265 nm and 280 nm can be used to cleave an ether bond between two aromatic rings, and that this process can be monitored with NMR techniques, UV-vis, and GC-MS. The comparison between non-sensitised reactions and reactions in the presence of benzophenone have so far not shown conclusive advantages for benzophenone sensitisation. However, this could be viewed as a “good” result, in the sense that use of additional reagents or chemicals which require recycling is something that we wish to avoid in a chemical process. Literature review into the area of photosensitisation has introduced us to the possibility that lignin itself may have photocatalytic properties, and we have seen this in oxidation of methanol to formate. Repeated reactions on Kraft lignin in aqueous alkaline solution have informed us about differences between lignin reactivity in acetonitrile and aqueous NaOH and have improved our understanding about which results seem to be relatively well controlled (selectivity), and which results are still difficult to understand (quantum efficiency). We have begun to investigate the relationship between water and atmospheric oxygen and reactive oxygen species like H<sub>2</sub>O<sub>2</sub>, hydroxy radicals, and singlet oxygen, and will continue to add to this data. Significant differences in photolysis behaviour between 2BP and Kraft lignin opens important questions about the mechanisms behind these differences. We have also gotten the impression that the wavelength difference between 265 nm and 280 nm does not cause dramatic differences in reaction behaviour, and we can apply this to future planning.



## 5. Future Work

In our system, we have several categories of photochemical events which can occur. One category is changes of lignin which result from the different electronic structure, molecular geometry, and activation energies which exist for organic molecules in an excited state (the domain of organic photochemistry). We need to understand more about what happens to an electron after it is excited. Photophysical properties of molecules like the likelihood of “losing” excited states through vibrational relaxation, the tendency to transfer energy within itself, the ability to exchange electrons with itself or other molecules, and the amount of time the molecule remains excited will govern the chemistry which follows. These photophysical properties can be measured with tools currently utilised in photochemistry research.

The fact that lignin is a heterogeneous mix of molecules will make it exceedingly difficult to understand its photophysical and photochemical properties in detail. These phenomena are already complex in molecules which are more easily defined. Although a mechanistic understanding of lignin photochemistry is probably out of reach with current technology, it may be possible to use multivariate analysis methods to find tendencies or relationships between a large set of input data (ex. NMR, FTIR, absorbance and fluorescence spectra, and reactor conditions) and specific results (ex. the rate of appearance of a desired molecule or functional group, or the avoidance of an undesired transformation measured by NMR). Methods for identifying significant variables out of a large set of input variables (ex. partial least squares regression and principal component analysis) are already used in chemistry (chemometrics), and are used in fields which have a large numbers of variables with highly complex interactions (quantitative finance, bioinformatics, signal processing, metabolomics, etc.). Like other fields with large numbers of variables and observations, dimensionality reduction becomes necessary. The work of finding appropriate techniques to process the lignin data will be continuously revisited as the data set grows.

In the meantime, there are several techniques which could be refined or introduced. Experiments on the amount of oxygen in the system could be an important factor, given the potential importance of reactive oxygen species. We will address this by introducing additional oxygen, or attempting to remove oxygen with flows of air or nitrogen gas into the reactor. The use of in-situ FTIR could be a useful tool for evaluating reaction kinetics, since we could obtain information about functional groups continuously throughout time. Both the gas flows, and the in-situ FTIR can be used at the same time due to the flexibility of the photoreactor apparatus. Data processing will also increase in importance given the high volume of FTIR data. Another area which needs improvement is the identification of small molecule products with GC-MS. Lignin fractionation will be used to create lignin samples with increased variability of functional group distribution and molecular weight distribution. Selecting for specific properties in “input” lignin will aid in testing hypotheses related to these properties. Finally, a better understanding about differences between solvents or pH in aqueous solutions would be helpful. This information could be obtained through literature review, since these topics have been addressed in other applications of photochemistry.



## 6. References

1. Tribot, A. *et al.* Wood-lignin: Supply, extraction processes and use as bio-based material. *Eur. Polym. J.* **112**, 228–240 (2019).
2. *Facts and Key Figures Swedish forest-based industry.* <https://www.forestindustries.se/news/publications-and-reports/> (2022).
3. Xiang, Z. *et al.* Photocatalytic Conversion of Lignin into Chemicals and Fuels. *ChemSusChem* **13**, 4199–4213 (2020).
4. Colmenares, J. C., Xu, Y.-J., Li, S.-H., Liu, S. & Carlos Colmenares, J. A sustainable approach for lignin valorization by heterogeneous photocatalysis. *Green Chem.* **18**, 594 (2016).
5. Chen, C., Volpe, R. & Jiang, X. A molecular investigation on lignin thermochemical conversion and carbonaceous organics deposition induced catalyst deactivation. *Appl. Energy* **302**, 117557 (2021).
6. Ksibi, M. *et al.* Photodegradation of lignin from black liquor using a UV/TiO<sub>2</sub> system. *J. Photochem. Photobiol. A Chem.* **154**, 211–218 (2003).
7. Cambié, D., Bottecchia, C., Straathof, N. J. W., Hessel, V. & Noël, T. Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment. *Chem. Rev.* **116**, 10276–10341 (2016).
8. Hynynen, J. *et al.* ‘Lignin and extractives first’ conversion of lignocellulosic residual streams using UV light from LEDs. *Green Chem.* **23**, 8251–8259 (2021).
9. Scaiano, J. *Photochemistry Essentials.* (American Chemical Society, 2022). doi:10.1021/acsinfocus.7e5031.
10. Albinsson, B., Li, S., Lundquist, K. & Stomberg, R. The origin of lignin fluorescence. *J. Mol. Struct.* **508**, 19–27 (1999).
11. Evstigneev, E. I. Factors affecting lignin solubility. *Russ. J. Appl. Chem.* **84**, 1040–1045 (2011).
12. Kärkäs, M. D., Bosque, I., Matsuura, B. S. & Stephenson, C. R. J. Photocatalytic Oxidation of Lignin Model Systems by Merging Visible-Light Photoredox and Palladium Catalysis. *Org. Lett.* **18**, 5166–5169 (2016).
13. Elliott, L. D., Kayal, S., George, M. W. & Booker-Milburn, K. Rational design of triplet sensitizers for the transfer of excited state photochemistry from UV to visible. *J. Am. Chem. Soc.* **142**, 14947–14956 (2020).
14. Wilkinson, F., Kelly, G. P., Ferreira, L. F. V., Freire, V. M. M. R. & Ferreira, M. I. Benzophenone sensitization of triplet oxazine and of delayed fluorescence by oxazine in acetonitrile solution. *J. Chem. Soc. Faraday Trans.* **87**, 547–552 (1991).
15. Naguib, Y. M. A., Steel, C., Cohen, S. G. & Young, M. A. Photoreduction of benzophenone by acetonitrile: Correlation of rates of hydrogen abstraction from RH with the ionization potentials of the radicals R•. *J. Phys. Chem.* **91**, 3033–3036 (1987).
16. Michelin, C. & Hoffmann, N. Photosensitization and Photocatalysis - Perspectives in Organic Synthesis. *ACS Catal.* **8**, 12046–12055 (2018).
17. Luo, N. *et al.* Visible-Light-Driven Self-Hydrogen Transfer Hydrogenolysis of Lignin Models and Extracts into Phenolic Products. *ACS Catal.* **7**, 4571–4580 (2017).
18. Cao, Y., Wang, N., He, X., Li, H. R. & He, L. N. Photocatalytic Oxidation and Subsequent

- Hydrogenolysis of Lignin  $\beta$ -O-4 Models to Aromatics Promoted by in Situ Carbonic Acid. *ACS Sustain. Chem. Eng.* **6**, 15032–15039 (2018).
19. Zhang, C. & Wang, F. Catalytic Lignin Depolymerization to Aromatic Chemicals. *Acc. Chem. Res.* (2020) doi:10.1021/acs.accounts.9b00573.
  20. Taylor, L. J. & Tobias, J. W. Accelerated Photo-Oxidation of Polyethylene. I. Screening of Degradation-Sensitizing Additives. *J. Appl. Polym. Sci.* **21**, 1273–1281 (1977).
  21. Hosono, K., Kanazawa, A., Mori, H. & Endo, T. Photodegradation of cellulose acetate film in the presence of benzophenone as a photosensitizer. *J. Appl. Polym. Sci.* **105**, 3235–3239 (2007).
  22. Gorman, A. A., Hamblett, I. & Rodgers, M. A. J. Time-Resolved Luminescence Measurements of Triplet-Sensitized Singlet-Oxygen Production: Variation in Energy-Transfer Efficiencies. *J. Am. Chem. Soc.* **106**, 4679–4682 (1984).
  23. Kim, K. H. & Kim, C. S. Recent Efforts to Prevent Undesirable Reactions From Fractionation to Depolymerization of Lignin: Toward Maximizing the Value From Lignin. *Front. Energy Res.* **6**, 92 (2018).
  24. Xiang, Q. & Lee, Y. Y. Oxidative cracking of precipitated hardwood lignin by hydrogen peroxide. *Appl. Biochem. Biotechnol. - Part A Enzym. Eng. Biotechnol.* **84–86**, 153–162 (2000).
  25. He, W., Gao, W. & Fatehi, P. Oxidation of Kraft Lignin with Hydrogen Peroxide and its Application as a Dispersant for Kaolin Suspensions. *ACS Sustain. Chem. Eng.* **5**, 10597–10605 (2017).
  26. Forsskl, I. Aspects of photosensitized lignin oxygenation. *J. Photochem.* **25**, 197–209 (1984).
  27. Makhotkina, O. A., Preis, S. V. & Parkhomchuk, E. V. Water delignification by advanced oxidation processes: Homogeneous and heterogeneous Fenton and H<sub>2</sub>O<sub>2</sub> photo-assisted reactions. *Appl. Catal. B Environ.* **84**, 821–826 (2008).
  28. Neumann, M. G., De Groote, R. A. M. C. & Machado, A. E. H. Flash photolysis of lignin: Part I. Deaerated solutions of dioxane-lignin. *Polym. Photochem.* **7**, 401–407 (1986).
  29. Neumann, M. G., De Groote, R. A. M. C. & Machado, A. E. H. Flash photolysis of lignin: II-Oxidative photodegradation of dioxane-lignin. *Polym. Photochem.* **7**, 461–468 (1986).
  30. Prado, R., Erdocia, X. & Labidi, J. Effect of the photocatalytic activity of TiO<sub>2</sub> on lignin depolymerization. *Chemosphere* **91**, 1355–1361 (2013).
  31. Murov, S. L., Carmichael, I. & Hug, G. L. Chemical Actinometry. in *Handbook of Photochemistry* 298–305 (Marcel Dekker Inc, 1993).
  32. Keeler, J. *Understanding NMR spectroscopy*. (John Wiley & Sons, Ltd, 2010).
  33. Allegretti, C. *et al.* Fractionation of Soda Pulp Lignin in Aqueous Solvent through Membrane-Assisted Ultrafiltration. *ACS Sustain. Chem. Eng.* **6**, 9056–9064 (2018).
  34. Cui, C., Sun, R. & Argyropoulos, D. S. Fractional precipitation of softwood kraft lignin: Isolation of narrow fractions common to a variety of lignins. *ACS Sustain. Chem. Eng.* **2**, 959–968 (2014).
  35. Toledano, A., Serrano, L., Garcia, A., Mondragon, I. & Labidi, J. Comparative study of lignin fractionation by ultrafiltration and selective precipitation. *Chem. Eng. J.* (2010) doi:10.1016/j.cej.2009.10.056.

36. García, A. *et al.* Characterization of lignins obtained by selective precipitation. *Sep. Purif. Technol.* (2009) doi:10.1016/j.seppur.2009.05.001.
37. Hwang, K. O. & Lucia, L. A. Fundamental insights into the oxidation of lignocellulosics obtained from singlet oxygen photochemistry. *J. Photochem. Photobiol. A Chem.* **168**, 205–209 (2004).
38. Machado, A. E. H. *et al.* Photoreactivity of lignin model compounds in the photobleaching of chemical pulps 2. Study of the degradation of 4-hydroxy-3-methoxy-benzaldehyde and two lignin fragments induced by singlet oxygen. *J. Photochem. Photobiol. A Chem.* **110**, 99–106 (1997).
39. Rahimi, A., Ulbrich, A., Coon, J. J. & Stahl, S. S. Formic-acid-induced depolymerization of oxidized lignin to aromatics. *Nature* **515**, 249–252 (2014).
40. Xu, W., Miller, S. J., Agrawal, P. K. & Jones, C. W. Depolymerization and hydrodeoxygenation of switchgrass lignin with formic acid. *ChemSusChem* **5**, 667–675 (2012).
41. Nguyen, J. D., Matsuura, B. S. & Stephenson, C. R. J. A photochemical strategy for lignin degradation at room temperature. *J. Am. Chem. Soc.* **136**, 1218–1221 (2014).
42. Rodrigues Pinto, P. C., Borges Da Silva, E. A. & Rodrigues, A. E. Insights into oxidative conversion of lignin to high-added-value phenolic aldehydes. *Ind. Eng. Chem. Res.* **50**, 741–748 (2011).
43. Guo, X. *et al.* Selective visible-light-driven oxygen reduction to hydrogen peroxide using BODIPY photosensitizers. *Chem. Commun.* **54**, 845–848 (2018).
44. Kang, J., Irmak, S. & Wilkins, M. Conversion of lignin into renewable carboxylic acid compounds by advanced oxidation processes. *Renew. Energy* **135**, 951–962 (2019).
45. Yao, B. *et al.* The Photodegradation of Lignin Methoxyl C Promotes Fungal Decomposition of Lignin Aromatic C Measured with <sup>13</sup>C-CPMAS NMR. *J. Fungi* **8**, (2022).
46. Riddell, A., Kvist, P. & Bernin, D. A 3D printed photoreactor for investigating variable reaction geometry, wavelength, and fluid flow. *Rev. Sci. Instrum.* **93**, (2022).
47. Montgomery, D. *Design and Analysis of Experiments*. (John Wiley & Sons, Inc., 2013).
48. Evstigneyev, E. I. & Shevchenko, S. M. *Structure, chemical reactivity and solubility of lignin: a fresh look*. *Wood Science and Technology* vol. 53 (Springer Berlin Heidelberg, 2019).
49. Miglbauer, E., Gryszel, M. & Głowacki, E. D. Photochemical evolution of hydrogen peroxide on lignins. *Green Chem.* **22**, 673–677 (2020).
50. Wang, S., Cai, B. & Tian, H. Efficient Generation of Hydrogen Peroxide and Formate by an Organic Polymer Dots Photocatalyst in Alkaline Conditions. *Angew. Chemie - Int. Ed.* **61**, 1–5 (2022).
51. Rönöls, J., Jacobs, A. & Aldaeus, F. Consecutive determination of softwood kraft lignin structure and molar mass from NMR measurements. *Holzforschung* **71**, 563–570 (2017).

