CHALMERS
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The potential of UV-light from LEDs to valorize lignin

Initial trials towards valorization of technical lignin

Master's thesis in innovative and sustainable chemical engineering

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Department of chemistry and chemical engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

In this report initial trials towards investigating the action of UV-light on three different technical lignins in different solvents were investigated. The solution phase of the samples were investigated by the use of Ultraviolet-Visible (UV/VIS) spectroscopy, Liquid Fourier-transformed Infrared (FTIR) spectroscopy and ^1H Nuclear magnetic resonance (NMR) spectroscopy. Solvents used in this work were Acetonitrile (AcN), Ethanol (EtOH), distilled water and alkaline distilled water at pH12. The results shows that ^1H-NMR spectroscopy is a useful tool to detect volatile products in the irradiated samples, some of which contained useful platform chemicals like methanol, formic acid and acetic acid. It was also found that the long term aging of samples can severely affect the results. For a complete analysis of the liquid phase a high concentration of the reaction products in the samples is necessary and it is expected that the analysis of the solid phase might give valuable information. The choice of solvent is highly important as the found differences between them were large.

Keywords: Lignin, UV-light, Valorization.

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Erik Alksnis, Gothenburg, June 2020

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Introduction

1.1 Background

The transition away from fossil resources as a raw material for chemical products is currently an important problem to solve. A subset of the chemicals used worldwide are aromatic compounds which are found in fossil resources like oil. A natural and renewable source of aromatics would be of great interest to facilitate the phasing out of fossil resources.
Lignocellulosic materials like wood and other plants are almost entirely made up of cellulose, hemicellulose and lignin. Lignin makes up overall around 20-30% of the dry wood mass depending on the species and variations within the tree [1], [2]. Lignin, which currently is a low value aromatic polymer, could facilitate such a source of aromatic compounds if pathways to valorize it are found. In general there are two categories of pulping. The first category is mechanical pulping were grinding the wood material into a pulp is the essential step, this results in a pulp with large amounts of lignin. The second category consists of chemical pulping methods which by the use of different chemicals separate the lignin from cellulose and hemicellulose. When liberating cellulose and hemicellulose from the wood composite material for purposes, such as making chemical paper pulp, a considerable amount of technical lignin is produced.
During 2015 the worldwide production of chemically separated

lignin was close to 100 millions tons and the expectations are that the production will continue to expand [3]. The largest share of this production belongs to a class of technical lignin called lignosulphonates while the two smallest shares belong to Kraft lignin and organosolv lignin. Kraft lignin is mainly used as fuel for heat with effort being put into exploring new areas of usefulness. Organosolv lignin is expected to grow fast due to new processes emerging like second generation bioethanol processes. These two technical lignins will possibly be important sources for materials in the future [3].

These technical lignins might be hard to utilize in other areas, due to the nature of the extraction method. If this problem is left unsolved the risk is that they will continue to be burnt for the energy content to provide heat and power instead of moving up the waste hierarchy. The hope is that these technical lignins could provide a valuable source of aromatic chemicals if valorizing pathways are found. Increasing the valuable yield of processes like chemical pulp mills by utilizing a previous waste stream would also be a benefit [4].

It has long been known in the paper industry that paper with a high lignin content can, when exposed to light, lose its brightness and turn yellow. Chemical reactions in lignin are facilitated by light. This has created interest in the research about these interactions and reaction pathways have been suggested [5]. Previous work with photoreactions has found that it is possible to depolymerize technical lignin with UV-light, both with and without a photocatalyst [6]. This interaction with light could be useful for depolymerizing lignin and breaking the large lignin polymer to smaller units which might serve as platform

chemicals to chemical industries. The hope is that by utilizing UV-light instead of thermochemical processes, energy and/or product improvements might possibly be achieved. Some of the thermochemical methods to depolymerize extracted lignin which are currently being researched are base catalyst depolymerization, super critical solvent depolymerization and ionic liquids [7]. However, the previous work with UV light used wavelengths above 290 nm and limited the exposure to 7 hours with limited conversion and yield. In this project longer reaction times, no catalyst and shorter wavelengths of the incoming light has been used. The hope is to improve the conversion without the need of a second catalyst removal step from the product. With the addition of a catalyst reactive hydroxyl radicals are often formed which can result in severe losses of aromatic rings [8]. Without the radicals formed by the catalyst the hope is that the reaction conditions are mild enough that the lignin products will be stable under the exposure of shorter wavelength UV. Preserving the aromatic compounds is important due to the scarcity of non-fossil aromatic sources for future applications.

1.2 Aim of the study

The overall aim of this study is to advance the research into the valorization of technical lignins into valuable small molecule products. This study aims to investigate the effect of direct irradiation of short wavelength UV-light on technical lignins. Differences in functional groups, molecular size distributions of technical lignins and potential identification of small molecule present in the solvent phase are aimed to be investigated.
A few questions tried to be answered during this study are:

Can UV/VIS spectrometry detect differences between samples and the control? Can UV/VIS spectrometry detect differences between samples with different exposures? Can an in-situ FTIR probe be used to detect differences between the samples and the control? Can an in-situ FTIR probe be used to detect differences between the samples of different exposures? Can ^1H - NMR be used to detect dissolved molecules in the solvent phase? What is the effect of UV light on the molecular size distribution of the solid phase measured by a Gel Permeation Chromatography? Is there a difference in the samples between the wavelengths used during the exposure?

1.2.1 Limitations

This study will limit itself to low UV absorbing solvents to better investigate the UV effects of lignin in different environments. The study will limit itself to only investigate the actual effect of the UV light and not investigate the economic or technical feasibility of any potential product or process. The study will limit itself to UV irradiation in batch exposures with the currently available equipment and exposure design and with a fixed exposure time. The study limits itself to only expose the samples to UV-light in ambient conditions under an atmosphere of air. Hence, the investigated parameters are: UV Wavelength, LED power output, Lignin source and solvent.

1.3 Lignin structures

Knowledge of the chemical structure is important to ease the research of lignin valorization. This is fundamental for later modifications and the understanding of why and how changes occur.

1.3.1 Native lignin

Native lignin is the lignin found in lignocellulosic material which has not been chemically or physically modified. It provides the lignocellulosic material with stiffness, and keeps the material water resistant by its hydrophobicity. Lignin is a complex polymer of undetermined size which is hard to extract unmodified. Lignin mainly consists of 3 repeating units. These are P-hydroxyphenyl (H), Guaiacyl (G) and Syringyl (S). These repeating units are derived from the three monolignols: P-Coumaryl alcohol, Coniferyl alcohol and Sinapyl alcohol respectively. See figure 1.1 for the monolignol structures. The ratio between these units differ depending on the origin of the source. Softwoods consist of nearly only G units while hardwood has a mix G and S units. Meanwhile grasses have a larger fraction of H units, in contrast to softwoods and hardwoods which only have a few percent of H units incorporated in the lignin structure. [9], [10]

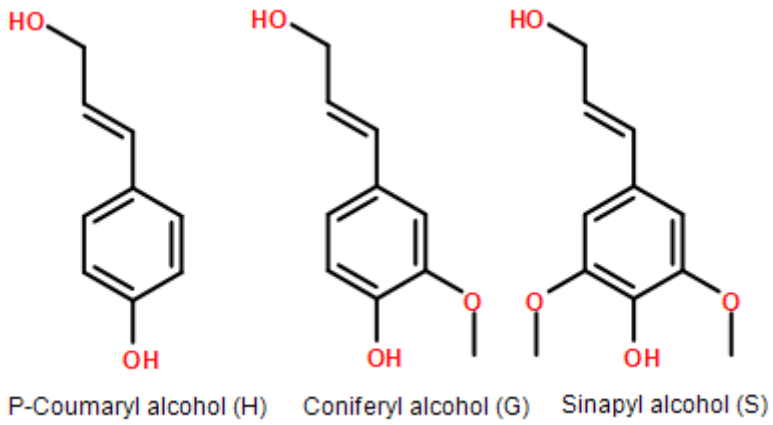


Figure 1.1: The most common monolignols in lignocellulosic materials: H, G and S units.

The proportions of the interunit linkages, in other words the bonds between the C_9 units of the aromatic ring and attached

three carbon tail, in native lignin depends on the species but in general softwoods have a lower percentage of $\beta-O-4$ type bond than hardwoods, at 50% respective 60%. This is the most important bond to cleave to facilitate the depolymerization of native lignin. Other linkages of lower frequency are $\beta-5$, $5-5$, $4-O-5$, $\beta-1$ and $\beta-\beta$. Structures of the linkages in native lignin can be seen in figure 1.2 [11], [10], [12], [5], [4], [13].

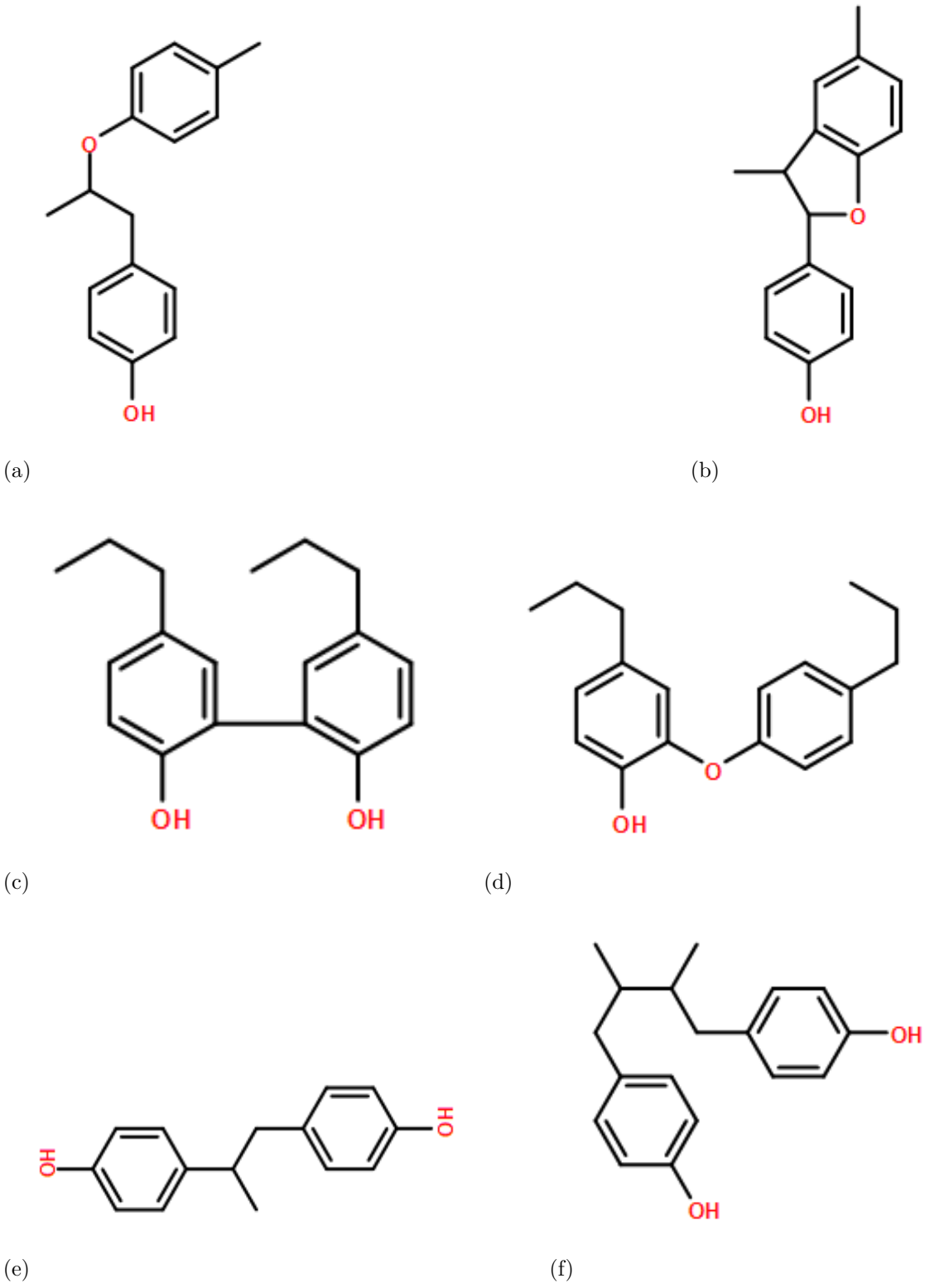


Figure 1.2: Structure of the interunit linkages in native lignin. (a) shows $\beta - O - 4$,(b) shows $\beta - 5$,(c) shows $5 - 5$,(d) shows $4 - O - 5$,(e) shows $\beta - 1$ and (f) shows $\beta - \beta$.

1.3.2 Kraft lignin

Kraft lignin is a heavily modified technical lignin extracted from the dominating pulp process world wide, the Kraft process. The high temperature, pressure and high pH of the process coupled with the long cooking times results in a harsh process. This yields a process which to a large extent cleaves the dominating interunit linkages in native lignin $\beta-O-4$ bonds. The cleavage of interunit linkages results in smaller lignin particles, which are solubilized in the cooking liquor. The increase of hydroxyl functional groups in the lignin molecules enhances the lignin solubility during the Kraft cook. Softwood lignin can have around 13 OH groups per 100 C_9 units while dissolved Kraft lignin around 65 to 100 C_9 units [12].
The Kraft cooking process is not a selective process for lignin, parallel reactions occur in the lignin besides the cleavage of the ether bonds and cellulose degradation. Condensation reactions occur during the pulping which result in stable carbon-carbon bonds between the aromatic units. A general problem with Kraft lignins is the heterogeneity of the formed products in regards to the functionality proportions and molecular size distribution. Lignin upon being fractionated by the use of different solvents show differences in terms of size distributions and functional groups. Other factors that provide different characteristics are the original amount of interunit linkages, molecular size distributions and further variations that can be due to the raw material source, seasonal and geographical changes and the cooking conditions. The complexity to determine the chemical structure of Kraft lignins yields few definitive answers but general relations [14]. Nevertheless, a large amount of the dominating $\beta - O - 4$ bonds are broken

during the cooking. Residual lignin left in the pulp which did not dissolve during the cook can have 20 bonds $\beta - O - 4$ per 100 aromatic units and the dissolved Kraft lignin down to 3.2 bonds $\beta - O - 4$ per 100 aromatic units. However, depending on how the Kraft lignin is fractionated before the quantitative analysis the $\beta - O - 4$ bond frequency differ and fall between 12.7 and 1.4 due to Kraft lignins heterogeneity [14]. A study by Constant et al. found softwood Kraft lignin having a content of 6.1 $\beta - O - 4$ per 100 aromatic rings [13]. These findings are further supplemented by a study from Olsen et al. which also presents the amount of condensed structures found in softwood Kraft lignin. This amounts to somewhere between 25-40 C_5-condensed bonds per 100 C_9 units [15]. The size distributions of the lignin molecules vary depending on the species and cooking conditions. On a weight basis the molecular weight can vary between 1000 and 12200 g/mol with polydispersities between one and 3.7 depending on the fractionation used [14]. When no fractionation is used values around 4300-6000, and even up to 19000 have been determined and polydispersities of 6.1 to 8.1 [14], [13], [15]. These large variations, due to cooking and raw material variations, show that determining the molecular size distribution of the substrate is important if the molecular size is influencing the process.

1.3.3 Organosolv lignin

Organosolv lignin is a technical lignin from the organosolv process which is a less frequently used process compared to the Kraft process. Organosolv lignin is typically very pure with respect to carbohydrate and sulfur content. The lignocellulosic material is exposed to organic solvents, often ethanol or ethanol/water. This process preserves the phenolic content in

lignin to a greater extent and also yields a narrower size distribution. The organosolv lignin is, similar to Kraft lignin, degraded during the process and condensation will occur creating carbon-carbon bonds between the C_9 units. The molecular weight of the organosolv lignin is in general lower than for Kraft lignin with a more narrow size distribution, due to the fact that the polydispersity is lower. The molecular size on weight basis can vary between 2000 and 4000 g/mol depending on the species and pulping method, even when using the same ethanol solvent. The polydispersity have been found between 2.8 and 3.8 [16], [13]. The residual amount of $\beta - O - 4$ in organosolv lignin can be between zero and 4.3 per 100 C_9 units depending on the lignocellulosic material source [13].

1.4 Lignin depolymerization

The breakage of interunit linkages into useful, smaller units is a key step for the valorization of lignin into useful products. There exists many different mechanisms which achieve this, some utilized in techniques which are already employed in reactors in various stages of development.

1.4.1 UV degradation

UV light is known to degrade wood materials, it has been shown that ether type bonds can be degraded during weathering of wood with UV exposure. This degradation leads to a decrease in the relative content between lignin and carbohydrates. It was found that for the conditions used, the $5 - 5$ carbon bonds in lignin were significantly more resistant to the degradation [17]. The photodegradation of lignin model compounds have been investigated and some pathways show

monomeric products from dimeric compounds. At the same time there exists a parallel possibility that the breakage of an ether bond results in a carbon-carbon linked dimeric compounds similar to a $5-5$ or $\beta-5$ [5]. However, the nature of the materials investigated are more similar to the dominating structures found in native lignin than technical lignin. Reaction conditions such as solvent, temperature and light intensity are important for the degradation of lignin. Different solvents will promote reaction steps differently, for example when using tetrahydrofuran as a solvent, ring opening reactions were achieved under UV light without a heterogeneous catalyst. Resulting in a heavily oxidised lignin after 200 hours of irradiation at 365 nm. The aromatic rings were broken and oxidized into aliphatic acids. The molecular size distribution was also pushed towards smaller molecules. A reaction mechanism was suggested which proposed that the solvent was promoted into a strong oxidizer by the UV light. It was shown that a solvent without the capability to form a peroxide did not reproduce the effect [18].

Lignin depolymerization by photocatalytic means, with the addition of TiO_2 to produce strong oxidizing compounds, have been investigated. In a study by Machado et al. it was found that under direct irradiation, in alkaline media, the content of free phenolic groups decreased with time, in contrast to when using hydroxyl radical promoting setups. When TiO_2 or hydrogen peroxide were used in conjunction with UV light the trend was an increase after an initial decrease of phenolic content. The presence of strong oxidizing agents allowed for other reaction pathways [8].

1.5 Analysis principles

The UV/VIS analysis can be useful to investigate the lignin samples as the aromatic lignin polymer includes highly absorbing conjugated bonds. The more conjugated bonds that are in close proximity the larger wavelength the molecule can absorb. The aromatic rings in lignin absorb UV light and the several functional groups attached can modify the specific absorption values depending on the groups. Several of the functional groups extend the conjugated area out from the aromatic ring.
The FTIR analysis can be useful to investigate the lignin samples as the different functional groups have different vibrational frequencies, potentially giving information on their content and nature. This could provide detail on functional group changes in the samples. In situ FTIR probes can be used in liquid phase samples while more commonly used FTIR instruments are optimized for solid phase samples.
The ^1H-NMR analysis can be useful to investigate the lignin samples as NMR measures on the spins of the nucleus of atomic species reporting on the chemical environment neighbouring the proton. For the solution-state NMR to be useful, molecules need to be able to freely move in solution. For a solid phase sample a different approach is needed to obtain an NMR signal.
Gel Permeation Chromatography can be useful to investigate the molecular size distribution of lignin by dissolving the residual solid phase and passing the solution through a column with a porous gel. The retention time in the column is correlated to the molecular volume and the mass. Larger molecules in general pass the column quicker then smaller ones which are

delayed by the more accessible pores they can enter.

2
Methods

2.1 UV source

The UV source used in the experiments are UV LEDs fitted to a heat sink, called a LED plate, and powered by a DC power supply. The UV light was introduced to the samples by the guiding action of an optical fibre, resting at the LED surface. The optical fibre entered through the cap of the closed vial as seen in figure 2.1. All LED plates were built according to the same circuit design but with varying wavelengths of the LEDs attached to the printed circuit board (PCB). The schematic of the electric circuit is shown in figure 2.2. The printed circuit board was attached to the heat sink by screws and a layer of thermal paste underneath the PCB is present to enhance the heat flow from the LEDs to the heat sink. The heat sink was in turn cooled by a flow of compressed air. In figure 2.4 a illustration of the LED plate can be seen.
Three LED plates were made with four LEDs each of either 267 ± 7 nm, 280 ± 5 nm or 308 ± 5 nm wavelengths. The 267 nm source were KL265-50S-SM-WD LEDs sourced from Crystal IS, Inc. The 280 nm and 308 nm were DUV280-SD356 and DUV310-SD356 respectively from reseller Roithner LaserTechnik Austria and the optical fibres were FG600AEA from Thorlabs, Inc. Up to four optical fibres could be inserted into the same vial.

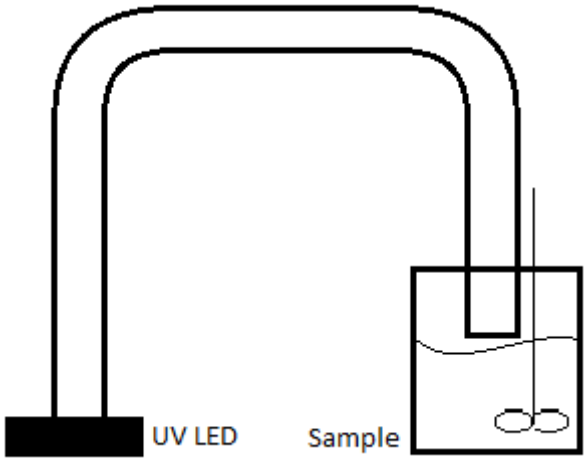


Figure 2.1: The flexible optical fibre guides light into the test sample on a stirring plate.

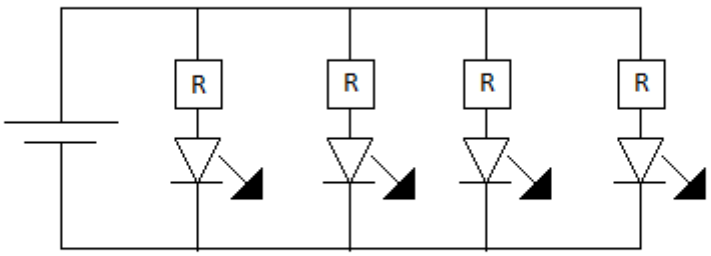


Figure 2.2: The schematic of the electric circuit for the LED plates.

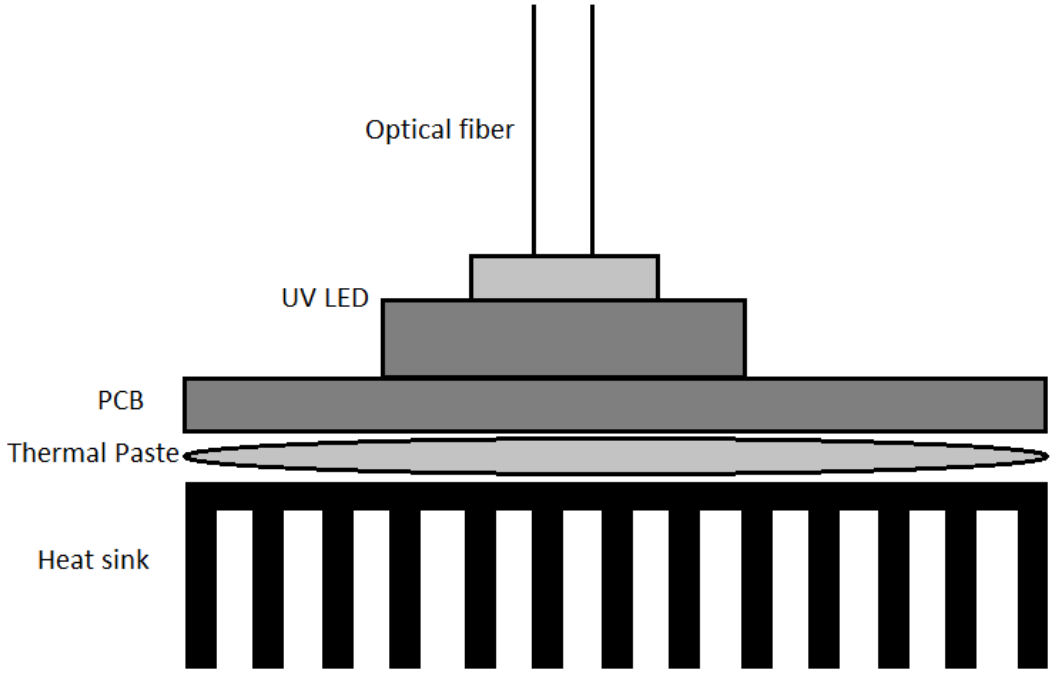


Figure 2.3: A overview of the assembled LED plates cross section.

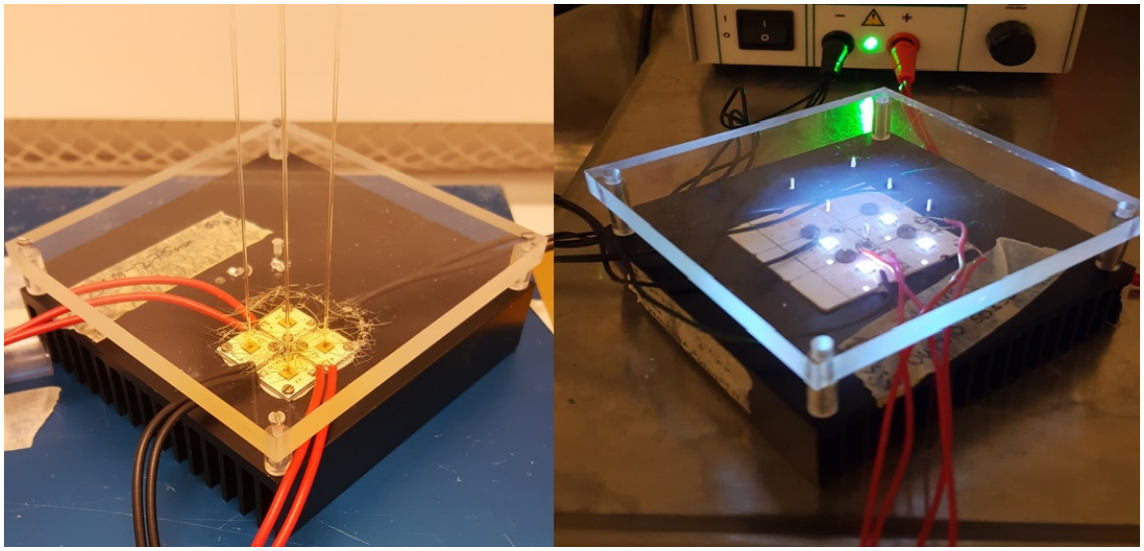


Figure 2.4: Two of the built and used LED plates during the study. To the left is the 267 nm plate and to the right is the 310 nm plate powered by a DC power supply. The 267 nm plate shows the optical fibres resting at the LED surface by the support of a plastic cover.

2.2 Sample preparation and exposure

All samples were prepared with the same method regardless of solvent and lignin type. 5 mg dry lignin powder were weighed and transferred to a 10 ml glass vial. 5 ml of solvent were transferred to the vial, which was closed with a lid, yielding a 1 g/l solution. The solution was stirred for a minimum of two hours in the dark before the UV exposure. Before the UV exposure the samples and control were wrapped in aluminum foil to limit cross contamination of UV light between the samples.

The irradiated samples were exposed to the UV light, guided by optical fibres inserted through the lid, 24 hours under stirring in a room temperature environment. The control samples were left to stir wrapped in aluminum foil with no optical fibre inserted during the same conditions. After the exposure the samples were left to sediment for a minimum of 24 hours. Notes were taken before and after the sedimentation step. In table 2.1 the experimental series for each dosage scenario can be found.

The Kraft lignin (K) used in this study were sourced from a Nordic pulp mill by the LignoBoost^{TM} process. It was extracted from a softwood fed Kraft process. Further characterization of the feed have been performed [19]. The two organosolv lignins (OS, OH) were produced by Attis Innovations LLC, Milton Georgia US. The solvent used in the study were Acetonitrile (AcN), anhydrous Ethanol (EtOH), distilled water at both neutral pH7 and alkaline pH12. Sodium hydroxide was used to increase the pH of the distilled water.

Table 2.1: The full set of combinations investigated, the experimental plan was repeated for a low dose and a high dose scenario.

Nr	Lignin type (0,1,2) K, OS, OH	UV wavelength [nm] (0,1,2,3) ctrl, 260, 280, 310	Solvent (0,1,2,3) EtOH, AcN,pH7, pH12	Code
1	0	0	0	K,ctrl,EtOH
2	0	1	0	K,260,EtOH
3	0	2	0	K,280, EtOH
4	0	3	0	K,310,EtOH
5	0	0	1	K,ctrl,AcN
6	0	1	1	K,260,AcN
7	0	2	1	K,280,AcN
8	0	3	1	K,310,AcN
9	0	0	2	K,ctrl, pH7
10	0	1	2	K,260, pH7
11	0	2	2	K,280,pH7
12	0	3	2	K,310,pH7
13	0	0	3	K,ctrl,pH12
14	0	1	3	K,260,pH12
15	0	2	3	K,280,pH12
16	0	3	3	K,310,pH12
17	1	0	0	OS,ctrl,EtOH
18	1	1	0	OS,260,EtOH
19	1	2	0	OS,280, EtOH
20	1	3	0	OS,310,EtOH
21	1	0	1	OS,ctrl,AcN
22	1	1	1	OS,260,AcN
23	1	2	1	OS,280,AcN
24	1	3	1	OS,310,AcN
25	1	0	2	OS,ctrl, pH7
26	1	1	2	OS,260, pH7
27	1	2	2	OS,280,pH7
28	1	3	2	OS,310,pH7
29	1	0	3	OS,ctrl,pH12
30	1	1	3	OS,260,pH12
31	1	2	3	OS,280,pH12
32	1	3	3	OS,310,pH12
33	2	0	0	OH,ctrl,EtOH
34	2	1	0	OH,260,EtOH
35	2	2	0	OH,280, EtOH
36	2	3	0	OH,310,EtOH
37	2	0	1	OH,ctrl,AcN
38	2	1	1	OH,260,AcN
39	2	2	1	OH,280,AcN
40	2	3	1	OH,310,AcN
41	2	0	2	OH,ctrl, pH7
42	2	1	2	OH,260, pH7
43	2	2	2	OH,280,pH7
44	2	3	2	OH,310,pH7
45	2	0	3	OH,ctrl,pH12
46	2	1	3	OH,260,pH12
47	2	2	3	OH,280,pH12
48	2	3	3	OH,310,pH12

2.3 UV/VIS analysis

The solvent reference, control sample and UV exposed samples were filtered prior to the UV/VIS analysis through a 0.2 μm filter. 50 μl of the filtered solutions were measured and diluted with additional solvent to 2.5 ml total volume. The diluted solutions were transferred to a 1 cm quartz cuvette and measured in an UV/VIS spectrophotometer against a reference sample of the same solvent. For some cases a different dilution ratio was used to achieve a higher or lower absorption spectra. The dilution ratios used are found in table 2.2.

Table 2.2: The dilution ratios used in the UV/VIS analysis for all the series of samples.

Lignin	Solvent	Dilution ratio
Kraft	AcN	2/50
OS	AcN	1/50
OH	AcN	2/50
Kraft	EtOH	1/50
OS	EtOH	1/50
OH	EtOH	1/50
Kraft	pH7	12/50
OS	pH7	4/50
OH	pH7	6/50
Kraft	pH12	1/50
OS	pH12	1/50
OH	pH12	1/50

Normalization of the spectras was done by scaling the whole spectra by a factor such that the chosen absorption peak equaled one. Two different absorption peaks were considered for normalization, the peak around 200 nm and 280 nm. The analysis was performed on a GBC double beam spectrophotometer with air as the background and pure unirradiated solvent as the reference sample. Two spectras were collected, one between 250-450 nm and one between 200-450 nm. The sampling in-

terval was 1.12 nm and the slit width 2 nm. The time between exposure and analysis was not controlled and varied between one day and 3 weeks. All the samples with the same lignin and solvent were performed on the same occasion.

2.4 FTIR analysis

The solvent reference, control sample and UV exposed samples were used without additional work up for the FTIR analysis. A FTIR probe measuring between $3000 - 500\ cm^{-1}$ was immerged in the sample solutions under stirring. A total of 128 scans were used per sample. The probe and tip was cleaned between each sample until judged clean by the instrument software. The unit used was a Mettler Toledo ReactIR 702L. The time between exposure and analysis was not controlled and varied between one day and 3 weeks. All the samples with the same lignin and solvent were performed on the same occasion.

2.5 ^1H-NMR analysis

900 μl of sample solution was transferred without further work up to the NMR tubes. A glass capillary filled with sodium trimethylsilylpropanesulfonate (DSS) dissolved in D_2O was flame sealed and transferred to the NMR tube. The solution in the capillary was used to obtain a good shimming, field homogeneity, and provide reference for quantitative estimates. The NMR tubes were placed in a sample rack for the use in a automated sampler. The ^1H-analysis were performed at Swedish NMR centre at Hasselblad Laboratory at the University of Gothenburg. A Bruker Avance III 700MHz pumped magnet unit with a 5 mm QCI probe was used for all analyses, the probe being proton optimized. The analyses used

single and multisolvent suppression for example by excitation sculpting with gradients and perfect echo. The time between exposure and analysis was not controlled and varied between three days and 3 weeks. All the samples were performed on the same occasion.

3
Results and discussion

Upon mixing the dry lignin with the different colourless solvents, some solutions turned coloured. The Kraft lignin solutions in general had a yellow colour, the softwood organosolv lignins a yellow and brown mix while the hardwood organosolv lignins had a more dominating brown colour. The neutral water solutions remained colourless, indicating very small amounts of lignin being dissolved. No lignin turned to be fully dissolved in any of the solvents except for Kraft lignin and hardwood organosolv lignin in pH12 solvent were the control samples. See table 3.1 for a summary of the visual appearance of the control samples.

Table 3.1: A summery of the visual appearance of the control samples. K, OS, OH refers to Kraft, softwood organosolv and hardwood organosolv lignin respectively.

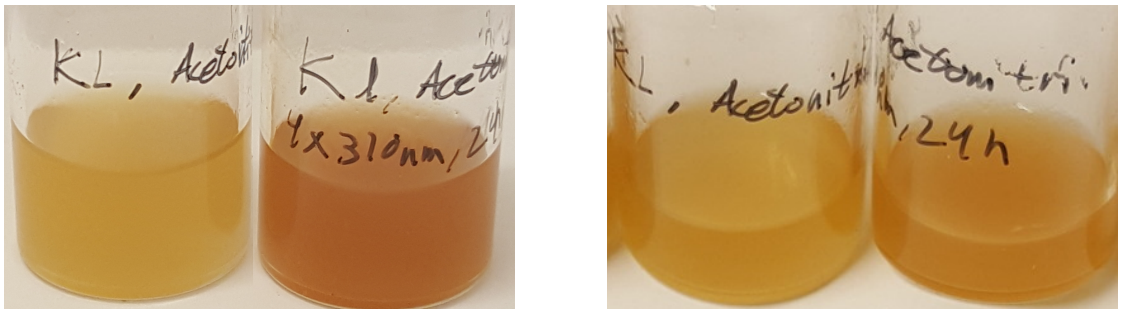
Solvent	Lignin type	Colour	Solid phase present
EtOH	K	Yellow	Yes
AcN	K	Yellow	Yes
Neutral water	K	Colourless	Yes
Alkaline water	K	Yellow	No
EtOH	OS	Yellow/Brown	Yes
AcN	OS	Yellow/Brown	Yes
Neutral water	OS	Colourless	Yes
Alkaline water	OS	Yellow/Brown	Yes
EtOH	OH	Brown	Yes
AcN	OH	Brown	Yes
Neutral water	OH	Colourless	Yes
Alkaline water	OH	Yellow/Brown	No

The experimental plan used was selected to explore the param-

eters dosage, wavelength, solvent and lignin type. In table 2.1 the experimental series for each dosage scenario can be found. The total plan includes 96 experiments however due to unforeseen circumstances the experimental plan was not finished and some experiments were never preformed. No experiments with 280 nm were done for the low dosage scenario and few with 260 nm were done for the high dosage scenario. In a handful of cases replicates at a low ampere setting were preformed, these samples were included and differentiated from the correct setting. 2A stands for the correct setting of two ampere and 1A stands for the faulty setting of one ampere.

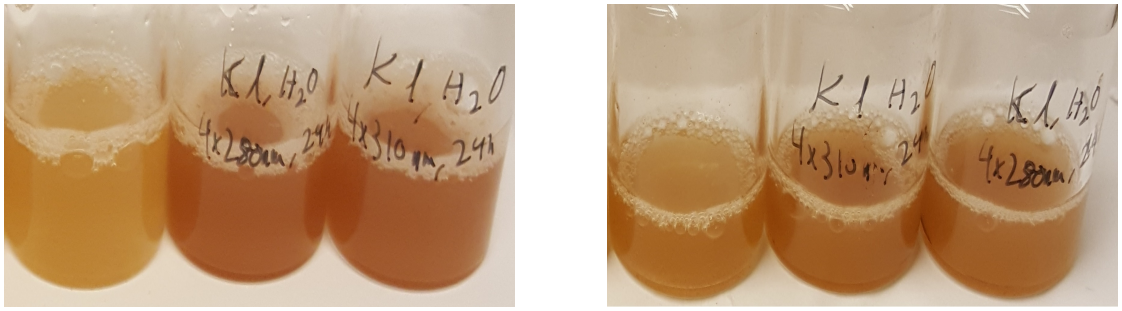
The samples were exposed to UV light of different wavelengths and intensity over a 24 hour period. Some samples changed colour compared to the unexposed control while others remained unchanged by visual inspection. With Kraft lignin in AcN at high doses the solutions turned visibly red, a colour which faded over weeks to be more similar to the control sample in the same series. A similar case can be seen in Kraft lignin in neutral water in which not the solution but the solid phase when shaken give the slurry a red colour which fades over weeks. This indicates that reactions continue in the samples after the exposure at a relatively slow rate to the exposure reactions. No difference in sample colour was noticed after a 24 hour rest. The change in AcN after four weeks are shown in figure 3.1 and in neutral water in figure 3.2. In the cases with fully dissolved control samples some solutions turned opaque seemingly due to an amount of particles. The created solid phase can be viewed in figure 3.3. After filtration through a 0.2 μm filter, all solutions were seemingly transparent and similar within each series of solvent and lignin type. The complete set of samples after several weeks of rest can be found in ap-

pendix A.



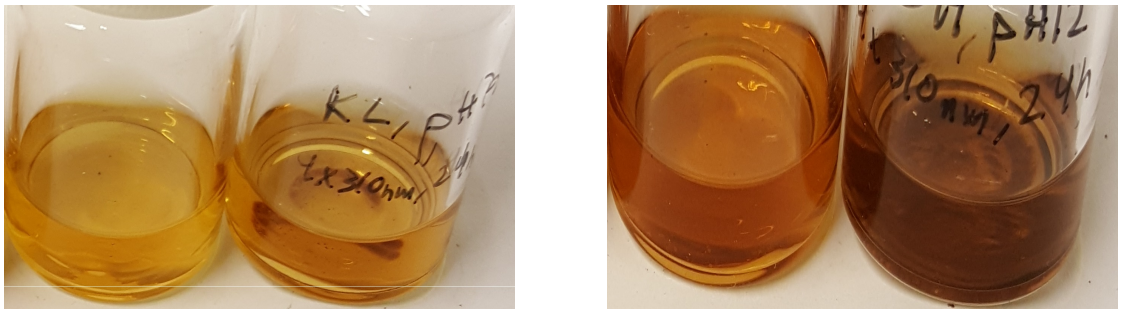
(a) (b)

Figure 3.1: An example of the reddening effect in AcN for Kraft lignin. (a) shows a high dosage sample directly after exposure to the right compared to the control to the left and (b) is the same set four weeks later in the same order.



(a) (b)

Figure 3.2: An example of the reddening effect in neutral water for Kraft lignin. (a) shows two high dosage samples directly after exposure compared to the control to the left and (b) is the same set seven weeks later with the control to the left.



(a) (b)

Figure 3.3: An example of the samples initially clear but after UV exposure a solid phase was present. In (a) Kraft lignin can be found compared to the clear control. In (b) Hardwood organosolv lignin can be found compared to the clear control.

3.1 UV/VIS results

To investigate a possible difference in the liquid phase the filtered solutions were diluted and analysed in a UV/VIS spectrophotometer. All analysed spectras showed the characteristic absorption peaks at 200 nm and 280 nm of lignin type molecules. Two series were done, one between 250-450 nm and one between 200-450 nm. The primary UV absorption peaks for lignin are shown in table 3.2 [20].

Table 3.2: Electronic transitions for lignin useable for UV/VIS characterisation. The exact wavelengths depends on the solvent phase of the sample. Reprinted with permission from [20], copyright © Yao Lu et al.

Absorption maxima [nm]	Electronic transition style	Chromophores and structures
200	$\pi - \pi^*$	Conjugated bonds in aromatic ring
240	$n - \pi^*$	Free OH
282	$\pi - \pi^*$	Conjugated bonds/aromatic ring
320	$\pi - \pi^*$	Aromatic ring conj. $C_\alpha = C_\beta$
320	$n - \pi^*$	$C_\alpha = O$ conj. aromatic ring
325	$n - \pi^*$	Etherified ferulic acid

Two different normalization methods have been utilized for which the whole spectras are multiplied by a factor such that the chosen normalization peak equals one. If the main UV absorbing chemical structure of such a peak is preserved during the irradiation procedure then it can be used to compare the ratios of the other absorption values to the chosen peak. This could remove the effect of initial concentration differences between samples within each lignin series. Since the absorption peak around 200 nm is related to typically stable aromatic rings that structure is possibly more resistant to change and to a higher degree preserved. If any other UV absorbing structure is created/changed or destroyed that could show up as a relative change compared to the normalized absorption peak at

200 nm, if the hypothesis that the aromatic rings are preserved is true which has not been shown. The normalization makes comparing different UV spectras and detecting differences in slopes and peaks easier.

In general no correlation between UV irradiation and the UV/VIS absorption spectra for all the solvents and lignins types were found. Partly because of difficulties to achieve a concrete answer with lignin solutions compared to other methods. to Within each series of lignin there was no correlation, suspected due to the different solvents used promoting molecules to dissolve into the liquid phase differently. Within each series of solvent some differences were noted. None of the spectras for a specific lignin-solvent combination showed any clear correlation with the UV exposure, suggesting that an increase in the number of peaks will be necessary to investigate the UV effect if any. An increase in the lignin concentration might also ease the analysis guaranteeing a homogeneous sample in cases for technical lignins with a large heterogeneity. The UV cutoff of water and AcN are all below the investigated ranges, however the UV cutoff of EtOH is 210 nm meaning the peak close to 200 nm roughly coincides with the cutoff and is possibly the reason for the sharper decline at lower wavelengths compared to the other spectras. This can be viewed in figure A.21. This means that the decrease after the threshold might be due to the solvent alone. After normalization to the 200 nm peak there is a significant difference between Kraft lignin and the two organosolv lignins in neutral water. The Kraft lignin has low absorption values between 215-270 nm relative to the 200 nm peak compared to the organosolv lignins in neutral water. The same samples were used in both the 200 and 250

nm series, however the series did not always agree on the absorption values in the overlapping area for the same samples. This indicates that the aging of the samples might be severe and care must be taken for future studies. The complete set of unnormalized UV spectras and normalized to the 200 nm peak between 200-450 nm can be found in appendix A.

3.2 FTIR results

To investigate a possible difference in the liquid phase the solutions were used as is and measured with a FTIR probe. No obvious difference between the samples and solvent references were discerned likely due to a too low concentration for the specific probe to be detected. An exception was that all of the AcN solutions showed a strongly separated peak around 1636 cm^{-1} compared to the reference regardless if the solutions showed any visual difference or not compared to the control sample. However AcN is a hygroscopic liquid and water has a high absorption peak around that wavenumber. Possible traces of water were confirmed in NMR showing a correlation between a large absorption signal in the FTIR probe and the water signal in the NMR spectra. The water might derive from a reaction, however it is suspected to be due to contamination due to the hygroscopicity of the AcN. In figure 3.4 an example of a FTIR spectra is shown for Kraft lignin in AcN.

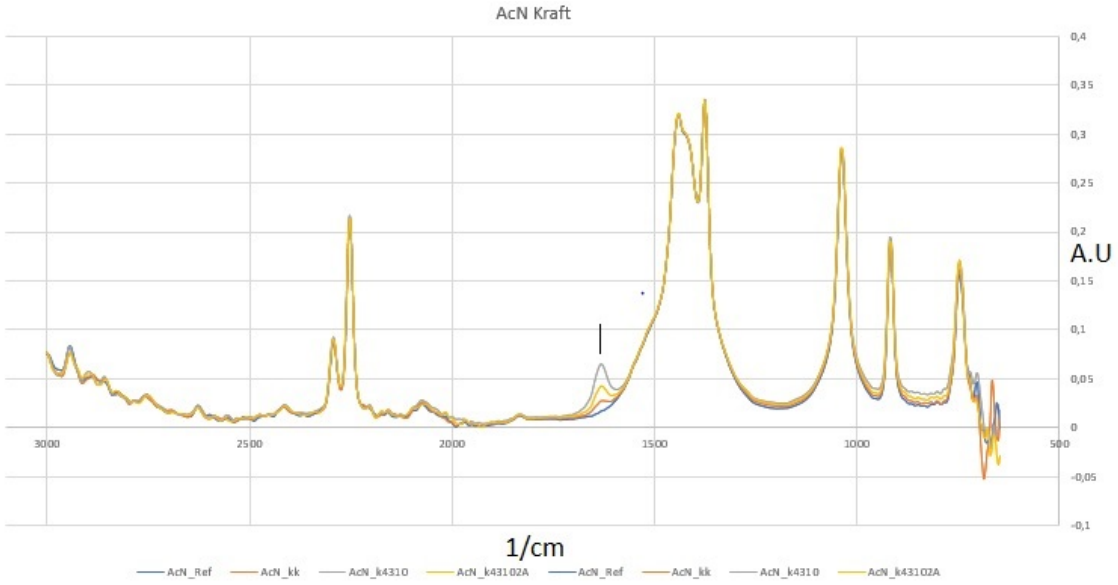


Figure 3.4: The FTIR spectra of Kraft lignin samples in AcN. The major difference between samples coincide with a major absorption peak of water around 1636 cm^{-1}.

3.3 NMR results

From the ^1H-NMR analysis it was found that many samples showed the presence of formic acid, methanol, acetic acid, different aldehyde compounds and phenolic compounds. Only the control samples and the high dose samples were analysed in the NMR, due to the expectation that the high dose samples would show the largest difference. However the spectras were complex and hard to identify due to the number of peaks and indications of broad peaks possibly due to large molecules without complete freedom of movement. It was found that the acetic acid peak overlapped severely with the AcN signal complicating this analysis. No significant difference of aldehyde content was found within each series, the amount was relatively low in all cases. Acetic acid was only confirmed in one of the controls, Kraft lignin in EtOH, while several of the high dose samples showed a medium high acetic acid content. Formic acid, acetic acid and methanol had an equal or higher

content in almost all irradiated samples compared to the control, indicating a oxidizing reaction. In lignin there already exists some aldehyde-like structures which might be the reason the aldehyde content is almost always found in the samples. An overview of the ^1H NMR results can be found in table 3.3.

Table 3.3: An overview of the ^1H - NMR results. A question mark means difficulties were present to assess the compound. - means that no presence was found, cross show a indication of the relative amount in the same series. Note that the UV dose shows the calculated output from the LED plate and not the actual received UV light to the sample delivered by the optical fiber.

Sample code	Lignin	Solvent	UV dose $[mW]$	Wavelength $[nm]$	Formic acid	Methanol	Acetic acid	Aldehydes	Phenols
EtOH K C	Kraft	EtOH	0	-	X	X	X	X	X
EtOH K 4280	Kraft	EtOH	192	280	X	X	X	X	X
EtOH K 4310	Kraft	EtOH	272	308	X	X	X	X	X
EtOH OS C	OS	EtOH	0	-	-	-	-	X	?
EtOH OS 4280	OS	EtOH	192	280	X	-	-	X	?
EtOH OS 4310	OS	EtOH	272	308	X	-	-	X	?
EtOH OH C	OH	EtOH	0	-	X	X	-	X	?
EtOH OH 4280	OH	EtOH	192	280	XX	XX	-	X	?
EtOH OH 4310	OH	EtOH	272	308	XXX	XXX	X	X	?
AcN K C	Kraft	AcN	0	-	-	-	overlap w. solv.	X	X
AcN K 4280	Kraft	AcN	192	280	XX	-	overlap w. solv.	X	XX
AcN K 43102A	Kraft	AcN	272	308	XX	-	overlap w. solv.	X	X
AcN K 43101A	Kraft	AcN	136	308	-	-	overlap w. solv.	X	-
AcN OS C	OS	AcN	0	-	-	-	overlap w. solv.	X	X
AcN OS 4280	OS	AcN	192	280	-	-	overlap w. solv.	X	XX
AcN OS 4310	OS	AcN	272	308	-	-	overlap w. solv.	X	X
AcN OH C	OH	AcN	0	-	-	-	overlap w. solv.	X	X
AcN OH 4280	OH	AcN	192	280	-	-	overlap w. solv.	X	X
AcN OH 43102A	OH	AcN	272	308	-	-	overlap w. solv.	X	X
AcN OH 43101A	OH	AcN	136	308	-	-	overlap w. solv.	X	X
pH7 K C	Kraft	pH7	0	-	-	X	-	-	-
pH7 K 4280	Kraft	pH7	192	280	XXX	XXX	-	X	-
pH7 K 4310	Kraft	pH7	272	308	-	XX	XXX	X	-
pH7 OS C	OS	pH7	0	-	-	XX	-	X	-
pH7 OS 4280	OS	pH7	192	280	XXX	X	XX	X	-
pH7 OS 4310	OS	pH7	272	308	-	XX	XX	X	-
pH7 OH C	OH	pH7	0	-	-	X	-	X	-
pH7 OH 4280	OH	pH7	192	280	-	XXX	-	X	-
pH7 OH 4310	OH	pH7	272	308	-	XX	-	-	-
pH12 K C	Kraft	pH12	0	-	X	X	-	X	-
pH12 K 4260	Kraft	pH12	200	267	X	X	X	X	-
pH12 K 4280	Kraft	pH12	192	280	X	X	XXX	X	-
pH12 K 43102A	Kraft	pH12	272	308	X	X	X	X	-
pH12 K 43101A	Kraft	pH12	136	308	X	X	XX	X	-
pH12 OS C	OS	pH12	0	-	X	X	-	X	-
pH12 OS 4280	OS	pH12	192	280	XX	XX	X	X	-
pH12 OS 4310	OS	pH12	272	308	X	X	X	X	-
pH12 OH C	OH	pH12	0	-	X	X	-	X	-
pH12 OH 4260	OH	pH12	200	267	X	X	XXX	X	-
pH12 OH 4280	OH	pH12	192	280	X	X	XX	X	-
pH12 OH 43102A	OH	pH12	272	308	X	X	-	X	-
pH12 OH 43101A	OH	pH12	136	308	-	X	XX	X	-

Additionally further analysis was preformed on the unexposed lignin samples in Dimethyl sulfoxide (DMSO) to characterize

the lignin control samples. The spectras can be found in figure 3.5. Two spectras of varying wavelengths are shown compared to their control sample in figure 3.6 for Kraft lignin in neutral water and in figure 3.7 for softwood organosolv lignin in EtOH. Similar spectras makes up the basis for the assignments in table 3.3.

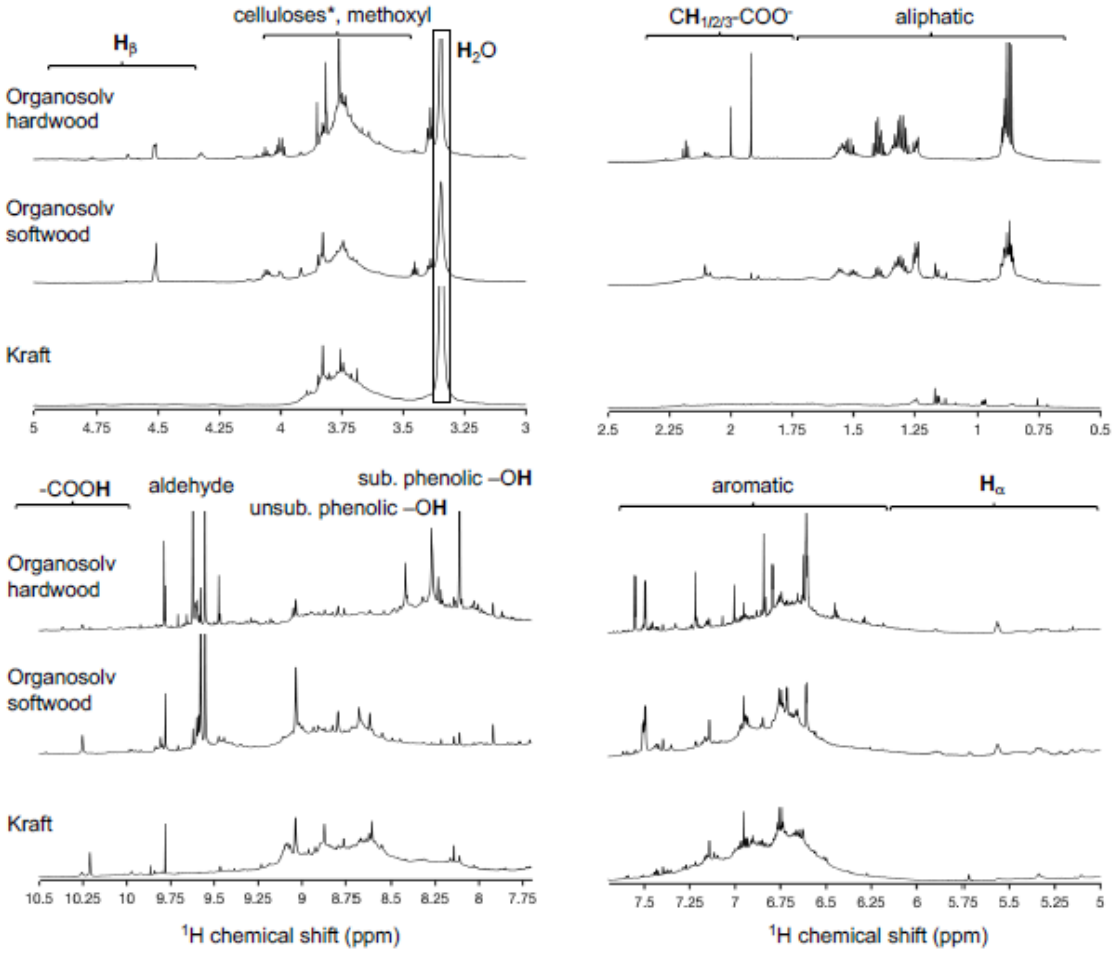


Figure 3.5: ^1H-NMR spectra for the three investigated technical lignins in DMSO. The region between 0.5 and 1.75 ppm is judged show signals from aliphatic structures, the peak at 0.8 ppm is judged to be methyl groups far removed from any oxygen. At 2.5 ppm the DMSO solvent signal is removed. The water signal in DMSO can be found around 3.3 ppm, methoxy groups on the aromatic rings are judged to be found around 3.75 ppm. Cellulose is expected to show one peak around this area, however cellulose should show additional signals which are not detected. The region marked as H_β is judged to be proton signal from a β carbon, were the kraft lignin don't show any signal compared to the organosolv lignins. The assignments are based on literature assignments.

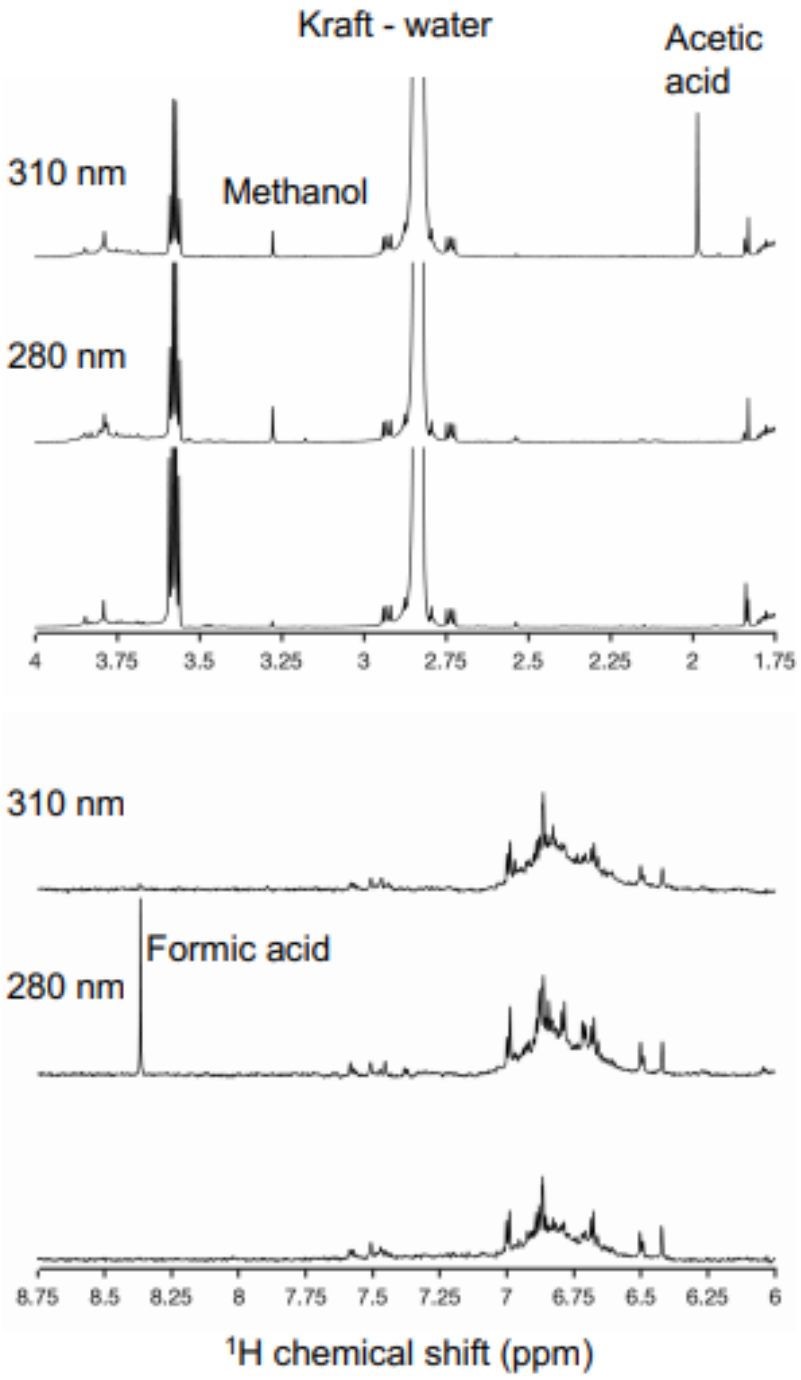


Figure 3.6: ^{1}H-NMR spectra for Kraft lignin exposed to high doses of 310 nm and 280 nm UV light compared to the control sample in neutral water. The presence of acetic acid in 310 nm sample is clearly shown and formic acid in 280 nm sample additionally. The presence of methanol is evident from the peak at 3.25 ppm.

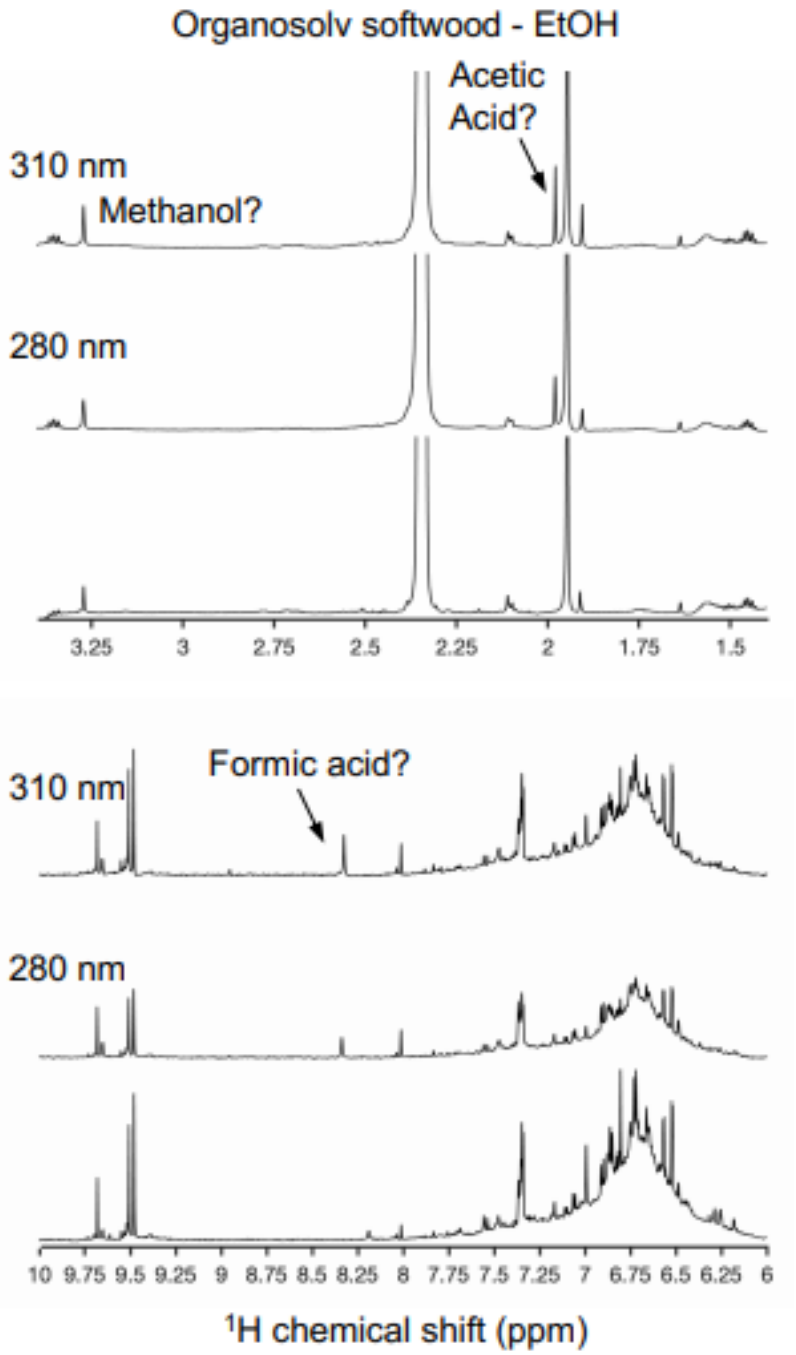


Figure 3.7: ^{1}H-NMR spectra for softwood organosolv lignin exposed to high doses of 310 nm and 280 nm UV light compared to the control sample in EtOH. Difficulties are present for the identification of compounds to the peaks, formic acid is judged to be found at 8.25 ppm.

3.4 Moving forwards

No analysis on any changes in the potential solid phase have been preformed in this study due to unforeseen circumstances and lack of time. To investigate the possibility of depolymerization or polymerization induced by the UV light a Gel Permeation Chromatography analysis could be preformed. The residual solid phase could be collected and the molecular size distribution analyzed. A change to the molecular size distribution between the irradiated samples and control samples could show if and polymerization occurs or not. IR spectroscopy on the residual solid samples could also be valuable information for characterization as IR units more sensitive than the one used in this study exists. The possibility to use a diffusive sphere in the UV/VIS spectrophotometer to allow for analysis of solid samples is currently looked into. Expanding the NMR analysis with the inclusion of solid state NMR analysis will also be preformed moving forward, an obstacle currently is the large sample size needed of 25 mg UV exposed solid phase.

It was found during the course of the project that the exposure set up as of now have possibly more influencing parameters then noted before. With a UV sensor module the light output from the optical fibers and LEDs were measured and it was found that the arc of the fibers had a large effect on the measured values. This is probably due to the way the light was captured at the LED surface and then emitted to the sensor surface were both surface defects and small changes in position showed a large difference. The position of the magnet in the test vial relative to the end of the optical fiber was also not controlled for. Possibly the magnet used for mixing might block the light diminishing the effective UV dose between different

samples. To solve these issues a new reactor design might be the best course of action which could utilize UV transparent quartz vials for the exposure. This would allow for the UV light to pass from the LEDs to the samples without the need for an optical fiber, and related light losses, to bypass the normally short wavelength UV blocking glass. To improve the situation with the current design might be to replan the experimental design to include more repeats to improve the statistical analysis. The lower dose experiments could also be left out since little to no change occurred saving resources and time for future work. For the current design the absolute quantification of the UV light reaching the samples remains a challenge to overcome. Currently only the calculated UV output from the LEDs can be tracked, only relative amounts can be found for the actual samples.

4
Conclusion

This project has not been able to say how the action of short wavelength UV-light alone effects technical lignin, dissolved or not in the solvent phase. Indications of a oxidizing reaction, possibly with dissolved oxygen, might be present due to the presence of different carboxylic acids but no affirmation of that has been done, it is expected from other UV degradation studies however. Progress have been done for a better designed follow up study. Many combinations of lignin and solvent did not provide any visual change upon exposure, indicating that if anything changes it is subtle. A high concentration will be an improvement for easier detection during analysis.

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A

Appendix

The complete set of all test samples after exposure and several weeks of rest.

A.1 Kraft lignin series:

Figure A.1: Complete set of Kraft lignin in AcN, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 1A, high dose 310 nm 2A, high dose 280 nm.

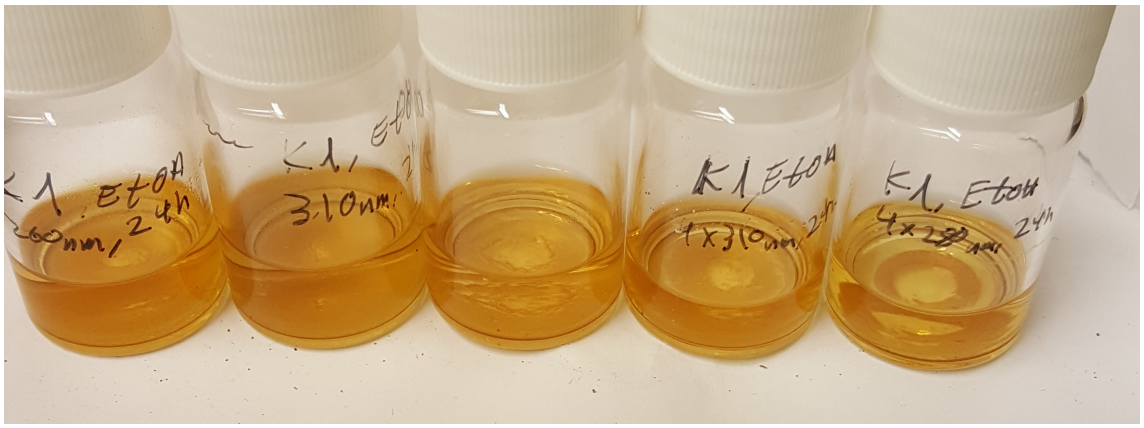

Figure A.2: Complete set of Kraft lignin in EtOH, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

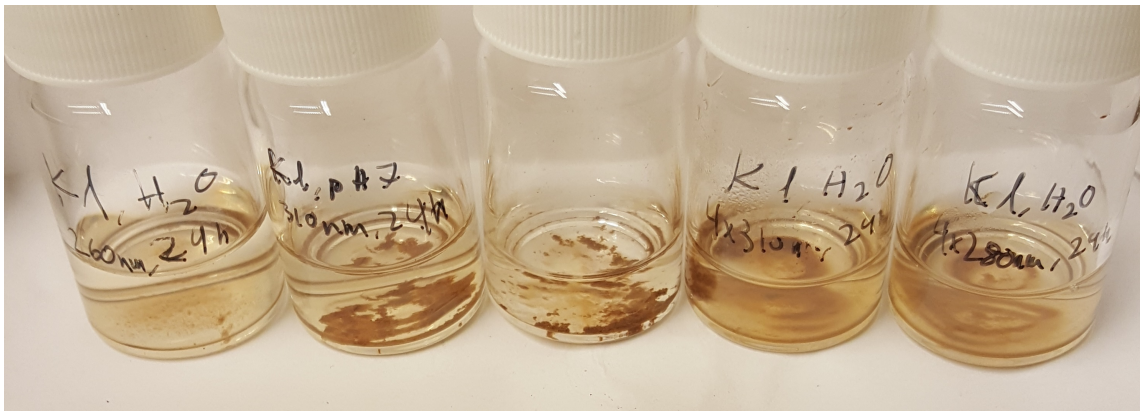

Figure A.3: Complete set of Kraft lignin in neutral water, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

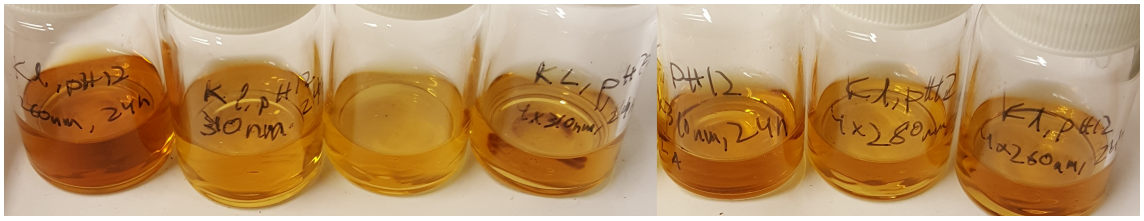

Figure A.4: Complete set of Kraft lignin in pH12 solution, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 1A, high dose 310 nm 2A, high dose 280 nm, high dose 260 nm.

A.2 Softwood Organosolv lignin series:

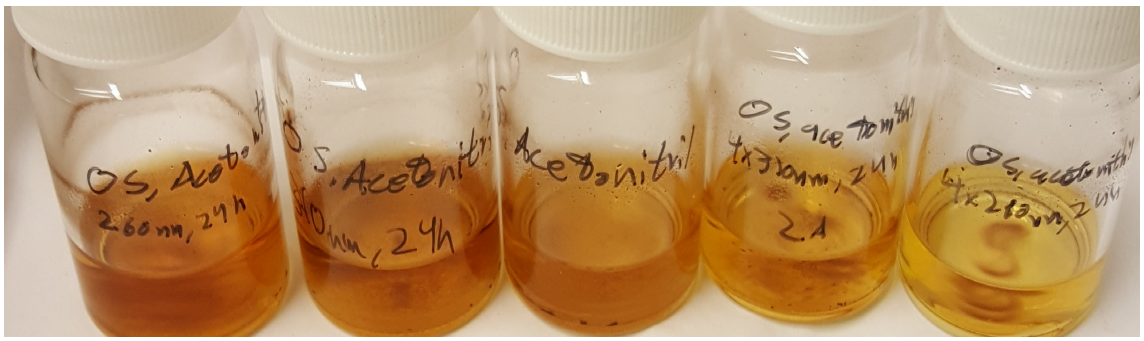

Figure A.5: Complete set of OS lignin in AcN, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

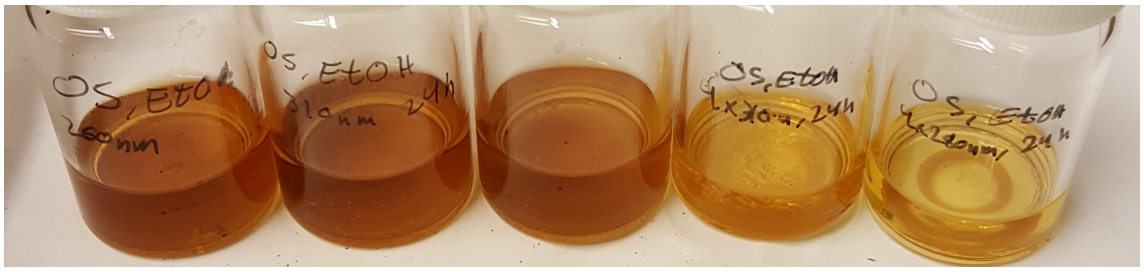

Figure A.6: Complete set of OS lignin in EtOH, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

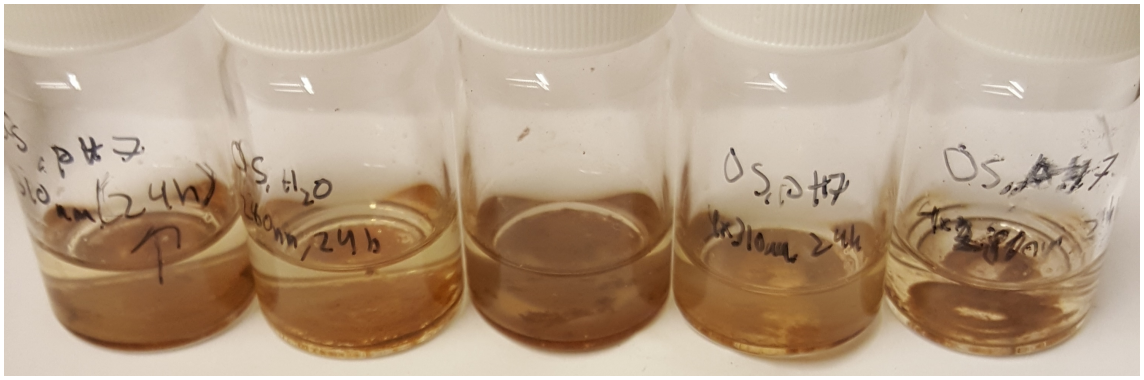

Figure A.7: Complete set of OS lignin in neutral water, From left to right: low dose 310 nm, low dose 260 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

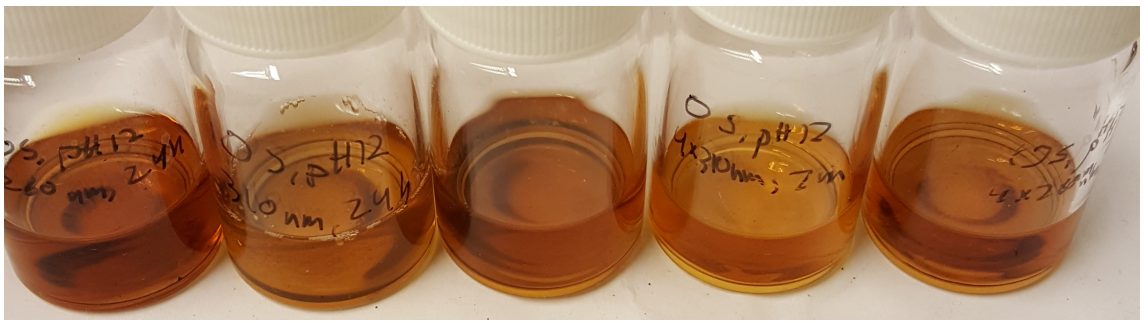

Figure A.8: Complete set of OS lignin in pH12 solution, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

A.3 Hardwood Organosolv lignin series:

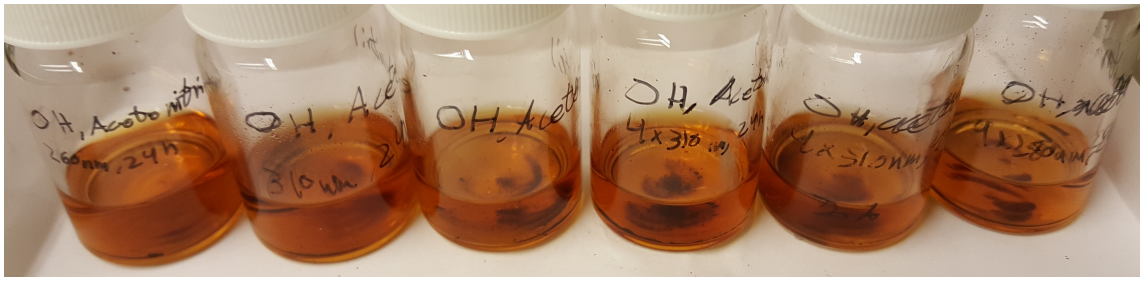

Figure A.9: Complete set of OH lignin in AcN, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 1A, high dose 310 nm 2A, high dose 280 nm.

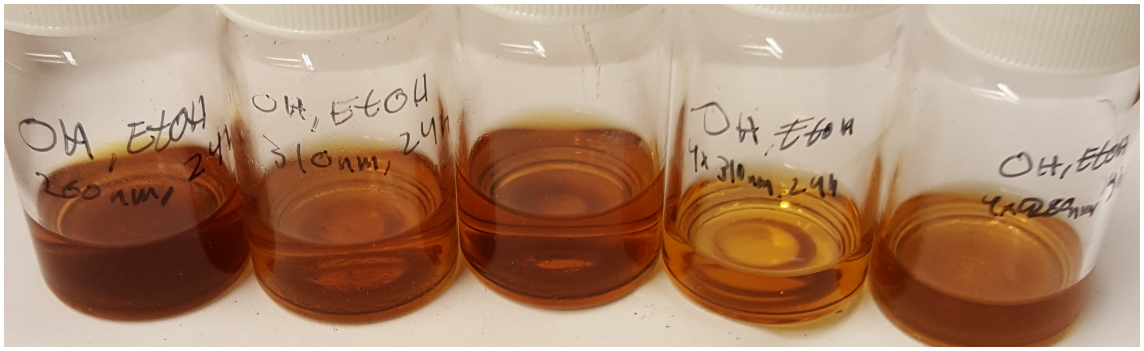

Figure A.10: Complete set of OH lignin in EtOH, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

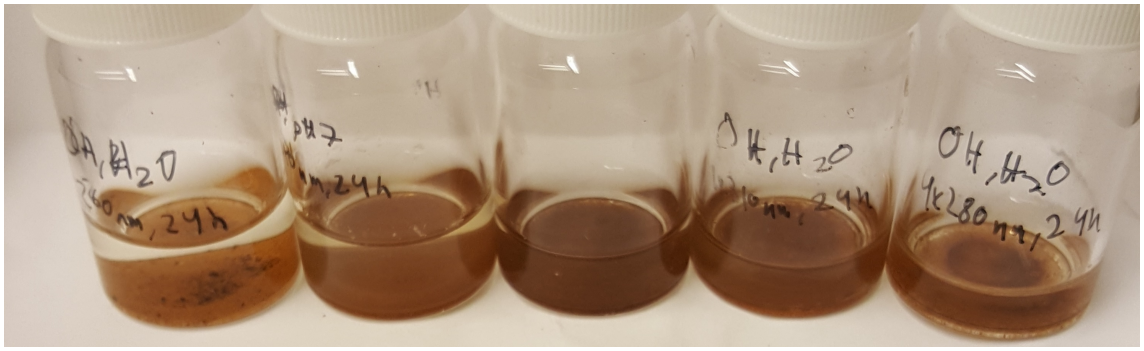

Figure A.11: Complete set of OH lignin in neutral water, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 2A, high dose 280 nm.

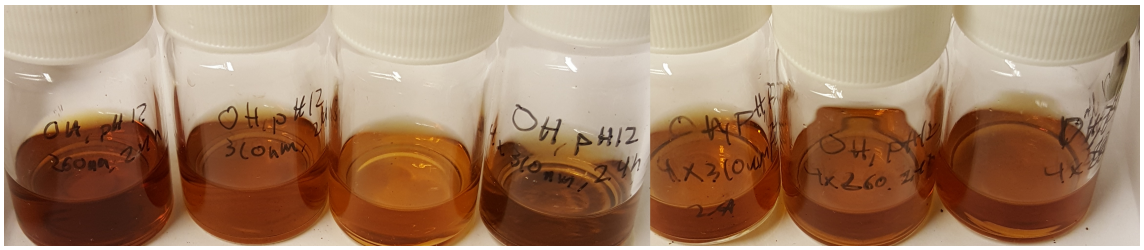

Figure A.12: Complete set of OH lignin in pH12 solution, From left to right: low dose 260 nm, low dose 310 nm, control sample, high dose 310 nm 1A, high dose 310 nm 2A, high dose 260 nm, high dose 280 nm.

A.4 UV spectras

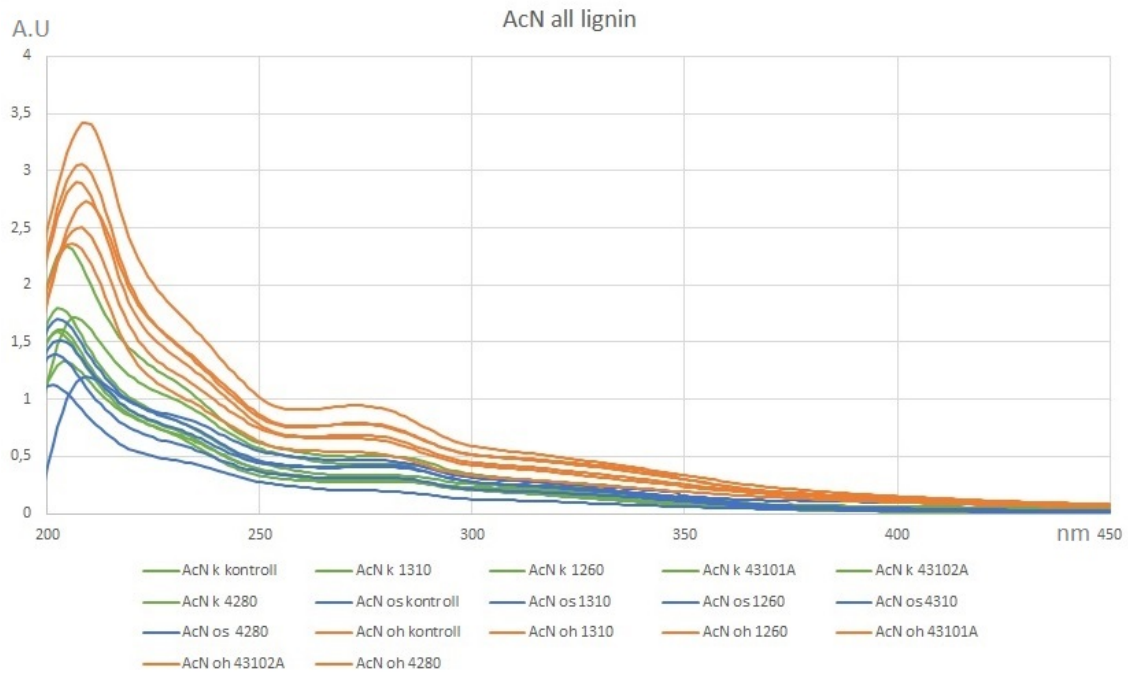

Figure A.13: UV spectra of all lignins in AcN. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively.

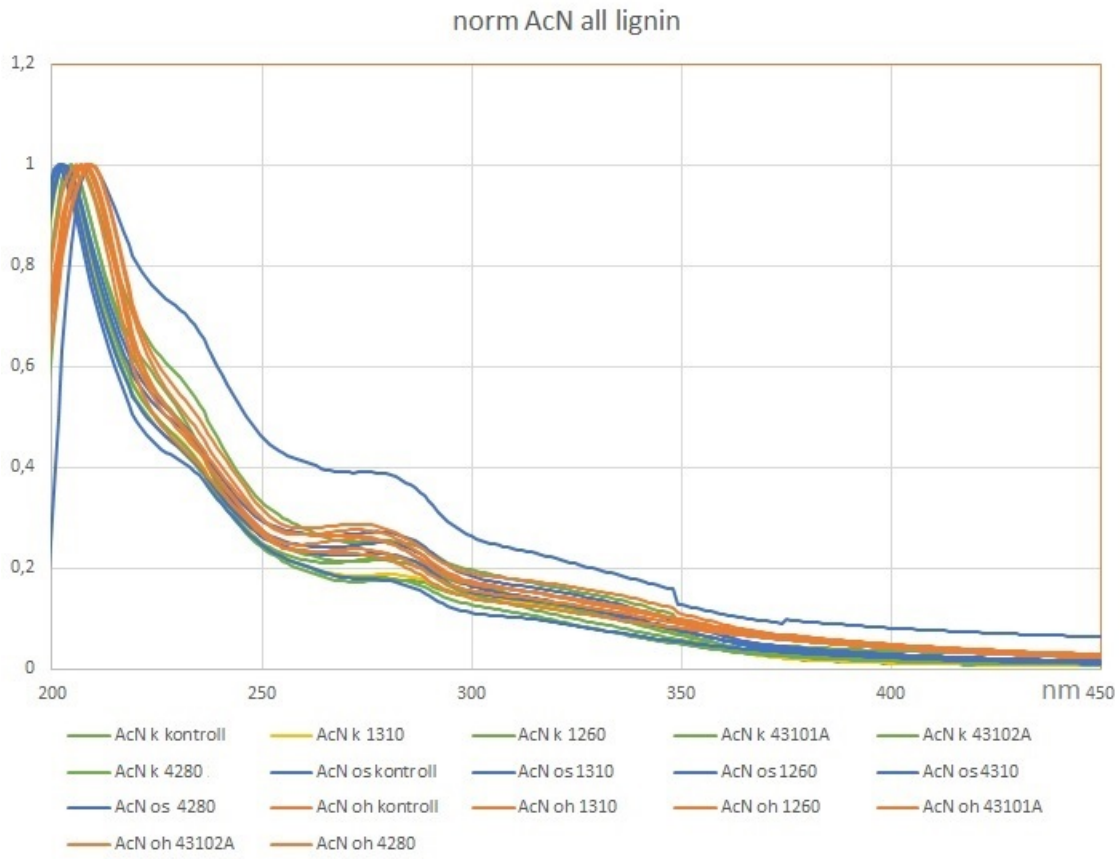

Figure A.14: The normalized UV spectra of all lignins in AcN. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively.

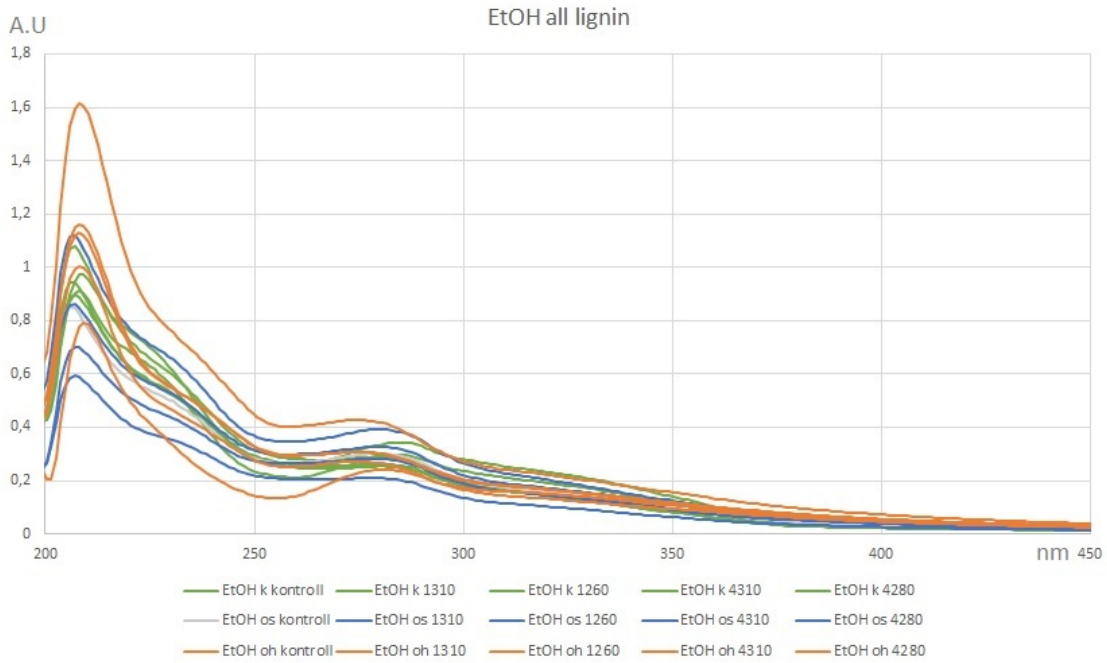

Figure A.15: UV spectra of all lignins in EtOH. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively. The peak close to 200 nm is close to the UV cutoff threshold of ethanol at 210 nm suggesting care should be taken at interpreting the peak.

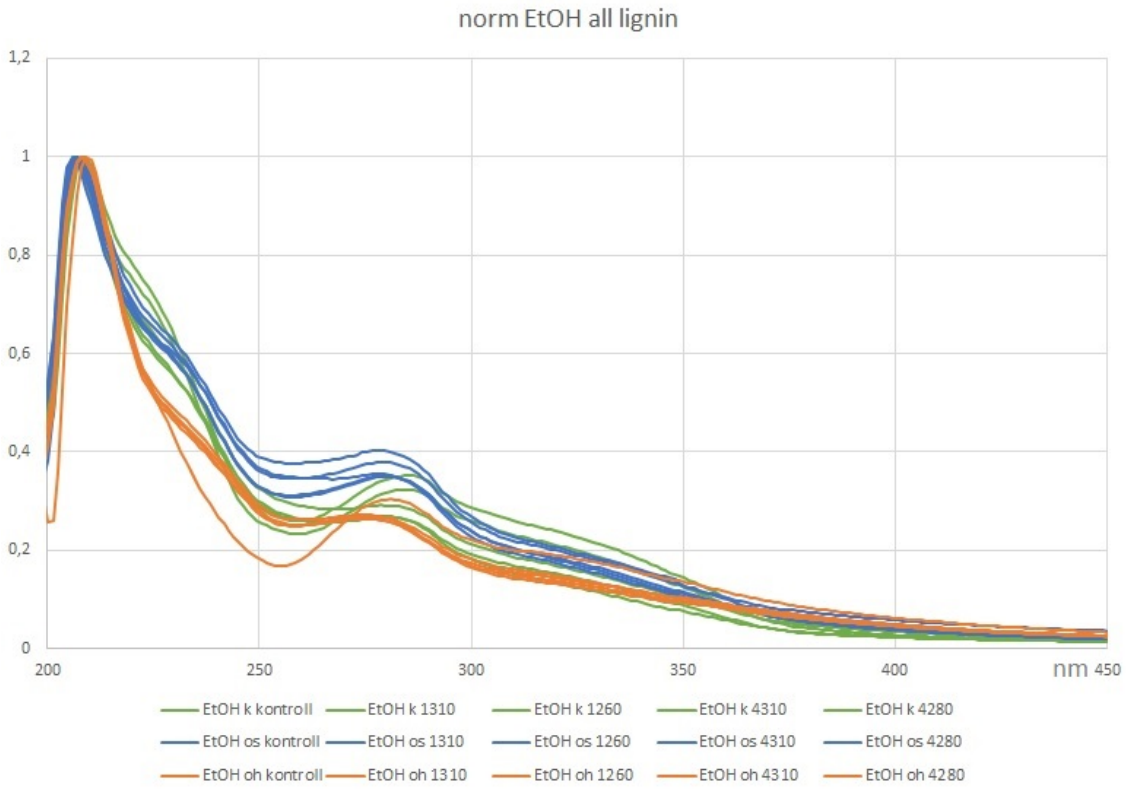

Figure A.16: The normalized UV spectra of all lignins in EtOH. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively. The peak close to 200 nm is close to the UV cutoff threshold of ethanol at 210 nm suggesting care should be taken at interpreting the peak.

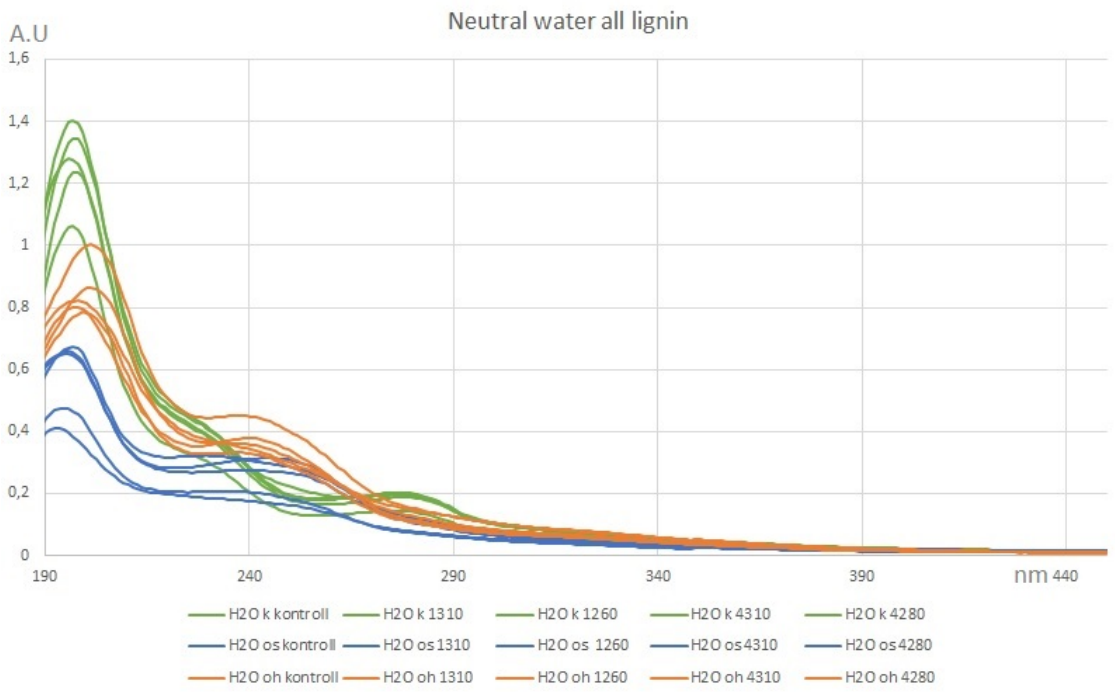

Figure A.17: UV spectra of all lignins in neutral water. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively.

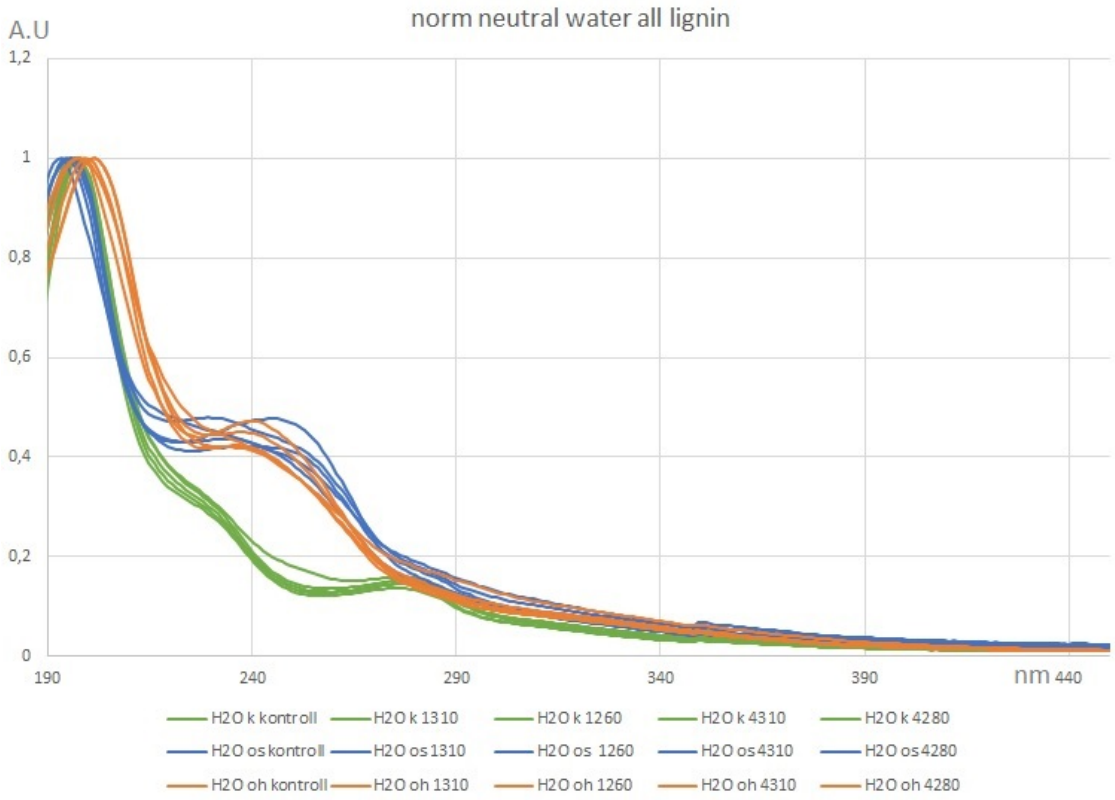

Figure A.18: The normalized UV spectra of all lignins in neutral water. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively.

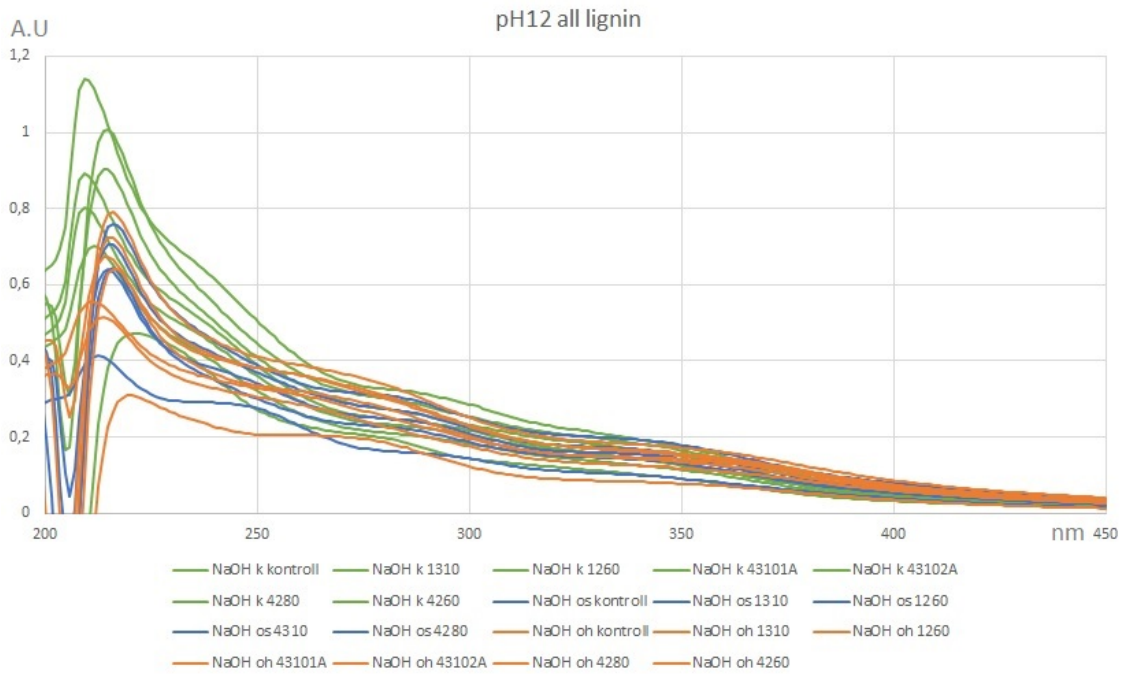

Figure A.19: UV spectra of all lignins in pH12 solvent. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively. It is not known why several of the curves cut the x-axis after several attempts to fix the problem.

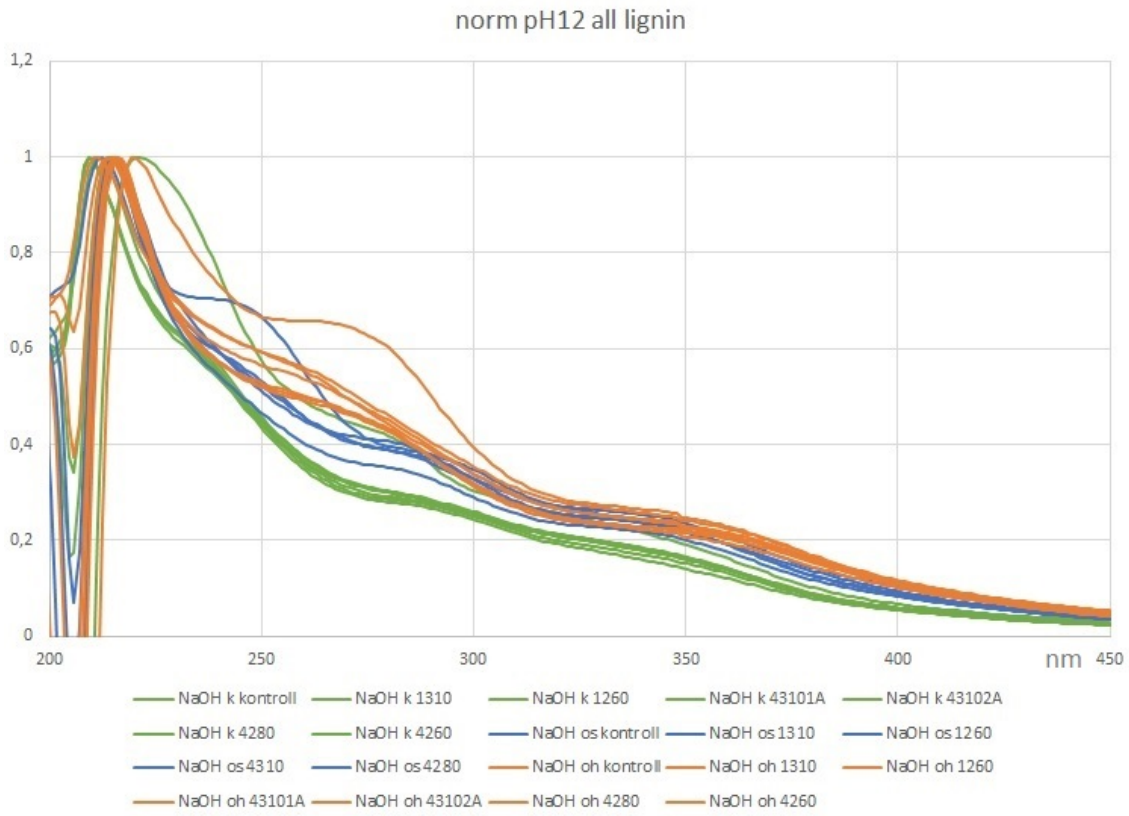

Figure A.20: The normalized UV spectra of all lignins in pH12 solvent. Kraft lignin, softwood and hardwood organosolv are green, blue and orange respectively. It is not known why several of the curves cut the x-axis after several attempts to fix the problem.

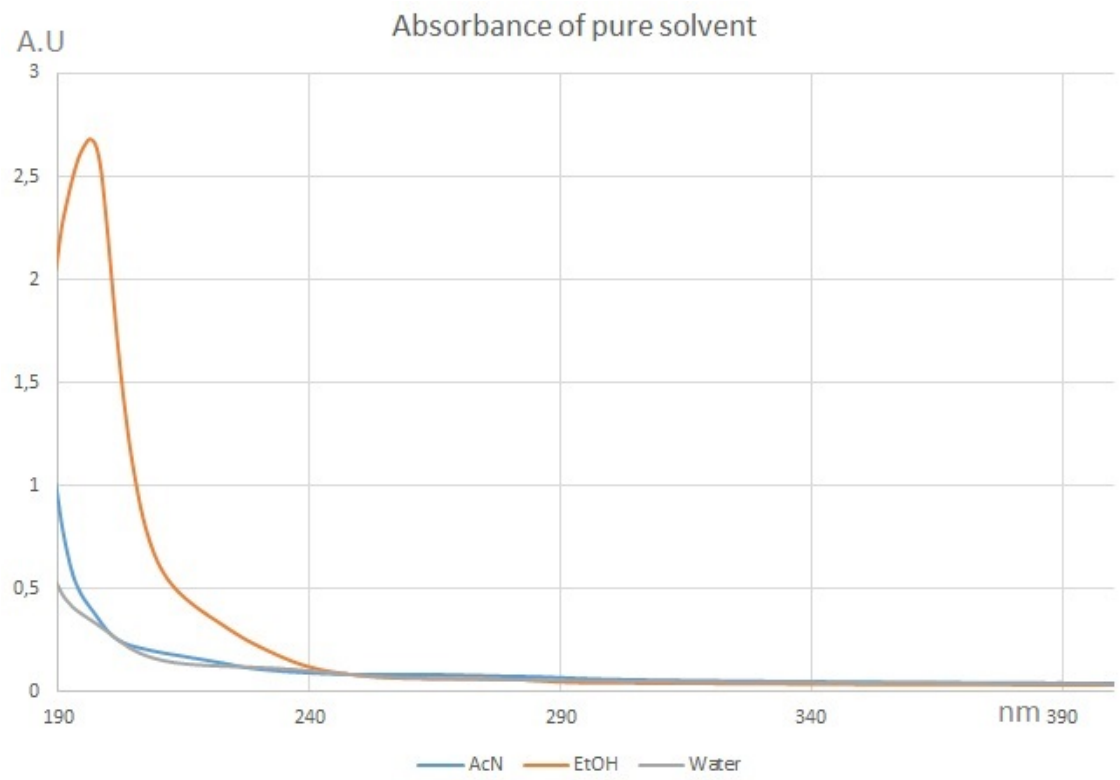

Figure A.21: The absorbance of the pure solvents compared to air without a reference cuvette. It is clear to see the UV cut off of EtOH at 205-206 nm and AcN close to 190 nm.