

Photochemical Cells Sensitized by Lignophenol Derivatives

Mitsuru Aoyagi, Nao Umetani and Masamitsu Funaoka

Graduate School of Bioresources, Mie University, Japan Science and Technology Agency (JST),

Solution Oriented Research of Science and Technology (SORST)

Fax: +81-59-231-9517, e-mail: aoyagi@biomie-u.ac.jp

Hinoki cypress (*Chamaecyparis obtusa*)-lignophenol(*p*-cresol type, HCLC) have been directly synthesized from lignocellulosics through the phase-separation system, which were surface reactions between 72 % H₂SO₄ and *p*-cresol under 1 atm at 30 °C. Because of rich phenolic hydroxyl groups in grafted phenols, various derivatives were designed from LPs. In the case of phenolic hydroxyl groups on *ortho*-positions for C₁-carbons in phenylpropane units in the native lignins, the function groups acted as recycling switches for cleavages of main chains of LPs under alkaline conditions with heat. Resulting derivatives (2nd der.) have showed new features in addition to properties of HCLC. Hydroxymethylation of HCLC (HCLC-HM) were easily carried out by treatment of methanal under alkaline conditions (60 °C). Resulting HCLC-HM were polymelyzed into network type derivatives (HCLC-HM-P) by heat treatments. HCLC-HM, HCLC-HM-P and their 2nd der. showed visible light conversion into electricity on the nano-TiO₂ electrodes. Especially 2nd der. showed good result (V_{oc} = 0.47 V, I_{sc} = 3.17 mAcm⁻², FF = 0.74 and η = 0.89%) probably because both absorption of light and adsorption on the electrodes were improved by productions of quinoid type structures on HCLC by alkaline treatments.

Key words: lignin, lignophenol, dye-sensitized solar cell, titanium dioxide, recycle

1. INTRODUCTION

Recently, biomass is well attracted to a lot of researchers as a substitution for fossil resources such as petroleum. Especially, lignocellulosics were expected to be used as substituted fuels for power generation because of the concept of "carbon free" based on sustainability by photosynthesis. In order to utilize lignocellulosics well, it is necessary to separate efficiently main components, cellulose, hemicellulose and lignin. But it was impossible to separate lignin without damages because native lignin has high sensitivity for change of circumstances. In 1988, novel separation method for components of lignocellulosics under mild condition has developed by Funaoka *et al* [1]. Through the phase-separation system composed of a heterogeneous surface reaction between a concentrated acid and a phenol analog, lignocellulosics is easily converted to carbohydrates in acid and phenolic lignin-based polymers (lignophenols) under 1 atm at room temperature (Fig.1) [1].

Lignophenols has 1,1-bis(aryl)propane-2-*O*-arylether type structures. This structure has high electron density, switching functionality and expansion for modification such as hydroxyl groups or *ortho*-positions of phenols. By switching functionality, both arylcoumaran type structures (second derivative-I) and stybene type structures (second derivative-II) were formed by neighbouring group participation and aryl migration under alkaline conditions, respectively (Fig.1) [2,3].

These derivatives acted as good photosensitizers for nano-porous TiO₂ electrodes for photochemical solar cells [4-7]. Dye-sensitized solar cells with ZnO electrodes have been discovered in latter 1970s, but efficiency was low (η = 1 %) [8]. In 1991, Grätzel *et al* has reported new sandwich type cell with nano porous TiO₂ electrodes (η = 7 %) with ruthenium dye [9]. After

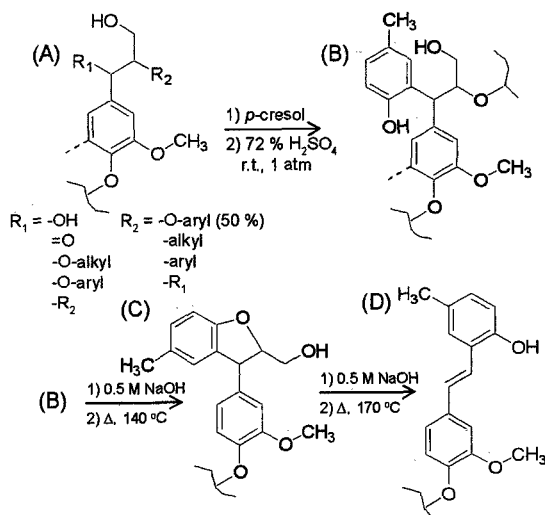


Fig. 1. Synthesis of lignophenol and its derivatives directly from lignocellulosics. (A) Softwood native lignin in lignocellulosics, (B) lignophenols (*p*-cresol type), (C) second derivative-I after neighboring group participation (phenol switching) and (D) second derivative-II after aryl migration.

this breakthrough, a lot of researches were focused on. However natural dyes also have been investigated [10-16], amounts of the dyes are small. On the other hand, stable supply of lignin-based polymer will be expected because lignin exists for 30 % based on lignocellulosics. Moreover, lignin is a sustainable material without restrict of consumption such as rare metals or fossil materials. Therefore, lignophenol and its derivatives are expected to be efficient and cheap photosensitizers for dye-sensitized solar cells.

Thus, in this study an attempt has been made to utilized various recycled lignophenols such as recycled phenolic resins based on lignophenols for

photosensitizers for photochemical cells under visible light irradiation.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols

Hinoki cypress (HC, *Chamaecyparis obtusa*) was used as Softwood materials for the phase-separation system. The woody materials were milled for 80 mesh passed. Extractives in the materials were removed by benzene/ethanol (2/1, v./v.) in a Soxhlet reflux system for 96 hrs. Lignophenols have been synthesized following the phase-separation system. Two-step method (process II) of the phase-separation system was also carried out for HC as follows [2]. The material (500 g) was thrown into acetone solution of *p*-cresol with concentration of 3 mol / phenylpropane units (C_9 units), which were subunits of native lignin. After evaporation of acetone, 72 % H_2SO_4 aq. solution was immersed into the material adsorbed by *p*-cresol at 30 °C. Then the mixture was stirred vigorously for 60 min soon after mixing. After 60 min, the mixture was thrown into 20 L of de-ionized water with vigorously stirring by a homogenizer for 5 min. Then the purple precipitation was washed until pH = 5. After drying the precipitation, lignophenol was extracted by acetone. The lignophenol in acetone was refined by thrown into diethylether (EtOEt) under vigorously stirring in chilled condition. After evaporating and drying on P_2O_5 , Hinoki cypress-lignophenol (*p*-cresol type, HCLC) was obtained.

2.2 Synthesis of derivatives

Acetylated lignophenol was synthesized by acetic anhydride in pyridine solution under room temperature for 48 hrs. The reaction mixture was dropped into chilled water under magnetic stirring. The resulting precipitation was washed by chilled water. After drying over P_2O_5 , acetylated lignophenol (LPAc) was obtained.

Hydroxymethylated lignophenol (HM-LP) was synthesized in 0.5 M NaOH solution by mixing 20 mol of formaldehyde for a amount of aromatic rings in lignophenol at 60 °C under N_2 atmosphere with a stirring system and a reflux condenser. After 3 hrs reaction, 1.0 M HCl was dropped into the mixture at 5 °C to pH = 2.0. The resulting precipitation was washed

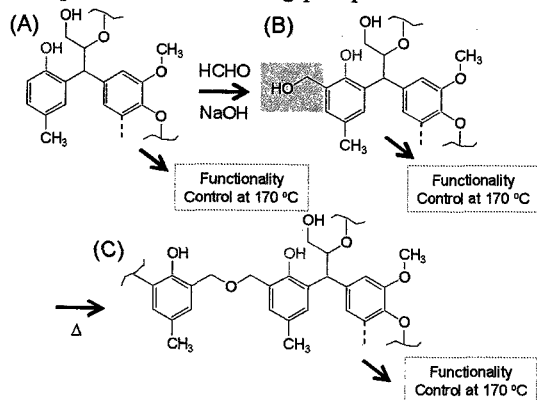


Fig. 2. Synthesis of lignophenol and its derivatives. (A) Hinoki cypress-lignophenol (*p*-cresol type, HCLC), (B) Hydroxymethylated HCLC(HCLC-HM) and (C) Polymerized HCLC-HM(HCLC-HM-P). Second derivative-II of (A), (B) and (C) after aryl migration were derived in 0.5 M NaOH at 170 °C.

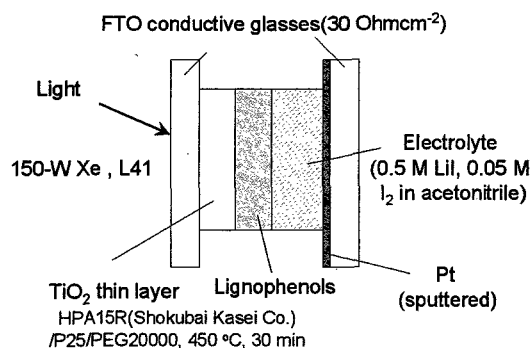


Fig. 3. A schematic model for photochemical cell with nanoporous TiO₂ thin layer on FTO glassed. The composition of cell was FTO-TiO₂-lignophenol-electrolyte (0.5 M LiI, 0.05 M I₂ in acetonitrile)-Pt-FTO. Both visible and infrared light was irradiated from 150-W Xe lamp through L41 UV-cut filter.

to pH = 5.0.

Polymerized HM-LP (HM-LP-P) was polymerized at 150 °C in SUS bat under aerobic condition.

2.2 Synthesis of derivatives

Hydroxymethylated lignophenol (HM-LP) was synthesized in 0.5 M NaOH solution by mixing 20 mol of formaldehyde for a amount of aromatic rings in lignophenol at 60 °C under N_2 atmosphere with a stirring system and a reflux condenser. After 3 hrs reaction, 1.0 M HCl was dropped into the mixture at 5 °C to pH = 2.0. The resulting precipitation was washed to pH = 5.0. The insoluble residue was dried over P_2O_5 .

Polymerized HM-LP (P-HM-LP) was obtained by heating HM-LP at 150 °C for 7 hrs.

2.3 Functionality control

Second derivatives of HCLC, HCLC-HM and HCLC-HM-P were derived under alkaline condition at 170 °C in SUS bombe. Lignophenol materials were dissolved in 0.5 M NaOH. The alkaline solutions were heated to 170 °C in SUS bombe. After 60 min, the alkaline mixtures were neutralized by 1.0 M HCl to pH = 2.0. The resulting precipitation was washed by chilled de-ionized water. The insoluble residue was dried over P_2O_5 .

2.4 Characterization of lignophenols

The structure of lignophenol was characterized by Gel Permeation Chromatography (GPC), ¹H-NMR and Thermal Mechanical Analysis (TMA). GPC was carried out by LC-10 with four columns (KF801, KF802, KF803 and KF804, Shodex Co.), using tetrahydrofuran (THF) after distillation as eluent. M_w and M_n were determined based on standard polystyrene. ¹H-NMR spectrum was measured by NMR500 (JASCO Co.) in CDCl₃ or CDCl₃ / C₃D₅N = 3 / 1 (v / v). TMA was also carried out by TMA-SS(SII Inc.) in the temperature range 50-280 °C at a rate of increase of 2 °Cmin⁻¹, using penetrating technique for a measurement. UV-vis spectroscopy was carried out on a UV-560 (JASCO Co.) with integral sphere apparatus. FT-IR spectroscopy was also carried out on a Spectrum GX (Perkin Elmer Co.), using the KBr pellet technique for sample preparation.

2.5 Preparation of lignophenol solar cell

Photochemical cells with TiO₂ thin film on FTO

glasses employing lignophenols were prepared. TiO₂ pastes were obtained by well mixing HPA-15-R TiO₂ dispersion (Shokubai Kasei Co.), P25(Nippon Aerogel Co.) and polyethylene glycol (Fw = 20 000) at a ratio of 100 : 10 : 4 (w/w/w). Well-ground pastes were coated on FTO-glasses (30 Ohmcm⁻²) using bar-coating technique with 63 μm spacers. The resulting films on FTO were sintered at 450 °C for 60 min under aerobic condition. After cooling to 80 °C, the films on FTO were immersed into lignophenol/acetone solutions. The TiO₂ electrodes employing LP-electrolytes (0.5 M LiI, 0.05 M I₂ in acetonitrile)-Pt-FTO was composition of cells (Fig.3). Performances of the cells were estimated by potentiostat(HA-105, Hokuto Denko Co.) under 150-W Xe lamp(Hamamatsu Photonics Co.) irradiation through L41 UV-cut filter.

3 RESULT AND DISCUSSION

3.1 Second derivative of lignophenols

The photochemical cell employing lignophenols showed good results under visible light irradiation. As shown in Table.I, second derivatives-II of HCLC by functionality control under alkaline condition at 443 K (HCLC443) tended to show better results than HCLC. In the previous reports[4-7], second derivative-I of Hinoki cypress-lignophenol (*p*-cresol type, HCLC413) with TiO₂ electrodes produced the best photo-electricity conversion performance, $V_{oc} = 0.51$ V, $I_{sc} = 10.23$ mAcm⁻², $FF = 0.59$ and $\eta = 3.61$ % under 85.0 mWcm⁻² of visible light irradiation[6]. Moreover, second derivative-II showed higher conversion ($\eta = 2.4$ %) than HCLC ($\eta = 0.81$ %). These improvements were based on two reasons. First, amounts of adsorption on the TiO₂ electrodes influenced the performances. In fact, the amounts of HCLC413 was three times larger than HCLC[6]. Probably the amounts of LP were influenced by size of molecules. By GPC analyses, HCLC has larger molecules ($M_w = 21$ 333, $M_w/M_n = 4.04$) than HCLC443 ($M_w = 1$ 606, $M_w/M_n = 2.14$). Because small fractions penetrated into inner space of nano-porous electrodes, re-combinations of excited electrons were restricted. Consequently, high photovoltage was observed for HCLC443.

Second, visible absorption range based on conjugated structures such as arylcoumaran type structure or

Table I Photo-electricity conversion of photochemical cells with nanoporous TiO₂ electrodes sensitized by Hinoki cypress-lignophenol(*p*-cresol type, HCLC) and its derivatives under visible light irradiation: Acetylated HCLC(HCLCOAc), second derivative-II of HCLC(HCLC443), hydroxymethylated HCLC(HCLC-HM), second derivative-II of HCLC-HM(HCLC-HM-443), polymethylated HCLC-HM(HCLC-HM-P) and second derivative-II of HCLC-HM-P(HCLC-HM-P-443).Electrolyte was 0.5 M LiI, 0.05 M I₂ in acetonitrile.

Lignophenols	Photovoltage V_{oc}/V	Photocurrent $I_{sc}/mAcm^{-2}$	Fill factor (FF)	$\eta/\%$
HCLC	0.48	2.86	0.60	0.81
HCLCOAc	0.43	1.33	0.60	0.33
HCLC443	0.52	2.67	0.58	0.79
HCLC-HM	0.52	2.38	0.64	0.77
HCLC-HM-443	0.45	1.29	0.74	0.41
HCLC-HM-P	0.40	1.38	0.62	0.33
HCLC-HM-P-443	0.47	3.17	0.74	0.89
N3(Ru complex)	0.57	7.33	0.66	2.71

Under 101.0 mWcm⁻² of visible light through L41 filter, 150-W Xe lamp

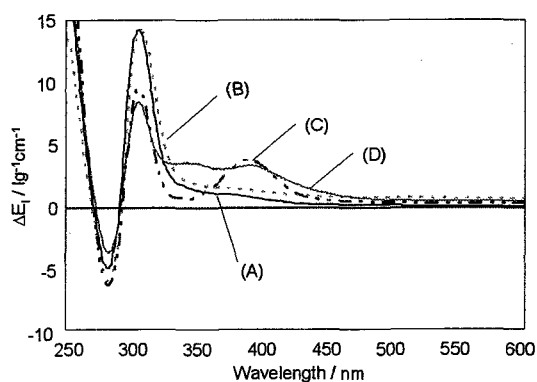


Fig. 4. Ionization difference spectra for lignophenols: (A)Hinoki cypress-lignophenol (*p*-cresol type, HCLC), (B)Hydroxymethylated HCLC (HCLC-HM), (C) second derivative-II of HCLC (HCLC443) and (D) second derivative of polymerized HCLC-HM (HCLC-HM-P443).

styrene type structure (Fig.1) also contributed to high photo-currents.

3.2 Hydroxymethylated lignophenol

Hydroxymethylated HCLC(HCLC-HM) also acted as a good photosensitizer for TiO₂ electrodes, $V_{oc} = 0.52$ V, $I_{sc} = 2.38$ mAcm⁻², $FF = 0.64$ and $\eta = 0.77$ % (Table.I). But performance of second derivative-II of HCLC-HM (HCLC-HM-443) was lower. Although molecular weight of HCLC-HM ($M_w = 17$ 639, $M_w/M_n = 3.42$) was equal to HCLC, high amounts of both aliphatic hydroxyl group (1.37 mol/C₉) and hydroxymethyl group (0.60 mol/C₉) exist in the molecules. In contrast, HCLC-HM-443 ($M_w = 11$ 155, $M_w/M_n = 6.25$) has 0.32 mol/C₉ and 0.05 mol/C₉, respectively. Since intermolecular hydrogen bonds between HCLC-HM and TiO₂ were more easily produced, high photovoltage was produced. Because the interactions of HCLC-HM were occurred by hydroxymethyl groups linked to *p*-cresolic groups on C₁, frontier orbitals stacked on the electrodes. As approaching 1,1-bis(aryl)propane units to TiO₂, efficiency of electron transfer would increase. Moreover, decrease of distance proceeded to decrease re-combination of excited electrons.

As shown in Table I, acetylated HCLC showed low conversion because all hydroxyl groups were blocked by acetyl groups. This result indicated interactions of both hydroxyl groups and aromatic rings influences on cell performances.

3.3 Polymethylated hydroxymethylated lignophenol

Second derivatives of HCLC-HM-P also showed better conversion, $V_{oc} = 0.47$ V, $I_{sc} = 3.17$ mAcm⁻², $FF = 0.74$ and $\eta = 0.89$ % (Table.I). HCLC-HM-P was a kind of resol type phenolic resin. Generally, it is hard phenolic resin with strong three dimensional linkages to be recycled by cleavage of intramolecular linkages. But HCLC-HM-P was easily small-sized by the switching functionality based on phenolic hydroxyl groups. Although HCLC-HM-P was not dissolved perfectly, the switch realized to cleavage C₂-O-C₄ linkages in an alkaline medium with heating for only 170 °C. In fact, 71.1 % of derivatives with $M_w = 7$ 393, $M_w/M_n = 4.25$ obtained from resulting alkaline solution by neutralization. This derivative has darker appearance than HCLC because of conjugated system such as

quinone-type or stilbene type structures. The new antenna structures probably contributed to increase injected electrons excited by visible light. Although structural arrangements were occurred on the main flames of HCLC, the amounts of *p*-cresols and phenolic hydroxyl groups were kept for 0.71 mol/C₉ and 1.29 mol/C₉, respectively. Therefore interactions between HCLC-HM-P and TiO₂ were also occurred same as HCLC. As this result showed, additive values were obtained by recycling of lignophenol derivatives on the downstream of the material flows from lignocellulosics. Since these derivatives were easily obtained with high yield, this utilization was expected.

Fig.4 illustrates ionization difference UV-vis spectra measured between 2-methoxyethanol and NaOH solution. Distinguished variations are observed between 300-500 nm. In these range, both HCLC and HM-HCLC had small broad peaks based on π - π transitions of phenoxide ions (Fig.4 A and B). Moreover, HCLC443 had large peak at $\lambda = 400$ nm. This suggested that some conjugated structures such as arylcoumaran type or stilbene type were produced by switching functionality (Fig.5A and B). Furthermore, second derivative of P-HM-HCLC had two new peaks at 350 and 400 nm. The former peaks were probably based on quinoid type structures such as Fig.5C. The conjugated structures were produced on methylene bridges combined to *p*-cresols under alkaline condition. The latter was same as HCLC443. These peaks increased with decreasing the peak at $\lambda = 320$ nm. This result implied new peaks were produced by rearrangements of 1,1-bis(aryl)propane type structures. These conjugated derivatives will be applied other fine chemical uses such as electronics devices or synthetic precursors

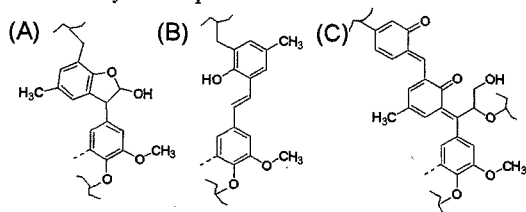


Fig. 5. Conjugated structures for second derivatives of polymerized hydroxymethylated Hinoki cypress-lignophenol (*p*-cresol type) synthesized in alkaline media: (A) arylcoumaran type, (B) stilbene type and (C) quinoid type.

4. CONCLUSION

Photochemical cell sensitized with lignophenol derivatives showed stable photo-electricity conversion. HM-HCLC with high amounts of hydroxymethyl groups showed higher photovoltages by strong interaction with TiO₂ surfaces. Second derivative of polymerized HM-HCLC showed higher performance than HCLC. Therefore the recycled materials on the downstream of material flow through the phase-separation system from lignocellulosics acted as good photosensitizers. This will show new material circulation and new variation for recycling system.

5. REFERENCES

- [1] M. Funaoka and I. Abe, *Tappi.*, 72(8), 145-149 (1989).
- [2] M. Funaoka, *Polym. Int.*, 47, 277-290(1998)
- [3] M. Funaoka, *Macromol. Symp.*, 201, 213-221(2003)
- [4] M. Aoyagi, M. Funaoka, *J. Photochem. Photobiol. A. Chem.*, 164, 53-60(2004)
- [5] M. Aoyagi, M. Funaoka, *Jpn. J. Polym. Sci. Tech.*, 62(6), 283-290(2005)
- [6] M. Aoyagi, M. Funaoka, *J. Photochem. Photobiol. A. Chem.*, 181, 114-119(2006)
- [7] M. Aoyagi, M. Funaoka, *Journal of Network Polymer*, 27(1), 20-29(2006)
- [8] H. Tsubomura, M. Matsumura, Y. Nomura, T. Amamiya, *Nature*, 261, 402-403(1976)
- [9] B. O' Regan, M. Gratzel, *Nature*, 353, 737-740(1991)
- [10] N. J. Cherepy, G. P. Smestad, M. Grätzel, J. Z. Zhang, *J. Phys. Chem. B*, 101, 9347-9351(1997)
- [11] G. P. Smestad, C. Bignozzi, R. Argazzi, *Sol. Energy Mater. Sol. Cells*, 33, 259-272(1994)
- [12] K. Tennakone, G. R. R. A. Kumara, A. R. Kumarasinghe, P. M. Sirmanne, K. G. U. Wijiyantha, *J. Photochem. Photobiol. A Chem.*, 94, 217-220(1996)
- [13] K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottagoda, V. P. S. Perera, P. S. R. S. Weerasundara, *J. Photochem. Photobiol. A Chem.*, 117, 137-142(1998)
- [14] C. G. Garcia, A. S. Polo, N. Y. M. Iha, *J. Photochem. Photobiol. A Chem.*, 160, 87-91(2003)
- [15] R. Mosurkal, J-A. Hea, K. Yanga, L. A. Samuelson, J. Kumara, *J. Photochem. Photobiol. A Chem.*, 168, 191-196(2004)
- [16] S. Hao, J. Wu, Y. Huang, J. Lin, *Solar Energy*, 80, 209-214(2006)

(Received February 16, 2007; Accepted July 12, 2007)