

1 Article

2 Lignin-Depolymerisation via UV-Photolysis and 3 Titanium Dioxide Photocatalysis

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11 **Abstract:** Today, more than 70 million tons of lignin are produced by the pulp and paper industry
12 every year. However, the utilization of lignin as a source for chemical synthesis is still limited due
13 to the complex and heterogeneous lignin structure. The purpose of this study was a selective
14 photodegradation of industrially available kraft lignin in order to obtain appropriate fragments
15 and building block chemicals for further utilization, e.g. polymerization. Thus, kraft lignin
16 obtained from soft wood black liquor by acidification was dissolved in sodium hydroxide and
17 irradiated at a wavelength of 254 nm with and without the presence of titanium dioxide in various
18 concentrations. Analyses of the irradiated products via SEC showed decreasing molar masses and
19 decreasing polydispersity indices over time. At the end of the irradiation period the lignin was
20 depolymerised to form fragments as small as the lignin monomers. TOC analyses showed minimal
21 mineralisation due to the depolymerisation process.

22 **Keywords:** kraft lignin; photolysis; photocatalysis; actinometry; OH-number; SEC; UV-VIS;
23 ATR-FTIR; XRD
24

25 1. Introduction

26 Currently 95 % of all chemical substances are produced from petroleum. In view of the limited
27 occurrence and the rapid exhaustion of fossil resources, the efforts of many scientists are focusing on
28 the use of alternative sources [1]. One of the most promising alternatives could be lignin, which is
29 the third most common biopolymer on earth. Lignin is a complex, three-dimensional irregularly
30 cross-linked polymer which, as a constituent of woody plants, makes up one third of the dry mass of
31 the wood in addition to cellulose and hemicellulose [2]. Being produced as a by-product in the pulp
32 and paper industry in an amount of about 70 million tons per year, it is currently used solely as a
33 renewable combustible raw material for energy generation [3]. Despite recovery, some of the lignin
34 still finds its way into the environment with the wastewater. Since lignin is very resistant to
35 microbial degradation, it cannot completely be removed by conventional wastewater treatment
36 techniques [4].

37 An approach to overcome this difficulty is to irradiate the effluents with ultraviolet light (UV)
38 in the presence of titanium dioxide (TiO₂) as a catalyst. By indirect photolysis and heterogeneous
39 photocatalysis, organic impurities such as lignin can completely be mineralised to carbon dioxide
40 and water [5]. However, the mechanism for wastewater treatment can also be used for controlled
41 depolymerisation of lignin. As it is a natural aromatic macromolecule, organic chemicals and
42 valuable substances can be extracted. Current work by Hansen *et al.* investigating the degradation
43 process on solid organosolv lignin using pyrolysis GC/MS showed pure lignin fractions and
44 phenolic products originating from monolignols [6]. Alvarado-Morales *et al.* performed
45 TiO₂/UV-based photocatalytic degradation and quantified vanillic acid and ferulic acid as main
46 organic products. They found different yields of these products by varying reaction parameters such

47 as irradiation time and catalyst concentration [7]. Nair *et al.* studied the photocatalytic lignin
48 fragmentation to enhance the contact between lignin and TiO₂ and thus improved the degradation
49 process. The phenolic products were identified via GC/MS [8]. Xu and colleagues recently
50 summarized recent advances in the selective decomposition of lignin-based compounds via
51 photocatalysis in a critical review [9].

52 This scientific work includes the photolytic and photocatalytic degradation of lignin at the
53 molecular level. Influences of irradiation time and photocatalyst concentration on the degradation
54 process were investigated. The degradation products were analysed by chromatography (SEC),
55 spectroscopy (ATR-FTIR, UV-VIS) and wet-chemistry (OH-number, total organic carbon (TOC)).

56 2. Results

57 2.1. X-Ray Powder Diffraction of the Photocatalyst

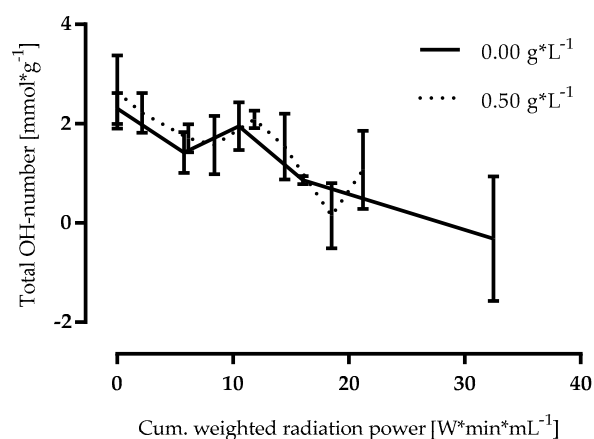
58 The photocatalyst used for the experiments was analysed using X-ray powder diffraction.
59 Using the software Bruker Diffrac.EVA, the crystallinity was determined. The provided AEROXIDE
60 P25® shows a crystalline and amorphous share of 90.5 % and 9.5 %, respectively. As titanium
61 dioxide naturally exists in three different crystal modifications, namely anatase, rutile and brookite
62 [9], and these have different photocatalytic activities, the three modifications were quantified using
63 Rietveld refinement (Bruker Diffrac.TOPAS). The provided titanium dioxide is found to be 85.49 %
64 anatase, 14.30 % rutile and 0.21 % brookite. Considering the amorphous share, the total composition
65 is 77.4:12.9:0.2:9.5 (anatase:rutile:brookite:amorphous share).

66 2.2. Characterisation of the Annular Reactor

67 As the radiation output of the used UV-lamp is not constant over its entire life span, the
68 performance of the lamp was evaluated before and after the experimental program using
69 Hatchard/Parker-actinometry. The UV-radiation output was 15'800 mW at the beginning and 12'200
70 mW at the end. To estimate the actual output at the beginning of each irradiation experiment, the
71 determined outputs were interpolated in a linear fashion.

72 2.3. Total Hydroxyl Group Determination

73 For future synthesis of polyurethanes, the knowledge of the total hydroxyl group content is
74 important. Therefore, this parameter was determined using a method based on ISO 14900:2001 (E).
75 Figure 1 shows the development of the hydroxyl group content over the course of the irradiation
76 experiment. As the withdrawn sample volume of 300 mL each compared to the starting volume of
77 5'000 mL is not insignificant and the radiation output remains almost constant during the
78 experiment, the radiation power needs to be weighted for the volume which is irradiated. With
79 proceeding irradiation times, a decrease in total hydroxyl group content can be observed,
80 independent from the catalyst concentration being used.

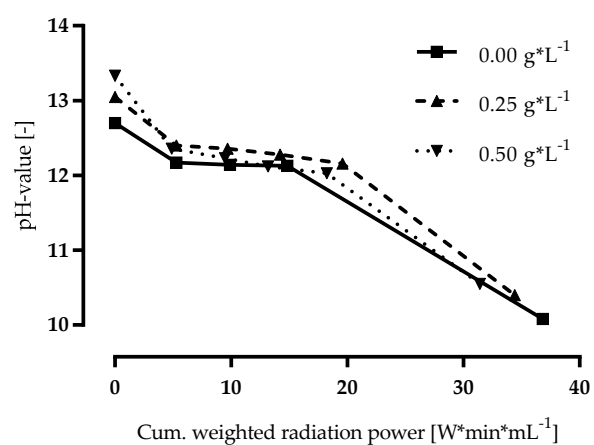


81

82 **Figure 1.** Total hydroxyl group content of the irradiated lignins plotted versus the cumulated
83 weighted radiation power.

84 2.4. pH-Value

85 The pH-value of the lignin solutions was monitored during the irradiation process and is
86 depicted in Figure 2. A decrease in pH-value can be observed for all experiments, independent from
87 the catalyst concentration being used.

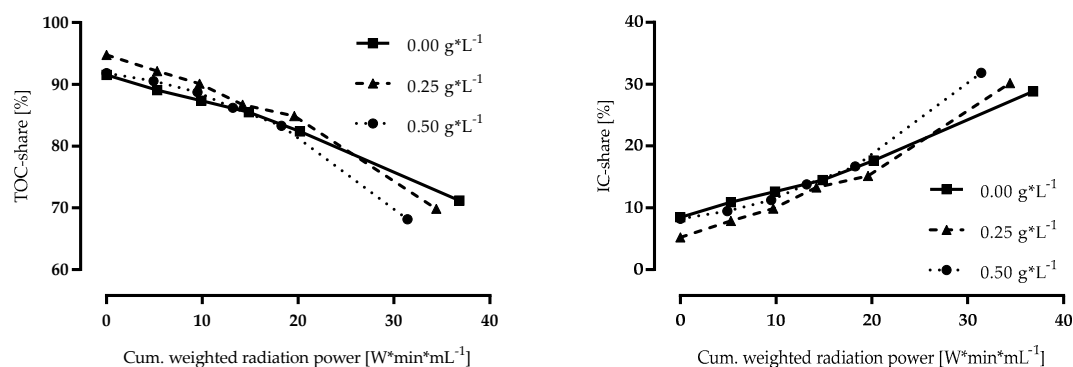


88

89 **Figure 2.** pH-values of the lignin solutions during the irradiation process.

90 2.5. Total Organic Carbon

91 As depicted in Figure 3 the content of total organic carbon (TOC) decreases with the proceeding
92 irradiation process while the content of inorganic carbon (IC) increases. A correlation between the
93 catalyst concentration and decrease of TOC or increase of IC cannot be observed.



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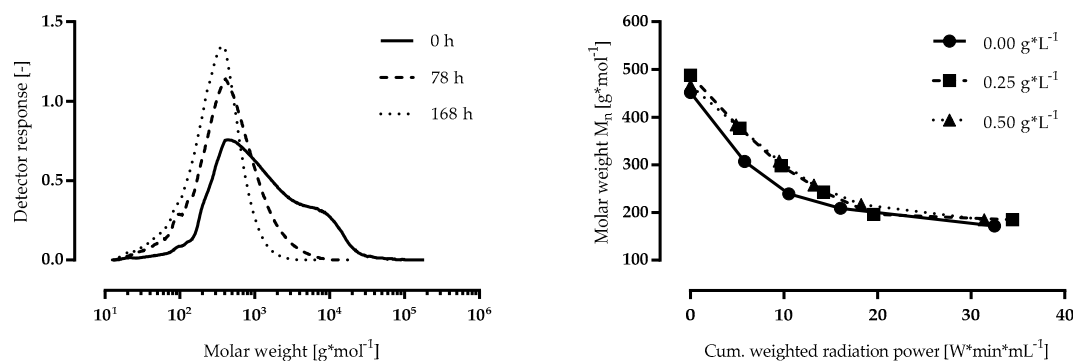
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Figure 3. (a) TOC and (b) IC of the lignin solutions during the irradiation process.

96

2.6. Size Exclusion Chromatography

97 To evaluate the impact of the irradiation process on the molecular weight of lignin, size
 98 exclusion chromatography was performed on the isolated samples. Figure 4a shows the molar
 99 weight distribution of the lignins isolated from the irradiation experiment using $0.25 \text{ g}^*\text{L}^{-1}$ of the
 100 catalyst. All curves are normalised so that changes in the shape of the curves can be evaluated more
 101 easily. The longer the lignin solution was irradiated, the more the maximum of the respective curve
 102 is shifted towards smaller molar weights. Furthermore, the width of the respective curve decreases
 103 with the proceeding irradiation process. Figure 4b shows the changes in the number average molar
 104 weight for all the irradiation experiments. All curves show the same trend. The number average
 105 molar weight decreases over the course of the irradiation experiment, independent from the catalyst
 106 concentration being used.



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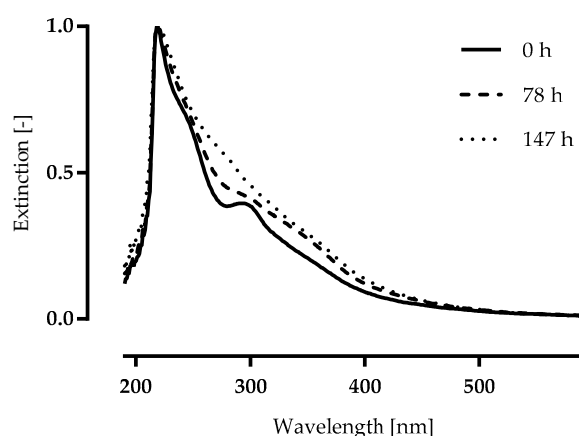
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Figure 4. (a) Molar weight distribution of the lignins isolated. The areas under the curves are normalised. (b) Changes in number average molar weight (M_n).

110

2.7. UV-VIS Spectroscopy

111 UV-VIS-spectra of the irradiated and isolated lignins were recorded in aqueous sodium
 112 hydroxide. As all spectra look similar, the spectra of the lignins from the irradiation experiment
 113 using $0.00 \text{ g}^*\text{L}^{-1}$ of the catalyst are depicted in Figure 5. For easier comparison, the spectra are
 114 normalised to their maximum. The unirradiated lignin shows an absorption shoulder at 280-295 nm,
 115 which gradually disappears with the proceeding irradiation process until it cannot be identified
 116 anymore.



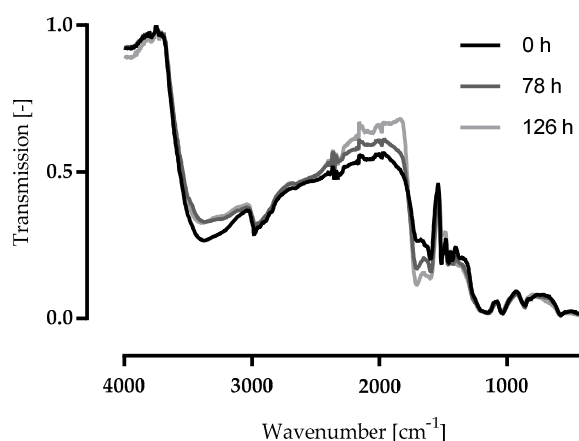
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Figure 5. UV-VIS-spectra of the irradiated lignins. Spectra are height normalised.

119 2.8. ATR-FTIR Spectroscopy

120 FTIR-spectra of the lignins were recorded using the ATR technique. Since the spectra of the
 121 different irradiation experiments almost look the same, only the spectra of the experiment using 0.25
 122 g*L⁻¹ are depicted in Figure 6.



123

124

Figure 6. ATR-FTIR-spectra of the irradiated lignins.

125 An assignment of the absorption bands to the functional groups is shown in Table 1.
 126 Comparing the FTIR-spectra shows that the absorption band at 3'380 cm⁻¹ which is caused by the
 127 hydroxyl group in relation to the band at 2'980 cm⁻¹ decreases with the irradiation progress. Relating
 128 the band at 1'700 cm⁻¹ to the band at 1'600 cm⁻¹ an increase of the band at 1'700 cm⁻¹ can be observed.
 129 A decrease of the bands at 1'510 cm⁻¹ and 1'460 cm⁻¹ can also be observed.

130

131

Table 1. Assignment of the absorption bands to the functional groups.

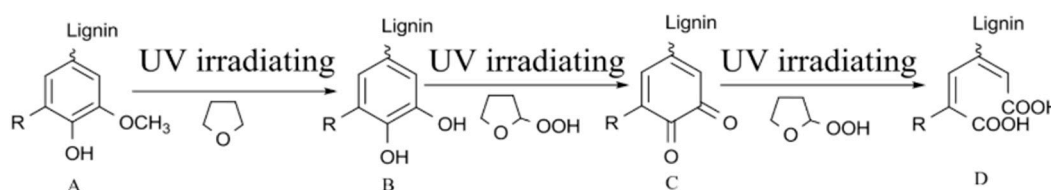
Measured wavenumber [cm ⁻¹]	Typical wavenumber [cm ⁻¹]	Vibrational mode
3'380	3'650-3'200	O-H stretching vibration
2'980	3'000-2'840	C-H stretching vibration in -CH, -CH ₂ or -CH ₃
1'700	1'707-1'690	C=O stretching vibration (conjugated)
1'600	1'625-1'575	arC-C vibration
1'510	1'525-1'475	arC-C vibration
1'460	1'475-1'430	Asymmetric deformation vibration of -CH ₂ and -CH ₃

132 3. Discussion

133 Analysis of the degraded lignins showed that the total hydroxyl group content decreases with
 134 increasing irradiation times. This observation was also made by Wang *et al.* who discovered a
 135 reduction of phenolic hydroxyl group content by up to 41 % [11]. The herein presented results
 136 suggest a reduction of total hydroxyl group content by up to 100 %.

137 These results must be interpreted with caution, as all samples were prepared by acidic
 138 precipitation without further washing. As acidity of the samples was not corrected for, remaining
 139 acid from the precipitation process might interfere with the results. However, the same trend could
 140 be validated by means of ATR-FTIR.

141 The recorded ATR-FTIR-spectra indicate a reduction of OH-stretching vibration (3'380 cm⁻¹) in
 142 relation to the aliphatic CH-stretching vibration (2'980 cm⁻¹) and simultaneously an increase of the
 143 conjugated C=O-stretching vibration (1'700 cm⁻¹). At the same time, a decrease of aromatic vibrations
 144 (1'510 cm⁻¹ and 1'460 cm⁻¹) can be observed. As the TiO₂/UV-process is described to have an
 145 oxidative mechanism it is plausible that hydroxyl groups are first oxidised to form carbonic acids
 146 and then ultimately mineralised to carbon dioxide and water [12]. Wang *et al.* postulated a
 147 mechanism for the formation of carbonic acids from lignin depicted in Figure 7.
 148



149

150 **Figure 7.** Reaction mechanism for the decolourisation of lignin via UV-irradiation in THF.

151 Reproduced from Wang *et al.* [11].

152 The formation of carbonic acids and carbon dioxide might also be a possible explanation for the
 153 decrease in pH-value. Figure 7 shows the destruction of the aromatic ring which is consistent with
 154 the findings obtained by ATR-FTIR as well as UV-VIS spectroscopy.

155 UV-VIS spectroscopy shows an absorption shoulder for untreated lignin at 280-295 nm which
 156 can be assigned to the structure of the monomers coniferyl alcohol and sinapyl alcohol [13]. The
 157 dissolution of this absorption shoulder correlates with the decrease of aromatic vibrations and
 158 strengthens the evidence for the destruction of the aromatic ring suggested by Wang *et al.* [11].

159 The formation of carbon dioxide was proven by TOC measurements indicating an increase of
 160 inorganic carbon content. This observation can be explained by partial mineralization of lignin (30
 161 %), further proving the oxidative character of the TiO₂/UV process. Carbon dioxide formation could
 162 also be observed by Ohnishi *et al.* by means of gas chromatography [12].

163 As it was intended to depolymerise lignin, size exclusion chromatography is the method of
 164 choice for evaluating the lignin fragments. Prado *et al.* investigated the depolymerisation of
 165 organosolv lignin showing a reduction in molar weight from 941 g*⁻¹mol down to 763 g*⁻¹mol [14].

166 As a matter of fact, our results even show a decrease from approx. 500 g^{*}mol⁻¹ down to 170 g^{*}mol⁻¹
167 correlating with the average molar weight of the lignin monomers of 180 g^{*}mol⁻¹ (paracoumaryl
168 alcohol: 150 g^{*}mol⁻¹, coniferyl alcohol: 180 g^{*}mol⁻¹, sinapyl alcohol: 210 g^{*}mol⁻¹).

169 Since the commercial catalyst AEROXIDE P25® is a mixture of titanium dioxide modifications
170 with anatase being the photocatalytically most active one, the composition was determined using
171 x-ray powder diffraction together with Rietveld refinement. The total composition of the provided
172 AEROXIDE P25® was 77.4:12.9:0.2:9.5 (anatase:rutile:brookite:amorphous share) confirming the
173 findings of Ohtani *et al.* reporting a composition of 78:14:8 (anatase:rutile:amorphous share) [15].

174 Although the provided photocatalyst could positively be identified as the highly active
175 AEROXIDE P25®, no significant differences regarding the analytical results could be observed,
176 when comparing the catalyst concentrations used. One plausible explanation could be that on the
177 one hand the used catalyst:lignin ratio was too low and on the other hand the lignin concentration
178 was too high. Previous studies reported catalyst:lignin ratios of 50:1 [11], 5:1-200:1 [16] or 1:1,8-1,6:1
179 [17]. The catalyst:lignin ratios used by us (0:1-1:10) and the high lignin concentration might result in
180 total absorption of UV-radiation solely by lignin, thus leading to a pure photolysis instead of
181 photocatalysis, rendering the photocatalyst ineffective as described by Kansal *et al.* [16]. A reduction
182 of chemical oxygen demand and UV-absorption was also observed by Chang *et al.* who investigated
183 the degradation of lignin via pure photolysis [5].

184 4. Materials and Methods

185 4.1. Precipitation of Lignin from Black Liquor

186 Kraft-lignin was isolated from soft wood black liquor by acidic precipitation. Prior to
187 acidification, the black liquor provided by ZPR (Rosenthal, Germany) was vacuum filtrated using
188 filter papers with 12-15 µm particle retention. Under constant stirring sulfuric acid (25 vol. %) was
189 added dropwise. After reaching a pH-value of 2 the suspension was stirred for another 1 h before it
190 was centrifuged at 3'000 rpm for 15 mins. For washing, the supernatant was discarded, replaced
191 with deionised water, re-suspended and centrifuged again. The washed lignin (3 times) was then
192 freeze-dried for 48 h.

193 4.2. Irradiation Experiments

194 For the irradiation process a reactor comprising a water-cooled quartz annulus with an
195 UV-lamp (UVX 60 by UV-Technik, Germany), a 5 L reservoir and a centrifugal pump was used. The
196 previously prepared lignin was dissolved in aqueous sodium hydroxide solution (5 g^{*}L⁻¹ in 0.1
197 mol^{*}L⁻¹) and added with different amounts of AEROXIDE P25® (0.00 g^{*}L⁻¹, 0.25 g^{*}L⁻¹ and 0.50 g^{*}L⁻¹).
198 5 L of the solution were irradiated at room temperature for up to 7 days and samples of 300 mL were
199 taken daily.

200 4.3. Isolation of Fragmented Lignins

201 For further analysis, the irradiated lignins were isolated in a process analogue to the process
202 mentioned above. Instead of precipitating the irradiated lignins at a pH-value of 2, which usually
203 gives the highest yield [18], a pH-value of 1 was chosen, as some of the irradiated lignins remain
204 dissolved at a pH-value of 2. Also, the precipitated lignins were not washed, as some of the lignins
205 even were soluble in deionized water. Prior to acidification the AERODIDE P25® was removed by
206 vacuum filtration using filter papers with 0.45 µm particle retention.

207 4.4. Hatchard/Parker Actinometry

208 The characterisation of the annular reactor was performed as described by Hatchard and Parker
209 1953. Before the actinometry could be performed, the apparatus including all sample containing
210 glassware were completely covered in aluminium foil, as the reaction used to determine the
211 UV-power is sensitive to light. For the quantification of Fe²⁺-ions in form of the ferriox-complex a
212 calibration in a range of 0.04-8.00 mg^{*}L⁻¹ was prepared. In addition, 5 L of a 50 mmol^{*}L⁻¹

213 potassium-ferrioxalate solution was prepared. After a pre-heating phase of the UV-lamp 12 samples
 214 of 3 mL were taken within 12 mins and incubated with phenanthroline for 1 h. The samples were
 215 then analysed using a UV-VIS-spectrometer at 510 nm (Lambda 19 by Perkin Elmer, USA).

216 4.5. OH-Number Determination via Acetylation

217 For the determination of the OH-number a procedure based on ISO 14900:2001 (E) was used.
 218 Modifications were made regarding the acetylation temperature and time as well as the sample
 219 amount and the amount of the acetylation reagent. Thus, 25 mg of the lignins were weighed into a
 220 1.5 mL reaction vessel and added with 850 μ L acetylation reagent. Inspired by Clauss *et al.* [19] and
 221 Baumberger *et al.* [20], who acetylated their samples at room temperature for 20 h and 6 days,
 222 respectively, an acetylation time of 72 h at room temperature was chosen. Excess of acetic anhydride
 223 was titrated with 0.2 mol*L⁻¹ sodium hydroxide using an automated titrator (Stabino PMX 400 by
 224 Particle Metrix, Germany). All measurements were repeated 6 times.

225 4.6. Total Organic Carbon (TOC)

226 For TOC analysis, all samples taken from the reactor were diluted 1/20 in 0.1 mol*L⁻¹ aqueous
 227 sodium hydroxide and measured in triplicates (TOC-L by Shimadzu, Japan).

228 4.7. Size-exclusion Chromatography (SEC)

229 To evaluate the depolymerisation of the lignins SEC was performed using the parameters
 230 shown in Table 2. Samples with a concentration of 2 mg*mL⁻¹ were prepared in THF and filtrated
 231 with 0.2 μ m PTFE filters prior to analysis. For molar weight evaluation polystyrene was used as a
 232 calibration standard.

233 **Table 2.** SEC set up and parameters.

Component	Description	Parameter
Eluent	THF p.a.	HPLC-grade
Pump	Agilent 1100 Series	Flowrate: 1.000 mL*min ⁻¹
Injector	Rheodyne 7725i sample loop	Injection volume: 100 μ L
Oven	Agilent 1100 Series	Temperature: 35 °C
Column	1x PSS SDV 8*50 mm pre-column	Particle size: 5 μ m
	2x PSS SDV 8*300 mm Linear M 5 μ	Particle size: 5 μ m Molar weight range: 50-10'000'000 g*mol ⁻¹
Detector	Agilent 1100 Series VWD	Wavelength: 280 nm
Calibration	PSS ReadyCal-Kit Polystyren	Calibration range: 376-2'570'000 g*mol ⁻¹

234 4.8. UV-VIS Spectroscopy (UV-VIS)

235 UV-VIS-spectra were recorded in a wavelength range of 190-800 nm (DR 6000 by Hach Lange,
 236 Germany) using 10 mm quartz cuvettes. Therefore 5 mg of the lignins were dissolved in 100 mL of
 237 0.1 mol*L⁻¹ aqueous sodium hydroxide [21].

238 4.9. ATR-FTIR Spectroscopy (ATR-FTIR)

239 ATR-FTIR-spectra were recorded in a wavenumber range of 4'000-400 cm⁻¹ with a resolution of
 240 4 cm⁻¹ (Vertex 70 and Platinum ATR Diamond by Bruker, USA). For noise reduction, each sample
 241 was measured 96 times. Since the irradiated lignins were not washed after precipitation all spectra
 242 had to be compensated for the presence of sodium hydrogen sulphate.

243

244 4.10. Powder X-ray Diffraction (XRD)

245 The characterisation of AEROXIDE P25® was performed using a bench top x-ray diffractometer
246 (D2 PHASER by Bruker, USA) with the parameters described in Table 3.

247 **Table 3.** XRD set up and parameters.

Parameter	Settings
Detector	Lynxeye, 5.86002946944° opening angle
Tube	Cu-anode, 1.54184 Å, 30 kV, 10 mA
Scan type, mode	Coupled two theta/theta, continuous PSD fast
Rotation	0 rpm
2 Theta	10.002026596-65.002026596°, Δ=0.010173662275°
Theta	5.001013298-32.501013298°, Δ=0.005086831138°
Steps	5'407
Time per step	0.500 s

248 **5. Conclusions**

249 This study aimed to describe the impact of UV irradiation time and catalyst concentration on
250 the photocatalytic or rather the photolytical depolymeration of lignin into valuable chemical
251 building blocks. Using a variety of analytical methods (chromatography, spectroscopy and
252 wet-chemistry) it could be shown that the lignin was selectively depolymerised to the size of its
253 monomers and even partially mineralised proving the oxidative character of the degradation
254 process. For the chosen catalyst concentration no significant differences could be found confirming
255 the photolytical origin of the lignin fragmentation process.

256
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261 photocatalytic experiments, in particular long-term studies; Christian Jung: conducting the experimental setup
262 for photolysis and photocatalysis; Steffen Witzleben: planning studies, lignin isolation and XRD studies; Margit
263 Schulze: planning studies, conducting experimental investigation and results discussion, coordination of
264 writing and editing.

265 **Conflicts of Interest:** The authors declare no conflict of interest.

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