

# Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



[www.rsc.org/greenchem](http://www.rsc.org/greenchem)



## Reduction of lignin color via one-step UV irradiation

Jingyu Wang, Yonghong Deng, Yong Qian,\* Xueqing Qiu\* and Dongjie Yang

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Abstract:** The dark color of industrial lignin is the main obstacle for their high value-added use in areas such as sunscreen or dyestuff dispersant. Here, a one-step method for reducing the color of lignin is presented and the structure changes of whitened lignin are characterized by UV, FTIR, NMR, GPC, DLS, AFM, HS-GC and potentiometric titrator. Results show that the contents of aromatic ring, methoxyl and phenolic hydroxyl group in alkali lignin (AL) decrease, while the content of carboxylic group increases when it is exposed to UV in THF. AL experiences a darker process before it is gradually whitened. The blue shift of UV spectrum and decreases of size and molecular weight indicate AL is not only intermolecular and intramolecular disaggregated, but also partially depolymerized when light colored lignin is obtained. This simple but efficient whitening method is successfully practiced in bleaching. The white degree of raw paper increases from 0.438 to 0.917 after being irradiated under sunshine for 3 days.

### Introduction

Lignin, one of the essential biomass, is the second most abundant and the unique renewable aromatic polymer on the globe.<sup>1–3</sup> Value-added utilization of lignin has attracted increasing attention in the last few decades, such as dyestuff dispersants, pesticide adjuvants, depolymerized chemicals and carbon fiber,<sup>4–8</sup> although most are just burned as a fuel source. Evaluation of lignin as natural broad-spectrum sunscreen pushes lignin into high-end utilization.<sup>9</sup> Lignin is not only good UV absorbent, but also excellent antioxidant and antibacterial agent.<sup>10–13</sup> However, the dark color of industrial lignin hinders the market promotion of lignin-based sunscreens and limits the application performance of liginosulfonate dyestuff dispersants.

Lignin is almost colorless in wood, while industrial lignin such as alkali lignin or liginosulfonate has dark color.<sup>14,15</sup> Varieties of chromophores are introduced into the structure via lignin isolation procedure and pulping process, but the mechanism for the formation of chromophores is not completely known. Five possible chromophores have been proposed: (1) carbon–carbon double bonds conjugated with the aromatic ring; (2) quinone methides and quinones; (3) chalcone structures; (4) free radicals; (5) metal complexes with catechol structures.<sup>16,17</sup> Although the contents of quinone methide and quinone structures are not large, they contribute most of the color of lignin.<sup>18</sup>

In order to push high value-added utilization of lignin, it is important to whiten it to acceptable color. Qian et al. whitened lignin to light yellow by blocking the free phenolic hydroxyl groups of alkali lignin and then self-assembling into colloidal spheres.<sup>19</sup> Lin et al. faded the color of liginosulfonate and sulfonated alkali lignin by two steps.<sup>14</sup> They also blocked the free phenolic hydroxyl first

and then oxidized the blocked lignin with air, molecular oxygen or hydrogen peroxide. The light colored sulfonated alkali lignin and liginosulfonate were still useful as dispersants for dyestuffs and the fiber staining capacity of the prior art products was as low as 20%.<sup>14</sup> Both methods need two-step processes and have to block the phenolic hydroxyl groups first.

In this work, we whiten lignin by one-step method, irradiating AL by UV in THF solution. Furthermore, this method is successfully applied in paper bleaching. Since THF can be recycled and UV can be replaced by sunshine, this one-step whitening method is green, little energy-consuming and effective.

### Experimental Section

#### Materials

Pine alkali lignin (AL) was obtained from Xiangjiang Paper Co., Ltd (Hunan, China). The AL sample was treated by acidification and filtration. THF (HPLC grade) was purchased from Kermel Chemical Reagent Co., Ltd (Tianjin, China) and used as received without further purification. Deionized water (resistivity  $\geq 18$  M $\Omega$ /cm) was obtained from a Millipore water purification system and was used for the experiments conducted in this work. Other reagents and solvents were purchased commercially as analytical grade products and used as received without further purification unless otherwise indicated.

#### Irradiating AL in THF

2 g purified AL was dissolved in 0.5 L THF. Then the AL/THF solution was irradiated by 365 nm ultraviolet, which was provided by 200 W cold cathode UV lamp (B-100AP, UVP, America). After 200 hours light irradiation, the solution was added into 2 L petroleum ether. The product was collected, washed with deionized water, and freeze-dried for 24 hours.

<sup>a</sup>School of Chemistry and Chemical Engineering,  
South China University of Technology,  
Guangzhou, 510640, P. R. China.  
E-mail: qianyong86@163.com; xueqingqiu66@163.com

### Bleaching paper raw material

We prepared two pieces of paper raw material with size of 5×5 cm in scale. One piece was soaked in THF with 50 hours light irradiating and another was set as control. The white degrees of two pieces of paper were measured by colorimeter (Datacolor 110, Datacolor, America).

### Characterization

Fourier transform infrared (FTIR) spectra of AL before and after irradiating were recorded in the range 4000-1000  $\text{cm}^{-1}$  by a FT-IR spectrometer (Vector 333, Bruker, Germany). Disks were prepared by mixing 1 mg of AL sample with 100 mg KBr. Both samples and KBr were dried to avoid the influence of water, and the mixture was pressed at 10 MPa for 2 min.

The nuclear magnetic resonance (NMR) spectra of AL before and after irradiating were recorded on a nuclear magnetic resonance spectrometer (Bruker, AVANCE HD III 600, Germany) using  $\text{DMSO-}d_6$  as the solvent. For the  $^{13}\text{C}$  NMR, 100 mg of lignin was dissolved in 0.5 mL of  $\text{DMSO-}d_6$ . The  $^{13}\text{C}$  NMR spectra were recorded in the FT mode at 150.9 MHz with the following parameters: 30° pulse angle, 2 s relaxation delay and 20,000 scans.

UV-vis absorption spectra of AL before and after irradiating were performed in range of 200-800 nm with a UV-vis spectrophotometer (UV-2450, Shimadzu Co., Japan). For the samples with THF as the solvent, THF was scanned at the same wavelength as a baseline.

The contents of the phenolic hydroxyl, methoxyl, carboxyl group of AL before and after irradiating were measured respectively. Content of phenolic hydroxyl was measured by Folin-Ciocalteu (FC) method.<sup>20</sup> Phenolics such as lignin and vanillin react with FC reagent and the products have characteristic peak (760 nm) in UV spectrum. The UV absorbance at 760 nm is proportional to the content of phenolic hydroxyl groups. 15 mg lignin sample was dissolved in 100 mL of NaOH solution (pH=10). Then 1 mL AL solution, 1.5 mL FC reagent and 15 mL deionized water were mixed in a 25 mL volumetric flask. After 8 min, 5 mL of 20% (w/v)  $\text{Na}_2\text{CO}_3$  aqueous solution was added and the volume was adjusted to 25 mL with deionized water. The mixture was stirred for 2 h at 30 °C, and then the UV absorbance at 760 nm was measured. Calibration experiment was conducted with vanillin solutions. Content of methoxyl group was measured by headspace gas chromatographic (HS-GC).<sup>21</sup> HS-GC experiments were performed with a headspace sampler (DK-3001A, Beijing Zhongxing Huili Science & Technology Co., Ltd, China) and capillary gas chromatograph (Model GC9800, Kechuang Co., China). GC was running under 100 °C with 3.8 mL/min high-purity nitrogen as carrier gas. The flame ionization detector was running under 270 °C with 25 mL/min hydrogen and 300 mL/min air. Before HS-GC measurement, 10 mg lignin should be dissolved in 0.5 mL hydroiodic acid (57%) in a sealed headspace test vial. After being heated in 130 °C for 2 hours, 0.5 mL of sodium hydroxide solution (6 mol/L) was injected into the vial and then started the measurement. Content of carboxyl group was measured by aqueous potentiometric titration using the automatic potentiometric titrator (809 Titrando, Metrohm Corp., Switzerland).<sup>22</sup> 1 g/L lignin/potassium hydroxide solution with p-hydroxybenzoic acid as internal standard was titrated by

hydrochloric acid with fixed concentration. Before titrating lignin, control experiment should be performed by using hydrochloric acid to titrate pure p-hydroxybenzoic acid solution with same concentration in samples. Detailed calculation processes and related data of contents of these three functional groups could be found in supplementary information.

Molecular weight ( $M_w$ ) of AL and LCAL was determined by Agilent 1100 series gel permeation chromatography (Agilent Technologies Corp., Santa Clara, USA) with PLgel 5  $\mu\text{m}$  1000 Å and PLgel 5  $\mu\text{m}$  500 Å columns. The mobile phase was THF with a flow rate of 1 mL/min and polystyrene was employed as standard.

Dynamic light scattering (DLS) experiments were performed with ZetaPALS instrument (Brookhaven Instruments Co., America). All the experiments were performed at 25 °C. To ensure that light scattering measurements were not affected by dust, the stock solutions were filtered through Whatman filters with pore size of 0.45  $\mu\text{m}$ .

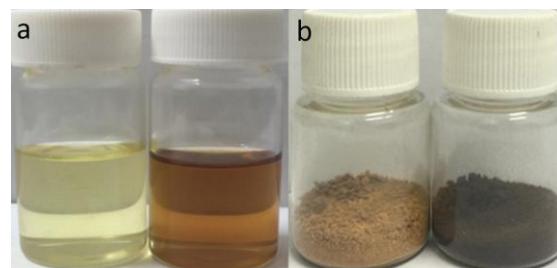
AFM (Park XE-100, Park Systems Co., Korea) with tapping mode was used to observe the morphology and size of AL before and after irradiating. The AFM samples were prepared by dropping the solutions onto a mica plate directly and dried under room temperature.

## Results and discussion

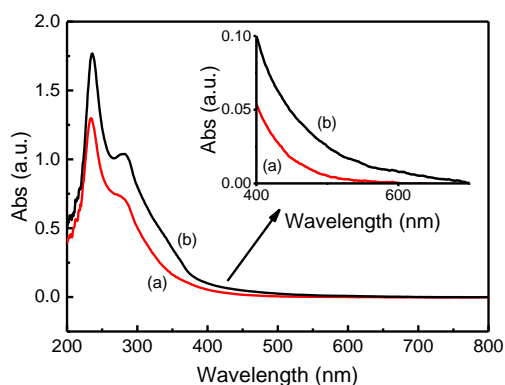
### Whitening lignin in THF by UV irradiating

It was surprised to find that the dark brown AL in THF was whitened to light yellow when it was exposed to UV light for certain time, as shown in figure 1a. The color of AL/THF solution faded seriously after 40 hours light irradiating. The wavelength of UV light was 365 nm. After freeze-drying, light colored AL (LCAL) was obtained (figure 1b). UV-vis absorption of LCAL and AL is shown in figure 2. Compared with AL raw material, the absorption at visible region of LCAL has a significant decrease.

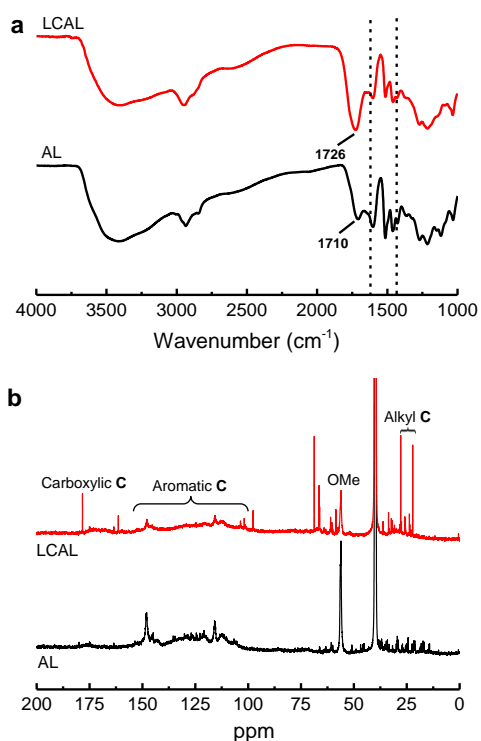
To explore what happened to AL when it was irradiated in THF, the structure changes of AL before and after irradiating were investigated by FTIR and  $^{13}\text{C}$  NMR. As shown in figure 3a, the vibration of aromatic ring (1600-1400  $\text{cm}^{-1}$ ) in LCAL is weaker than that in AL. At the same time, more obvious stretching vibration of carbonyl group (C=O) in LCAL appears at 1726  $\text{cm}^{-1}$ , while stretching vibration of carbonyl group (C=O) in AL at 1710  $\text{cm}^{-1}$  looks less obvious. FTIR results suggest that more carboxyl groups are formed in LCAL, but the content of aromatic ring decreases after UV



**Figure 1.** (a) Photos of AL before (right) and after (left) UV irradiation, the concentration of AL in THF was 0.5 g/L; (b) Corresponding LCAL (left) and AL (right) solids.



**Figure 2.** UV-vis spectra of (a) LCAL and (b) AL. The concentration of LCAL and AL in THF was 0.05 g/L. The insert image: the absorption from 700 to 400 nm.



**Figure 3.** FTIR and  $^{13}\text{C}$  NMR spectra of LCAL and AL.

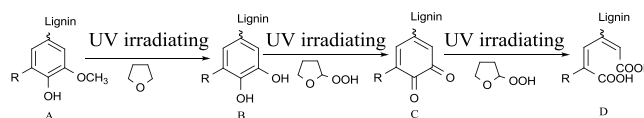
irradiation, which can be confirmed by  $^{13}\text{C}$  NMR spectra. As shown in figure 3b, the aromatic (100–160 ppm) and methoxyl (56 ppm) signals weaken after UV irradiation, while signals of carboxylic (178.5 ppm) and alkyl chain (22–28 ppm) become more obvious and very strong.

Therefore, contents of functional groups such as phenolic hydroxyl, methoxyl and carboxyl groups were measured. As shown in table 1, the contents of phenolic hydroxyl and methoxyl groups decrease 40.92% and 38.13%, respectively, while the content of carboxyl group has a 36.46% increase. UV-vis absorptions at 280 nm and 450 nm are recorded from figure 2. Here these absorptions represent the contents of aromatic ring and the color degree of

**Table 1.** Functional group content and specific UV-vis absorption changes of AL before and after irradiation.

Functional groups	AL (mmol/g)	LCAL (mmol/g)	Change rate (%)
Phenolic hydroxyl	2.842	1.679	-40.92
Methoxyl	4.980	3.081	-38.13
Carboxyl	2.475	3.895	+36.46
UV-vis@280nm*	1.0377	0.7177	-31.99
UV-vis@450nm*	0.0483	0.0171	-64.65

\*Dimensionless quantity



**Figure 4.** Structural mechanism of AL being whitened into LCAL during the irradiation process.

lignin, respectively.<sup>8</sup> The change rates of aromatic ring and the color degree are calculated according to eq. 1:

$$\text{Change rate} = (L-A)/A \times 100\% \quad (1)$$

where L represents group contents or UV-vis absorption of LCAL and A represents group contents or UV-vis absorption of AL.

Obviously, the content of aromatic ring decreases 31.99% and the color fades 64.54% after UV irradiating, which is consistent with FTIR and  $^{13}\text{C}$  NMR results.

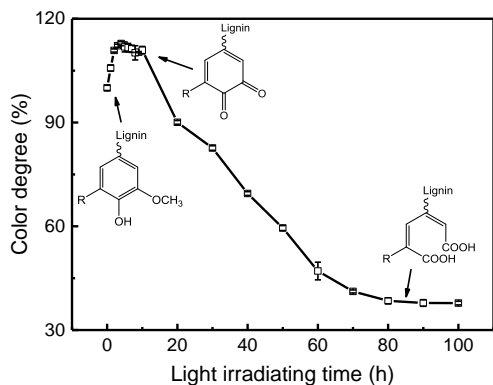
According to the above results, we speculated the whitening mechanism of AL in THF. As shown in figure 4, THF peroxide formed when it was irradiated by UV. It oxidized the methoxyl groups (A) of AL and catecholic structures formed (B). When lignin catecholic structures were exposed to UV irradiation, phenoxyl radical intermediate formed and then turned into colored quinone structures (C). However, quinone structures were not stable, and could be oxidized by THF peroxide. Finally, the aromatic ring opened and colorless aliphatic acid structure (D) formed.

To confirm the mechanism, we tracked the color change of the fading process by UV-vis spectrophotometry. The color change of AL in THF can be calculated by eq. 2:

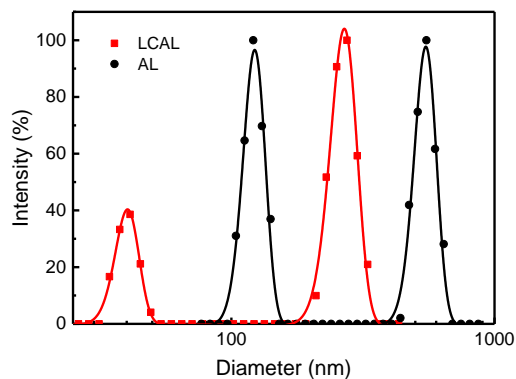
$$\text{Color change} = D450_i / D450_0 \times 100\% \quad (2)$$

where  $D450_i$  represents the absorbance of AL/THF solution at 450 nm after  $i$  hours irradiation and  $D450_0$  represents the absorption of AL/THF solution at 450 nm at the initial time.

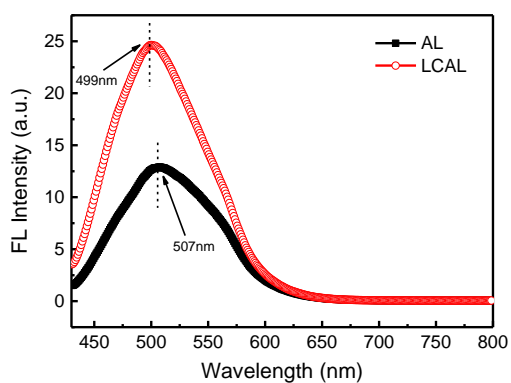
As shown in figure 5, the color of AL/THF solution becomes darker during the first 4 hours, which is induced by the photo-oxidation of phenolic hydroxyl and some methoxyl groups into quinone structures (from state A to state C in figure 4). When AL solution is further irradiated, quinone structures are photo-oxidized into aliphatic acid structures (state D in figure 4). Since quinone structures are the main chromophores of AL, the color of AL fades over 80% when aliphatic acid structures are formed. Comparatively, if solvents such as *N,N*-Dimethylformamide (DMF) cannot form peroxide under UV irradiation, they cannot oxidize the quinone structures and thus cannot whiten lignin. Comparative experiment is present in figure S2.



**Figure 5.** The color degree of AL at different UV irradiating times. The initial concentration of AL in THF was 2 g/L.



**Figure 7.** Diameter distribution of LCAL and AL in THF. The concentration of LCAL and AL in THF was 1 g/L.

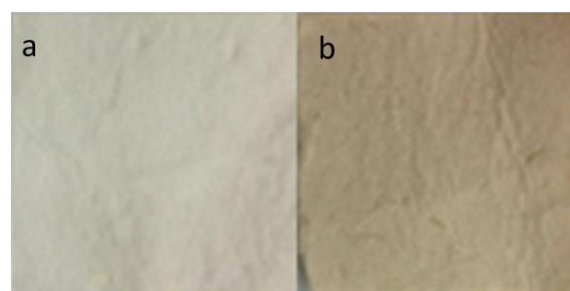


**Figure 6.** FL spectra of LCAL and AL. The concentration of AL and LCAL in THF was 500 mg/L. The excitation wavelength is 420 nm.

#### $\pi$ - $\pi$ disaggregation in LCAL

Another interesting finding was that insoluble AL disappeared and AL could be dissolved in THF completely after irradiation. AL tends to form aggregates in solution and those large aggregates make AL cannot be dissolved well in THF. There are two levels of aggregation in lignin:  $\pi$ - $\pi$  stacking (J-aggregation) between aromatic rings induced intramolecular aggregation and Van der Waals attraction induced intermolecular aggregation.<sup>23</sup> When AL in THF was irradiated by UV, some aromatic rings were broken and  $\pi$ - $\pi$  stacking in AL was disaggregated. As shown in figure 6, the peak of emission spectrum of AL moves from 507 nm to 499 nm (blue shift), which confirms J-aggregation in AL become weaker. However,  $\pi$ - $\pi$  disaggregation does not lead to completely intermolecular disaggregation. As shown in figure 7, size of AL decreases significantly, but the peak of aggregates still exists. AFM was applied to observe the morphology and size of AL before and after irradiating (figure S3). AL obviously disaggregated due to the breaking of aromatic rings and LCAL had smaller size of about 20 nm. AL and LCAL were both amorphous particles.

Being different from fast degradation in hydrogen peroxide,<sup>24, 25</sup> UV induced free radical depolymerization of AL in THF was mild.



**Figure 8.** Photos of (a) bleached paper and (b) raw paper.

The  $M_w$  value of AL decreased from 3000 to 2200 after irradiation. However, the color of AL whitened significantly due to the destruction of aromatic rings and remove of quinone structures.

#### Bleaching raw paper material

Bleaching process in pulp and paper industry is attempting to minimize the use of chlorine to satisfy environmental and healthy demands. Since the color of paper is induced by residual lignin,<sup>26, 27</sup> white paper was obtained by irradiating raw paper in THF, as shown in figure 8. The white degree of raw paper increased from 0.438 to 0.917 when it was irradiated under sunshine for 3 days. As THF can be recycled, UV irradiated whitening method, which fades lignin sufficiently, worths being tried in bleaching process.

#### Conclusions

Industrial lignin such as alkali lignin (AL) can be easily whitened by UV irradiating in THF. When AL is exposed to UV, phenolic hydroxy groups in AL become phenoxyl radicals and then form quinone structures. Since quinone structures are main chromophores, AL can be whitened when they are finally photo-oxidized into aliphatic acid structures. After irradiation, AL is not only disaggregated, but also partially depolymerized, while its characteristic structure is still retained. As THF is recyclable, this lignin whitening method is simple, effective, and green. Lignin is excellent UV absorbent and antioxidant, prepared light colored lignin can be used in high-end areas such as natural biomacromolecular sunscreen, although



numerous vitro and vivo tests are required to grant safety for lignin-based sunscreen to finally go market.

## Acknowledgements

We gratefully acknowledge the financial support from the National Basic Research Program of China (973 Program) (2012CB215302) and China Postdoctoral Science Foundation (2015M570714).

## Notes and references

- 1 J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552-3599.
- 2 Z. J. Wei, Y. Yang, R. Yang and C. Y. Wang, *Green Chem.*, 2012, **14**, 3230-3236.
- 3 R. ten Have and P. J. M. Teunissen, *Chem. Rev.*, 2001, **101**, 3397-3413.
- 4 J. F. Kadla, S. Kubo, R. A. Venditti, R. D. Gilbert, A. L. Compere and W. Griffith, *Carbon*, 2002, **40**, 2913-2920.
- 5 Y. X. Pang, W. Gao, H. M. Lou, M. S. Zhou and X. Q. Qiu, *Colloids Surf. A*, 2014, **441**, 664-668.
- 6 X. Y. Wang and R. Rinaldi, *Angew. Chem. Int. Ed.*, 2013, **52**, 11499-11503.
- 7 K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii and P. C. Ford, *Green Chem.*, 2010, **12**, 1640-1647.
- 8 D. J. Yang, H. Li, Y. L. Qin, R. S. Zhong, M. X. Bai and X. Q. Qiu, *J. Dispersion Sci. Technol.*, 2015, **36**, 532-539.
- 9 Y. Qian, X. Q. Qiu and S. P. Zhu, *Green Chem.*, 2015, **17**, 320-324.
- 10 W. P. Ban, J. G. Song and L. A. Lucia, *Ind. Eng. Chem. Res.*, 2007, **46**, 6480-6485.
- 11 X. J. Pan, J. F. Kadla, K. Ehara, N. Gilkes and J. N. Saddler, *J. Agr. Food. Chem.*, 2006, **54**, 5806-5813.
- 12 E. J. Shin, J. H. Kim, C. S. Park and K. Won, *J. Biosci. Bioeng.*, 2009, **108**, S56-S56.
- 13 A. Hambardzumyan, L. Foulon, B. Chabbert and V. Aguié-Beghin, *Biomacromolecules*, 2012, **13**, 4081-4088.
- 14 S. Y. Lin, *US Pat*, US4184845, 1980.
- 15 C. Atik and M. Balaban, *Cellul. Chem. Technol.*, 2003, **37**, 385-389.
- 16 P. Dilling, *US Pat*, US4454066, 1984.
- 17 S. I. Falkehag, J. Marton and E. Adler, in *Lignin structure and reactions*, ed. J. Marton, E-Publishing Inc., ACS, 1966, vol. 59, ch. 7, pp. 75-89.
- 18 L. Zhang and G. Gellerstedt, 3rd European Workshop on Lignocellulosics and Pulp, 1994.
- 19 Y. Qian, Y. H. Deng, H. Li and X. Q. Qiu, *Ind. Eng. Chem. Res.*, 2014, **53**, 10024-10028.
- 20 H. F. Zhou, D. J. Yang, X. Q. Qiu, X. L. Wu and Y. Li, *Appl. Microbiol. Biotechnol.*, 2013, **97**, 10309-10320.
- 21 H. Li, X. S. Chai, M. Liu and Y. H. Deng, *J. Agric. Food. Chem.*, 2012, **60**, 5307-5310.
- 22 M. S. Zhou, K. Huang, X. Q. Qiu and D. J. Yang, *CIESC J*, 2012, **63**, 258-265.
- 23 Y. H. Deng, X. J. Feng, M. S. Zhou, Y. Qian, H. F. Yu and X. Q. Qiu, *Biomacromolecules*, 2011, **12**, 1116-1125.
- 24 R. C. Sun, J. Tomkinson, F. C. Mao and X. F. Sun, *J. Appl. Polym. Sci.*, 2001, **79**, 719-732.
- 25 C. Crestini, P. Pro, V. Neri and R. Saladino, *Bioorg. Med. Chem.*, 2005, **13**, 2569-2578.
- 26 S. Camarero, O. Garcia, T. Vidal, J. Colom, J. C. del Rio, A. Gutierrez, J. M. Gras, R. Monje, M. J. Martinez and A. T. Martinez, *Enzyme Microb. Tech.*, 2004, **35**, 113-120.
- 27 J. H. Clarke, K. Davidson, J. E. Rixon, J. R. Halstead, M. P. Fransen, H. J. Gilbert and G. P. Hazlewood, *Appl. Microbiol. Biot.*, 2000, **53**, 661-667.

**Table of contents entry**

One-step irradiation in mild solvent caused lignin to be partially depolymerized and  $\pi$ - $\pi$  disaggregated and thus lignin was largely whitened.

