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# Exploiting the photocatalytic activity of TiO<sub>2</sub> towards the depolymerization of Kraft lignin<sup>†</sup>

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Lignin is a promising renewable source of aromatic chemicals. Described herein is a new photocatalytic methodology for depolymerization of oxidized Kraft lignin to industrially relevant aromatic platform chemicals. The photooxidation route begins with oxidation of alcohol moieties using a gold nanoparticle/ hydrotalcite composite. Next, the oxidized lignin is subjected to UVA irradiation in the presence of TiO<sub>2</sub>, leading to a 3-fold decrease of its molecular weight and to the formation of various monolignols. The products obtained in both steps were characterized using FTIR, SEC, GC-MS, and 2D NMR spectroscopy, which confirm the depolymerization of lignin to smaller molecular weight products. This method offers both energetic and chemical advantages over thermochemical processing for lignin valorisation.

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# Introduction

Lignin is the third main constituent of wood, after cellulose and hemicellulose.<sup>1</sup> During the milling process, cellulose is isolated and used in paper manufacture, while lignin is most commonly discarded and considered as waste. Indeed, lignin is often burned to produce heat for paper mill operations, contributing to a large excess of greenhouse gas emissions at the expense of the destruction of an abundant, natural source of aromatic compounds. The valorization of lignin presents an ecological option for sourcing aromatic molecules for industrial applications. The current focus of this valorization process has been three specific linkages in the lignin macromolecular backbone:  $\beta$ -O-4,  $\beta$ -5', and 4-O-5' (Fig. 1).<sup>2</sup> These linkages are most common in softwood lignin, but the percentage of each is source dependent.

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One approach to transforming lignin into value-added chemicals, involves breaking it into smaller molecules. Previous studies have reported both complete<sup>3</sup> and partial pyrolysis<sup>2</sup> of lignin as an alternative towards its valorisation, although most of the oxygenated functional groups are lost through these processes. Moreover, the large number of compounds formed make such thermochemical processes unsuitable for fine chemical production. A more targeted approach employs a catalyst to break specific bonds in lignin while retaining some



Fig. 1 Representation of the substructure of lignin highlighting the  $\beta\text{-O-4},\,\beta\text{-S}'$  and 4-O-5' linkages.

critical structural characteristics.<sup>2</sup> Metal-based catalysts and, in particular, photocatalysts, may allow for specific bond cleavage in lignin while preserving its functional groups, given previous successes on smaller molecules with similar substituents.<sup>4–8</sup>

To date, much of the work on lignin valorisation has been performed on small, model molecules, which are not fully representative of the lignin structure. In industry, most lignin waste is isolated from the Kraft process, which leads to the incorporation of sulfur functionalities in its molecular structure.<sup>9</sup> Sulfur's role in heterogeneous catalyst deactivation has likely hampered many past lignin transformation processes.<sup>10</sup> Nonetheless, the investigation of processes using bulk lignin is paramount towards improving the industrial relevance of valorisation pathways.

The valorisation of lignin through several photochemical approaches has been reported.<sup>7,11–15</sup> For instance, Chen et al. demonstrated the photo-depolymerization of a lignin model using In<sub>2</sub>S<sub>3</sub> nanoparticles.<sup>7</sup> In this case, aromatic monomers including acetovanillone and vanillin were obtained from guaiacylglycerol-β-guaiacyl ether after 12 h under visible light irradiation. Nevertheless, the application of this process to a real lignin fraction was not investigated. Additional examples rely on the use of the well-known photooxidant TiO<sub>2</sub> towards lignin depolymerization.<sup>16–19</sup> Wang et al. described a tandem method for cleaving C–O bonds of  $\beta$ -O-4 lignin models using Pd/ZnIn<sub>2</sub>S<sub>4</sub> and TiO<sub>2</sub>-NaOAc through photooxidation/hydrogenolysis.<sup>18</sup> In this one-pot strategy, selective oxidation of α-C-OH takes place over Pd/ZnIn<sub>2</sub>S<sub>4</sub> under a 455 nm light, while the TiO<sub>2</sub>-NaOAc system cleaves C-O bonds through hydrogenolysis by switching to a 365 nm light. Once again, lignin models were the sole targets of this study.

Herein, we present the use of UV-light activated  $TiO_2$  in real lignin depolymerization. More specifically, Kraft lignin is oxidized and then photodepolymerized to afford monolignol-like products. This approach results in value-added products from lignin through an economical, energy-efficient process as compared to traditional pyrolysis pathways.

## Methods and materials

#### Materials

Hydrotalcite (HT) was purchased from Sigma-Aldrich and used as received. TiO<sub>2</sub> P25 was obtained from Evonik Degussa and used as received. Tetrachloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O) was purchased from Alfa Aesar. Ammonia (28% v/v in H<sub>2</sub>O) was purchased from Fisher Scientific Canada. Toluene (Anachemia) and methanol (Fisher Scientific Canada) were used for all catalytic reactions. Ultrapure water was collected in-house (18.2 M $\Omega$  cm at 25 °C) and used in the synthesis of all nanoparticle composites. Hydroxylated Kraft lignin (FPInnovations Canada) was used in all oxidation and depolymerization reactions.

#### Instrumental analysis

ATR-FTIR analysis was performed on a Cary 630 Fourier transform infrared spectrometer with 8 scans per sample in wavenumbers between 4000–600 cm<sup>-1</sup>. Size exclusion chromatography (SEC) was carried out using an Agilent 1200 HPLC system fitted with a diode-array detector ( $\lambda_{detection} = 254 \text{ nm}$ ). Components were separated on a SUPREMA analytical Linear S column (8  $\times$  300 mm; 5  $\mu$ m) set to 40 °C and using a 20/80 CH<sub>3</sub>OH (HPLC grade, BDH) and 10 µM ammonium bicarbonate(aq.) (Sigma-Aldrich) eluent (flow rate =  $0.3 \text{ mL min}^{-1}$ ; injection volume = 40  $\mu$ L). SEC column calibration was performed using polystyrene sulfonate sodium salts, salicylic acid and acetone. 2D NMR spectra were acquired at room temperature using a Bruker AVANCE 500 MHz spectrometer, based on the method reported by Stahl et al.<sup>20</sup> In short, an aliquot of the reaction mixture was evaporated under reduced pressure and dissolved in 1 mL of DMSO-d<sub>6</sub>. The structural units of lignin were assigned by comparison with previously reported literature values.<sup>21</sup> GC-MS analyses were performed on an Agilent Technologies 6890N GC system equipped with an Agilent Technologies 5973 Network mass spectrometer. The chromatographic conditions were as follows: a Rtx-5 column (105 m  $\times$  0.32 mm  $\times$  1  $\mu$ m) from Restek was employed, and the injector temperature was set to 250 °C in split mode with an injection volume of 2 µL. Helium was the carrier gas at 1.6 mL min<sup>-1</sup>. The transfer line and source temperatures were set to 280 °C. The oven temperature was initially at 55 °C for 4 min, then increased at a rate of 35 °C min<sup>-1</sup> until 150 °C and held for 5 min. A second increase in temperature was then applied at 30 °C min<sup>-1</sup> until 250 °C, with a hold time equal to 5 min. The mass spectral database NIST/EPA/NIH EI (NIST05) was used for identification purposes.

# Synthesis of gold nanoparticles supported on hydrotalcite (AuNP/HT)

The synthesis of AuNP/HT was adapted from Gupta *et al.*<sup>22</sup> In a round-bottomed flask, 41.2 mg (0.11 mmol) of HAuCl<sub>4</sub>·3H<sub>2</sub>O was dissolved in 40 mL of ultrapure water. The pH was adjusted to 10 using an aqueous solution of NH<sub>3</sub> (28% v/v in H<sub>2</sub>O). The mixture was stirred for 6 h at room temperature and then heated to 100 °C for 30 min. The yellow solid (as a result of Au(OH)<sub>3</sub> precipitation and deposition) was filtered, washed with ultrapure water and dried in an oven at 200 °C for 4 h to yield 1.0 g a purple solid. The catalyst tended to lose activity a few weeks after synthesis, as was evidenced by no discernible variations in the lignin oxidation IR spectrum.

#### AuNP/HT-mediated oxidation of Kraft H-lignin

In a round-bottomed flask, 100 mg of H-lignin was dissolved in 20 mL of toluene. Next, 50 mg of AuNP/HT was added. The reaction mixture was stirred and refluxed for 4 h under a continuous oxygen purge. Different reaction times were investigated (*e.g.*, 2, 6, and 8 h), although 4 h afforded the best results. Control reactions (HT, no catalyst) were performed under the same reaction conditions to confirm the need for AuNP.

#### Photolysis in the presence of TiO<sub>2</sub>

In a glass vial, 30 mg of lignin (Kraft H-lignin or oxidized Kraft H-lignin; OKHL) was dissolved in 6 mL of methanol in the

presence of 10 mg of TiO<sub>2</sub>. The mixture was then irradiated for 6 and 18 h using two UVA LEDs centred at 365 nm (21.6 W m<sup>-2</sup>) and the irradiance was measured by a Luzchem Spectroradiometer. Control reactions were also performed in the absence of TiO<sub>2</sub> using the same reaction conditions.

### Results and discussion

#### **Oxidation of Kraft H-lignin**

The primary step of our depolymerization approach relies on the gold nanoparticle/hydrotalcite (AuNP/HT) catalyzed oxidation of the alcohol moiety in lignin. AuNP/HT was chosen as a catalyst based on the work of Mitsudome et al.<sup>23</sup> that clearly demonstrated its high activity towards alcohol oxidation reactions. A subsequent  $TiO_2$ -photoinduced scission of the  $\beta$ -O-4 linkages would then afford the desired aromatic building blocks as represented in Scheme 1 (lignin model is shown for clarification). The AuNP/HT-promoted alcohol oxidation was initially assessed using ATR-FTIR (Fig. 2). No significant changes were observed when comparing the spectrum of original H-Kraft lignin with the spectra collected after oxidation performed in the absence of catalysts or using pristine HT. However, in the presence of AuNP/HT, the OH stretching band at  $\sim$  3300 cm<sup>-1</sup> showed a significant decrease while the relative intensity of the band at  $\sim$  1700 cm<sup>-1</sup> increased. This is the first indication of successful OH oxidation generating carbonyl groups conjugated with an aromatic ring.<sup>16</sup> These preliminary screening trials suggest that AuNP/HT catalysts are capable of successfully oxidizing the alcohol moiety of the  $\beta$ -O-4 linkage under mild conditions (toluene reflux) and a short time (4 h). This finding is congruent with previous literature reports on the success of supported AuNP-mediated alcohol oxidation.23-26

Size exclusion chromatography (SEC) was performed to monitor the overall changes to lignin macrostructure through the detailed analysis of its molecular weight. Ideally, the simple oxidation of the  $\beta$ -O-4 linkage should not result in substantive changes in the lignin molecular weight, regardless of the reaction conditions. In all cases, the maximum MW remains relatively constant between 1500–1800 g mol<sup>-1</sup> (Fig. 3).

# Depolymerization of lignin H-Kraft using UV light-activated TiO<sub>2</sub>

The successful oxidation of the OH groups in the  $\beta$ -O-4 linkage is crucial for the effective depolymerization of lignin. To support this claim, a series of control reactions were performed on non-oxidized H-Kraft lignin with and without TiO<sub>2</sub> under an inert atmosphere. ATR-FTIR spectra collected after these experiments indicate some alcohol oxidation (Fig. 4). Here, a decrease in the relative intensity of the OH signal located between 3600–3000 cm<sup>-1</sup> was observed when



Scheme 1 Two-step reaction of depolymerization of  $\beta$ -O-4 lignin model 2-phenyl-1-phenylethan-1-ol.



Fig. 2 Normalized ATR-FTIR spectra of H-Kraft native lignin before and after oxidation under the following conditions: no catalyst, HT only and AuNP/HT. Highlighted: bands at  $\sim$  3300 and  $\sim$  1700 cm<sup>-1</sup>.



Fig. 3 SEC analysis of reaction mixtures following oxidation of Kraft lignin (black) oxidation (O<sub>2</sub>, 110 °C, 4 h) using the following catalytic conditions: no catalyst (yellow), HT only (green) and AuNP/HT (blue). Size exclusion chromatography (SEC) was performed to monitor the overall changes to lignin macrostructure through the detailed analysis of its molecular weight. Ideally, the simple oxidation of the  $\beta$ -O-4 linkage should not result in substantive.

 $TiO_2$  was employed as the catalyst under sample irradiation, suggesting that alcohol oxidation was the sole outcome of this experiment. SEC experiments were not performed due to lack of solubility in methanol, again indicating that depolymerization did not occur. When the reaction was carried out in the presence of oxygen, lignin was completely mineralized, as indicated by the presence of only few milligrams of starting material at the end of the reaction.<sup>27</sup>

#### Photodepolymerization of oxidized Kraft H-lignin (OKHL)

The photodepolymerization of OKHL was performed using UV-activated  $TiO_2$  over 6 and 18 h, with longer reaction times



Fig. 4 Normalized ATR-FTIR spectra of native Kraft H-lignin following UV irradiation with and without  $TiO_2$  (reaction conditions: N<sub>2</sub> atmosphere; 18 h).

giving rise to more effective valorization. The ATR-FTIR spectra (Fig. 5) highlight significant changes to the oxidized lignin following UV irradiation. First, OH stretching bands emerged at approximately  $3600 \text{ cm}^{-1}$  following UV light treatment of OKHL, presenting a higher intensity in the presence of TiO<sub>2</sub> photocatalyst. This trend can be attributed to the generation of phenolic compounds,<sup>28</sup> one of the major products of the lignin depolymerization process. Though initial assessments of reaction mixtures strongly suggest depolymerization is taking place, a more in-depth analysis using SEC and NMR spectroscopy was required.

SEC chromatograms presented in Fig. 6 show that UV light exposure promotes a substantial decrease in the molecular weight of the products, strongly supporting initial conclusions from IR spectra (Fig. 5). Two main conclusions can be drawn from the SEC data: first, OKHL depolymerization increased with longer irradiation period (*i.e.*, 6 vs. 18 h). Second, the depolymerization is highly dependent on the presence of the  $TiO_2$  photocatalyst. In the absence of  $TiO_2$ , UV exposure of the OKHL mixture afforded relatively low amounts of smaller MW products, given by the low signal intensity, suggesting that the products are likely oligomeric in structure. However, a higher depolymerization degree was reached using  $TiO_2$  as the photocatalyst after 18 h of UV irradiation, affording a high-intensity signal at considerably lower MW values than the OKHL starting material.

Using 2D NMR (<sup>1</sup>H–<sup>13</sup>C HSQC) we were able to closely examine the success of TiO<sub>2</sub>-mediated OKHL depolymerization and to give more insight into possible changes in the chemical structure of lignin.<sup>21</sup> Specifically, previous reports have suggested that the disappearance of certain resonances in the aliphatic region of the NMR spectra provide critical information regarding changes in the nature of specific linkages.<sup>29</sup> For instance, if alcohol oxidation occurs, we would observe the complete or partial disappearance of H $\alpha$  (Scheme 2A). The NMR resonances related to H $\alpha$  appear at around 75 ppm/6.1 ppm in the <sup>13</sup>C/<sup>1</sup>H NMR spectra.<sup>30</sup> In our case, no signals related to H $\alpha$ were observed in the HSQC spectrum of OKHL (Fig. 7A), indicating that significant alcohol oxidation took place in the first step (*i.e.*, the oxidation of H-Kraft lignin with AuNP/HT).

2D NMR spectra also point to significant structural changes in OKHL following photodepolymerization under UV irradiation with and without  $TiO_2$  (Fig. 7B and C, respectively). Since lignin is a polymer, its depolymerization will afford small oligomers or monomers with lower molecular weights (Scheme 2B), therefore reducing the chemical environment diversity and leading to smaller correlation peaks in HSQC or even the absence of these peaks. In fact, the OMe-related resonances are present in all spectra but are less predominant after UV irradiation (Fig. 7B and C), with new chemical shift correlations in the OMe region pointing to structural changes in OKHL.



OKHL 25 UV 6h UV 18h 20 UV + TiO<sub>2</sub> 6h  $UV + TiO_2$  18h UV Signal 15 10 5 0 2000 3000 4000 5000 0 1000 6000 7000 Molecular weight (g/mol)

Fig. 5 Normalized ATR-FTIR spectra of OKHL starting material, UV irradiated OKHL for 6 and 18 h, and UV irradiated TiO<sub>2</sub>/OKHL for 6 and 18 h. All reactions were performed under N<sub>2</sub>.

 $\begin{array}{lll} \mbox{Fig. 6} & \mbox{SEC chromatograms of OKHL starting material (blue), UV irradiated OKHL for 6 (black) and 18 h (gray) and UV irradiated TiO_2/OKHL for 6 (green) and 18 h (purple). All reactions were performed under N_2. \end{array}$ 



Scheme 2 (A) Alcohol oxidation and (B) depolymerization of lignin via C– O bond cleavage of the  $\beta$ -O-4 linkage.

In the case of OKHL after UV irradiation in the presence of  $TiO_2$ , a strong resonance at 8.0 ppm in the <sup>1</sup>H NMR spectrum could point to the presence of the monolignol, indicating lignin depolymerization<sup>21</sup> (see ESI† for <sup>1</sup>H NMR spectra of all samples, Fig. S1). The new correlation at 50 ppm/3.1 ppm observed after UV treatment can be related to a CH<sub>3</sub> group from methanol. Alternatively, it could also be assigned to the methoxy groups present in the lignin fragment generated following depolymerization.

Previous work has demonstrated the ability of AuNP supported on custom-made hydrotalcite-related materials to facilitate the transformation of lignin to monolignol-type products.<sup>31</sup> However, in our case significant formation of a monolignol-type product did not take place in the oxidation step in the presence of AuNP/HT, as previously discussed. Therefore, it is reasonable to assume that AuNP/HT itself is not able to depolymerise the H-Kraft lignin, which takes place upon UV irradiation in the presence of TiO<sub>2</sub>.

GC-MS analysis of the UV-irradiated OKHL reaction mixture in the presence of  $TiO_2$  likewise indicated lignin depolymerization and the generation of products which are consistent with monolignols (Fig. S4, ESI†). On the other hand, both OKHL and UV irradiated OKHL (in the absence of  $TiO_2$ ) did not present any peaks related to monolignol-like products, except a small peak related to vanillin. In these cases, the peaks observed in the chromatogram could be attributed to products with molecular weights that are not compatible with monolignols (Fig. S2 and S3, ESI†).

In agreement with previous reports by Scaiano and coworkers,<sup>32</sup> UV irradiation of OKHL by itself induces effective cleavage of the  $\beta$ -O-4 linkage through a photogenerated triplet state of the carbonyl moiety. However, the current work shows that addition of TiO<sub>2</sub> to the reaction media under UV irradiation favours the production of monolignol-like products. Therefore, considering that the end goal of lignin depolymerization is to obtain monolignol-like products, the use of TiO<sub>2</sub> is a definite advantage. In terms of the mechanism involved in this process, Reckenthäler et al.<sup>33</sup> demonstrated that electron transfer from TiO<sub>2</sub> to acetophenone can afford the ketyl radical. Thenceforth, a similar electron transfer event may also play a key role here, through interaction with OKHL to form a ketyl radical and undergo a similar  $\beta$ -O-4 cleavage as suggested by Netto-Ferreira and co-workers.34 The product formation in the presence of TiO<sub>2</sub> is summarized in Scheme 3 and is the basis for this proposed mechanism. In the current study, two free radical reactions are likely operating in parallel (i.e., the reaction



Fig. 7 HSQC 2D NMR spectrum of (A) OKHL, (B) OKHL following 18 h of UV irradiation. And (C) OKHL following 18 h of UV irradiation in the presence of  $TiO_2$ .

catalyzed by  $TiO_2$  and the direct reaction using UV). Given this, traditional radical scavenging experiments to identify free radicals generated throughout the course of the mechanism would lack precision.

Moreover, since monolignol products are more present when  $TiO_2$  was used rather than in its absence, further electron transfer events from  $TiO_2$  to lignin cannot be ruled out. Electron transfer to other bonds in the lignin chemical



Scheme 3 Proposed mechanism for photocatalyzed depolymerization by TiO<sub>2</sub> (activated by UV light) of a representative molecule present in lignin containing the  $\beta$ -O-4 bond.

structure, such as the  $\beta\text{-}5'$  and 4-O-5' linkages, could also contribute to further lignin depolymerization into smaller sub-units.

Barreto and co-workers<sup>35</sup> reported the TiO<sub>2</sub>-mediated photodegradation of methyl *t*-butyl ether into *tert*-butyl formate and *tert*-butyl alcohol. Considering that a comparable ether bond is present in lignin, a similar C–O–C cleavage is possible and may also contribute to its further depolymerization. 1D and 2D NMR data suggest that these pathways may be related to the extensive structural changes of OKHL under UV irradiation in the presence of TiO<sub>2</sub>. This assumption can be made taking into consideration the emergence of resonances at 52 ppm/3.7 ppm and 52 ppm/4.0 ppm and shifts of the peaks related to Hy (Fig. 7B and C).

## Conclusions

This contribution introduces a more energy efficient route of promoting oxidized Kraft H-lignin depolymerization to valueadded chemicals as compared to traditional thermochemical pathways. The oxidized version of the Kraft H-lignin was obtained via oxidation of the benzylic alcohol present in the β-O-4 linkage under simple reflux conditions in the presence of AuNP/HT heterogeneous catalyst and O2. Subsequent photoreduction and photocleavage of the carbonyl moiety via direct and/or TiO<sub>2</sub>-mediated UV excitation led to a decrease in the molecular weight of OKHL, as well as formation of smaller, monolignol-like molecules typical of lignin depolymerization. AuNPs were critical for the alcohol oxidation to carbonyl groups. In a second step, the carbonyl groups are then needed to depolymerize the lignin in the presence of UV light through direct TiO<sub>2</sub>-assisted photocleavage, for which further reactions were also observed *via* electron transfer from  $TiO_2$  to lignin.

# Conflicts of interest

The authors declare no conflicts of interest.

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