

Photocatalyzed degradation of lignin on TiO_2

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Abstract

In lignin solution with suspended TiO_2 lignin adsorbed to TiO_2 . The illumination of the suspension by UV ($\lambda > 310$ nm) brought about the desorption as well as the degradation of lignin. The tight adsorption was suggested by the suppression of CO_2 evolution, which accompanies the degradation, at high concentration of lignin. During the degradation the aromatic moiety was transformed faster than the aliphatic side chain. In the transformation process lignin was polymerized in the beginning and then converted to smaller molecule successively. Oxygenated compounds such as carboxylate and aldehyde were formed as intermediates. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Lignin; Degradation

1. Introduction

Lignin is natural polymer consisting of phenolic compounds as main units. Its degradation has been studied from environmental interest. Lignin is contained in pulp mill effluent, and is a major COD (chemical oxygen demand) component [1,2]. Its oxidative degradation has been studied by using ozone [3–5], permanganate [6,7] and UV-illuminated H_2O_2 [8]. These studies showed that such oxidation methods alone were not capable to reduce COD effectively. The further study has been carried out on the combination of oxidation with biological treatment [9].

Photocatalytic process may be an alternative method. This process has been newly developed for the treatment of waste water and polluted air [10], and has been known to be effective for the mineralization of many pollutants [11,12]. Photocatalytic degradation of lignin was first studied by Kobayakawa et al. [13]. They showed that the complete mineralization of lignin could be achieved. Whereas Ohnishi et al. [14] compared different photocatalysts for the decoloration of lignin solution and reported large activity of noble metal-loaded TiO_2 . It was also reported that photocatalytic pretreatment enhanced the biological bleaching of effluent from Kraft mill [15]. These authors' interests appear to be in practical aspect. In this article we report on the photocatalytic degradation process of lignin studied by means of UV, FTIR, NMR and GPC.

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2. Experiment

TiO₂ (TP-2 of Fujititan, anatase) was used as photocatalyst [16]. Ligninsulfonic acid sodium salt (coniferous wood lignin) was purchased from Tokyo Kasei and used without further purification. The chemical structure of its main monomer unit is shown in Fig. 1.

For the degradation experiment 0.1 to 2.0 g of TiO₂ was suspended in 300 ml of 0.003 to 0.03% aqueous solution of lignin in a cylindrical reaction vessel. A 100 W super-high pressure mercury lamp was placed in the center of the vessel. It was jacketed by Pyrex glass tube in which cooling water was run. Wavelength shorter than 310 nm was thus cut off by the water jacket. For the measurements of absorption spectrum, TOC (total organic carbon), GPC (gel permeation chromatograph) and the formations of organic acid, aldehyde and SO₄²⁻, samples were withdrawn periodically, and filtered by 0.22–0.45 μm millipore HV-type membrane. For FTIR and NMR analyses the suspension containing 1 g of TiO₂ and either 0.03% (FTIR) or 0.1% (NMR) lignin was illuminated, and the sample was centrifuged, the supernatant was filtered and evaporated to dryness through a rotary evaporator. For the measurement of CO₂ evolution, 75 mg of TiO₂ was suspended in 25 ml of lignin solution in a Pyrex vial. It was closed by a rubber septum and further shielded by an aluminum cap. The vial was illuminated by a 500 W super-high pressure mercury lamp through a water filter having Pyrex glass win-

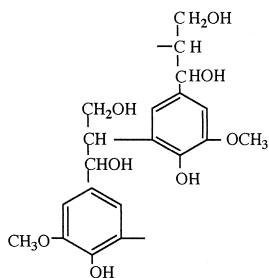


Fig. 1. Main monomer unit of coniferous wood lignin.

dows. Headspace gas was taken by a syringe and CO₂ in the gas was measured by GC.

Absorbance of the sample was recorded at 200 to 350 nm using a JASCO 670 UV–VIS spectrophotometer. TOC was determined by a Shimadzu TOC 500 analyzer. Organic acid was analyzed by a background-suppressing type ionchromatograph Yokogawa IC-7000. Aldehyde was detected by a HPLC comprised of a Shimadzu LC 9A pump and a Hitachi L 400 UV detector after coloring by 2,4-dinitrophenylhydrazine [17,18]. SO₄²⁻ was detected by an ionchromatograph comprised of JASCO 880-PU pump and Shodex CD-4 conductometer. Horiba FT-200 was used for the FTIR analysis. GPC was measured by the same HPLC as used for the analysis of aldehyde, and polystyrenesulfonate standard was used to calibrate molecular weight [7]. ¹H NMR spectrum was recorded by a Varian 300 BB.

3. Results and discussion

The absorption spectra of lignin at different illumination times were shown in Fig. 2. Illumination reduced the intensity of absorption in the entire wavelength from 200 to 350 nm. No appreciable additional band due to transformation of lignin appeared by illumination. In a separate experiment the absorbance at 280 nm plotted against the concentration of lignin gave a linear curve showing that the absorption measurement offers a convenient method to evaluate the degradation of lignin. On the basis of these preliminary experiment the extent of the degradation (transformation) of lignin was monitored by measuring the absorbance at 280 nm.

Fig. 3 illustrates the decrease in absorbance at 280 nm and TOC value, when the mixture was illuminated immediately after mixing (< 20 s). Following quick adsorption of lignin to TiO₂, the illumination appears to cause the desorption as well as the degradation as indicated by the slower apparent degradation in the beginning of illumination than the later time. To estimate

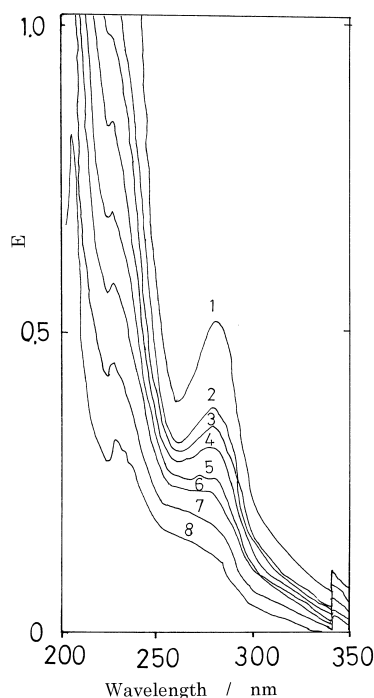


Fig. 2. Absorption spectra of lignin at different illumination times. Lignin 0.01%, TiO_2 3.3 g l^{-1} . (1) Before illumination, (2) 15 min, (3) 30 min, (4) 60 min, (5) 90 min, (6) 120 min, (7) 150 min, (8) 180 min.

apparent degradation rate TOC eliminated between first 15 and 90 min was calculated for different amounts of TiO_2 (Table 1). It was shown that the degradation rate decreased as the amount of TiO_2 increased, whereas the time required for the complete transformation (achievement of zero absorbance) was shortened

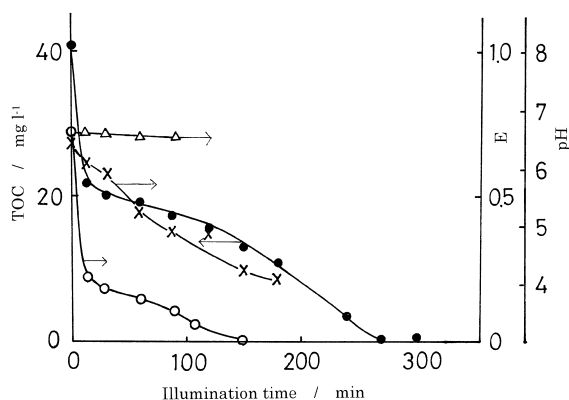


Fig. 3. Decrease in absorbance and TOC, and change in pH by illumination. Lignin 0.01%, TiO_2 6.6 g l^{-1} . \circ Absorbance, \bullet TOC, \times pH, Δ absorbance in the absence of TiO_2 .

Table 1
Effect of the amount of TiO_2 on photocatalytic degradation of lignin^a

TiO_2 / g	Rate of mineralization ^b / $\text{mg l}^{-1} \text{ h}^{-1}$ (TOC)	Time required for zero absorbance at 280 nm/min
0.5	5.2	
0.7	306	
1.0	3.4	260
1.5	3.2	200
2.0	1.9	150

^aLignin: 0.1%.

^bCalculated from the decrease in TOC between 15 to 90 min of illumination.

by the increase in the amount of TiO_2 . These contradictory results may be due to the large desorption of lignin upon illumination. Relation between degradation rate and the initial concentration of lignin was analyzed by the following Langmuir–Hinselwood equation.

$$1/r = 1/k_1 KC + 1/k_1. \quad (1)$$

Where r is degradation rate, k_1 rate constant, K adsorption constant and C initial concentration of lignin. r was calculated in the same manner as in Table 1. The plot of r^{-1} against C^{-1} gave a nearly straight line, from which $K = 4.3 \text{ l g}^{-1}$ was obtained. On the other hand, in dark the adsorption of lignin to TiO_2 followed Langmuir's adsorption isotherm given by Eq. (2).

$$C/w/m = 1/Kk_2 + C/k_2. \quad (2)$$

Where w is the amount of adsorbed lignin, m the amount of TiO_2 , k_2 constant, and others the

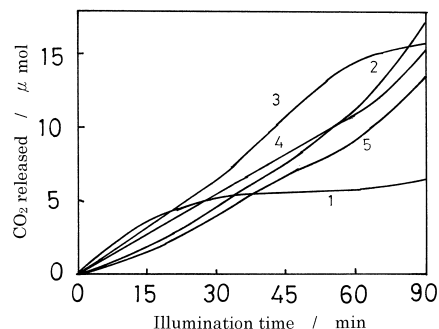


Fig. 4. Effect of the concentration of lignin on CO_2 evolution. Lignin: (1) 0.001%, (2) 0.002%, (3) 0.003%, (4) 0.01%, (5) 0.03%.

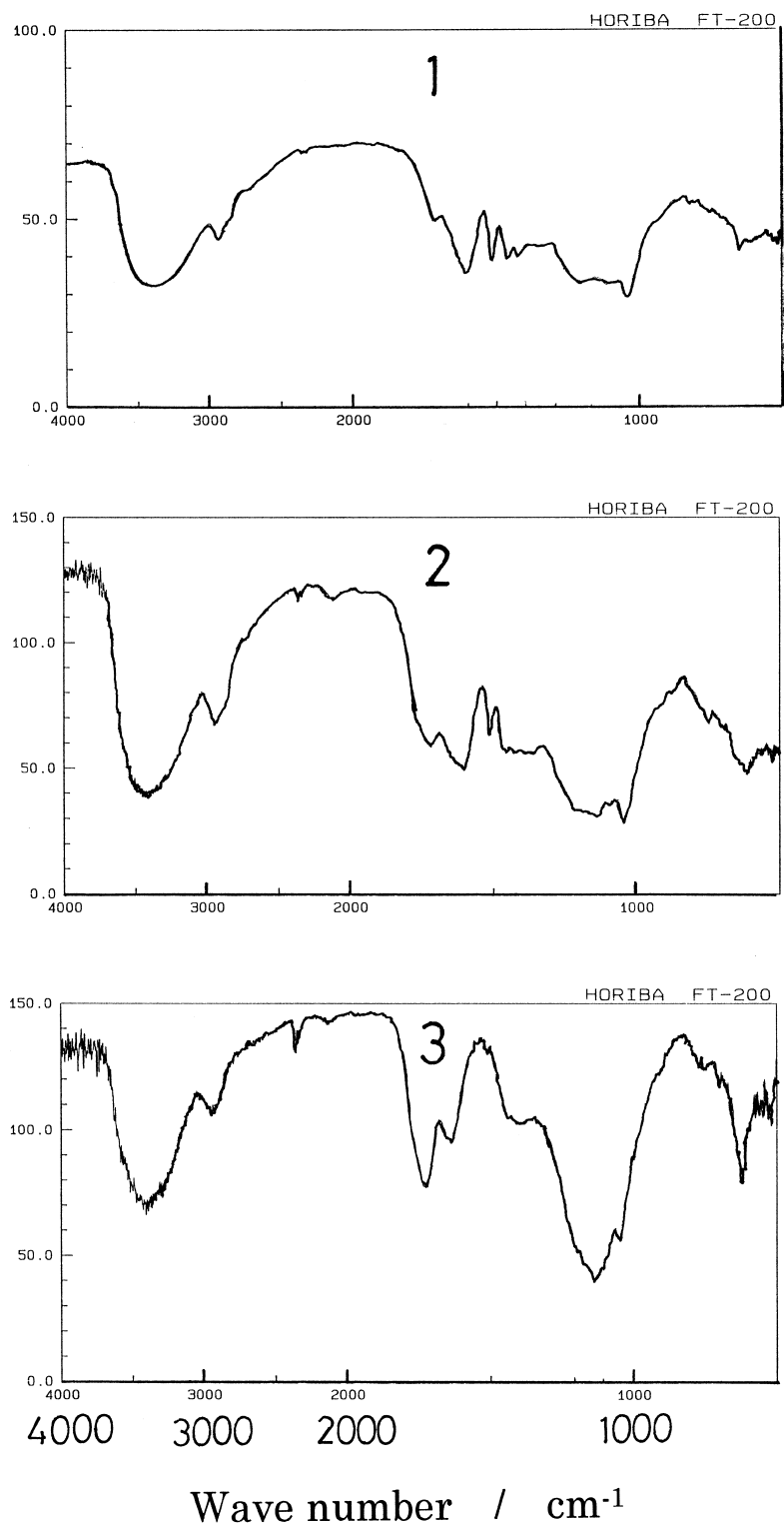


Fig. 5. FTIR spectra at different illumination times. (1) Before illumination, (2) 5 h, (3) 16 h.

same as in Eq. (1). $K = 14 \text{ l g}^{-1}$ was obtained from this equation. K obtained from the dark experiment is larger than that from the photocatalytic experiment. Such discrepancy has already been pointed out for other compounds in the

literatures [19–21], in which the former value is larger than the latter, and was attributed to photoadsorption besides other factors. Obviously our result is attributed at least partially to the photodesorption.

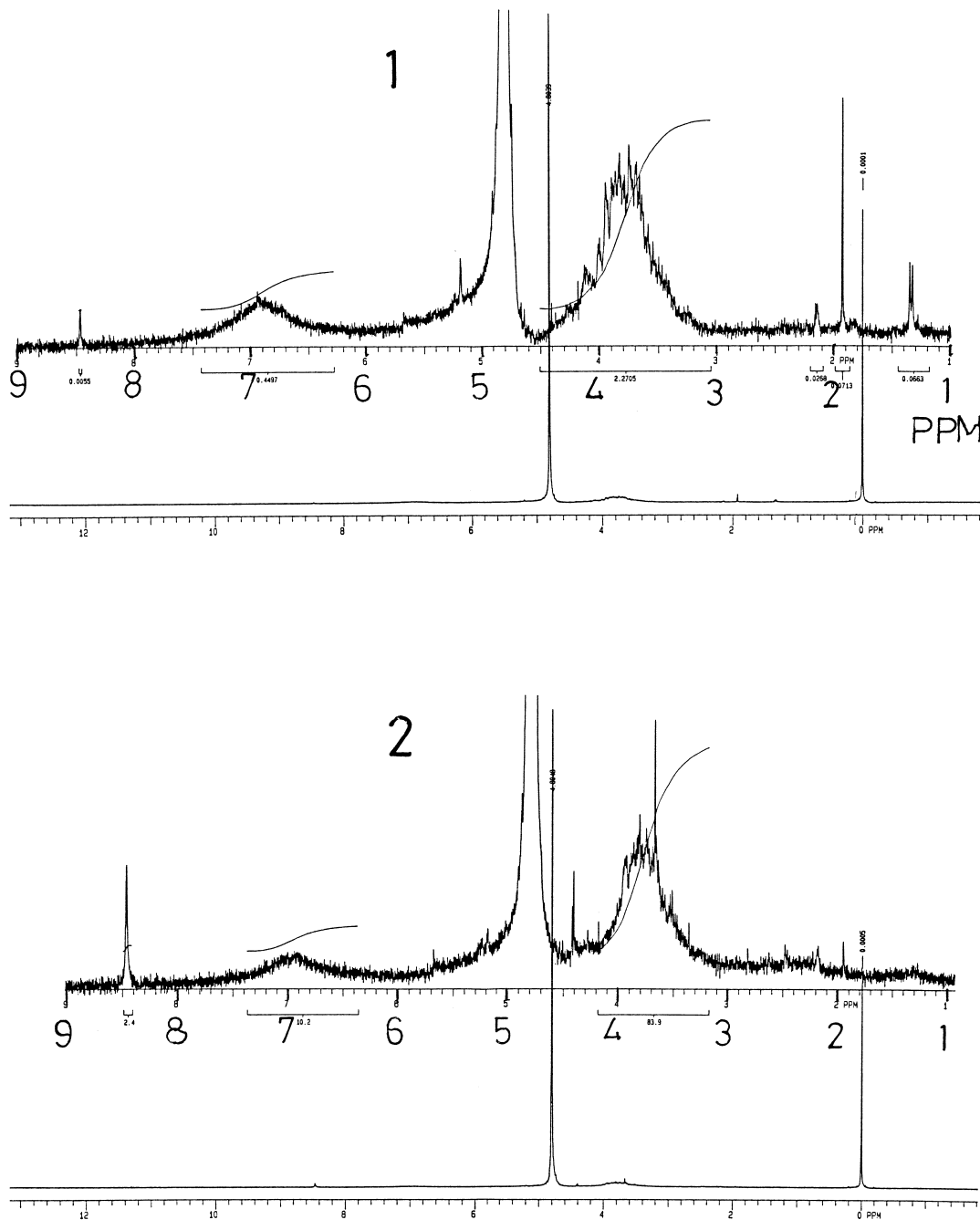


Fig. 6. NMR spectra before and after illumination. (1) Before illumination, (2) 24 h.

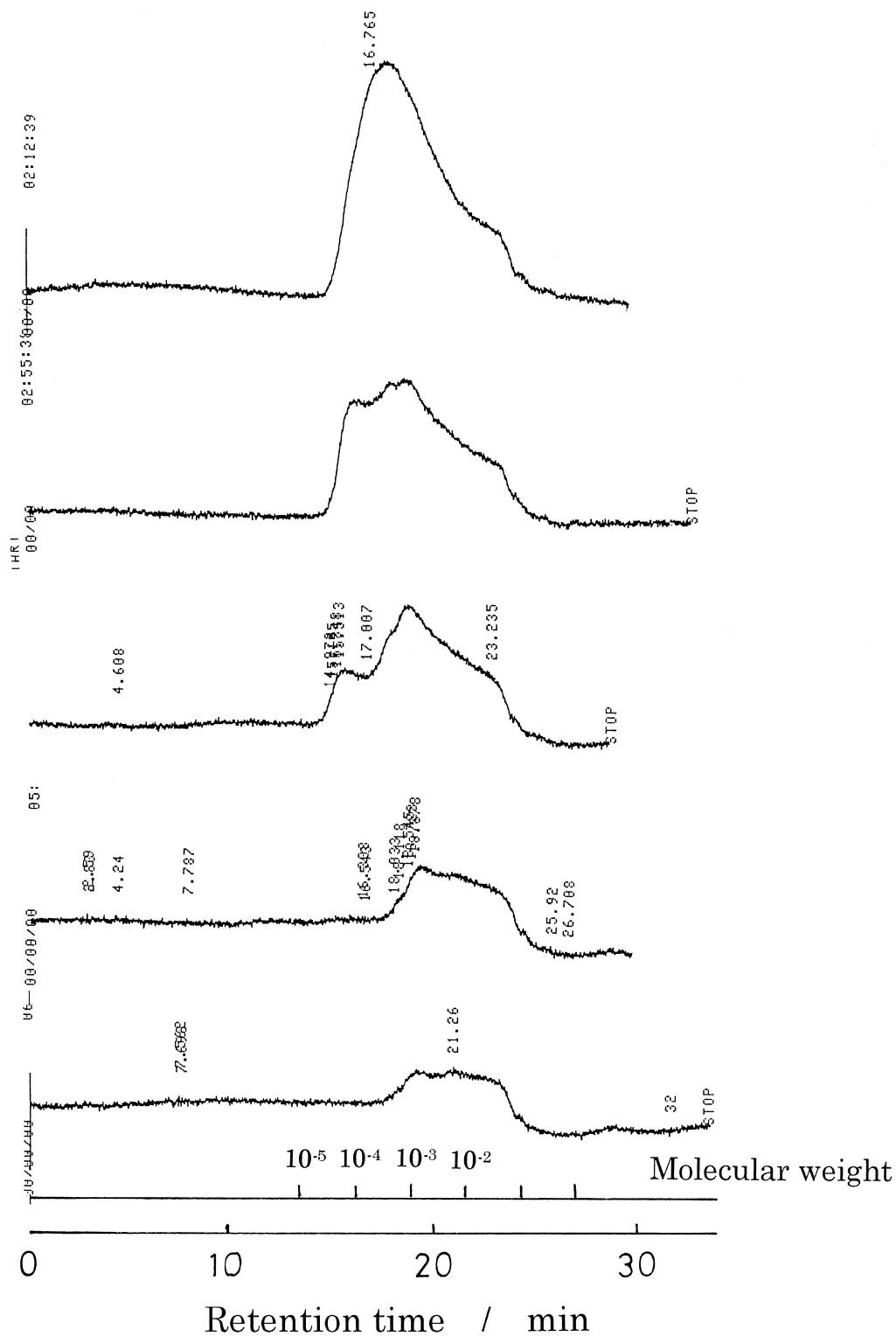


Fig. 7. Gel permeation chromatograms at different illumination times. (1) Before illumination, (2) 15 min, (3) 60 min, (4) 120 min, (5) 180 min.

Degradation of lignin was accompanied by the formation of SO_4^{2-} and a decrease in pH. Just stirring the suspension without illumination resulted in the release of SO_4^{2-} , and illumination brought about a slow increase in its concentration.

CO_2 evolution decreased with the increasing concentration of lignin as shown in Fig. 4. This peculiar result leads us to assume that CO_2 is trapped by lignin layer formed on TiO_2 grains. This layer might retard the degradation of lignin by reducing the supply of O_2 to the surface of TiO_2 which is essential for photocatalytic degradation [22].

Absorption maximum at 280 nm in UV spectrum can be assigned to aromatic ring. This assignment indicates that the reduction in the absorbance is due to the transformation of aromatic ring. Thus Fig. 2 shows that all the aromatic rings were transformed after 150 min of illumination.

FTIR measurement indicated the fast transformation of aromatic ring. Fig. 5 shows FTIR spectra before illumination and after 5 h and 16 h illuminations. Bands at 1600, 1505 and 1425 cm^{-1} before illumination are assigned to aromatic ring [23]. They disappeared by illumination, while a broad band appeared around 1150 cm^{-1} . This new band might be due to SO_4^{2-} . Whereas band at 2920 cm^{-1} is assigned to CH_3 , CH_2 and CH [23]. They remained unchanged after illumination. Band at 1030 cm^{-1} is assigned to aromatic C–H, C–O of primary alcohol and C=O [23]. This band remained unchanged after 16 h of illumination. Other new band appeared around 1720 cm^{-1} , which may be assigned to carbonyl group. This assignment suggests the formation of carboxylate and/or aldehyde. These FTIR results demonstrate that aromatic ring is transformed and oxygenated compounds were formed thereby.

^1H NMR spectra of the samples before illumination and after 24 h illumination were shown in Fig. 6. Band around 3.9 ppm is assigned to methoxy and aliphatic side chains [24,25] and that at 6.9 ppm to aromatic ring. Ratios of the

areas of two peaks were 5.0, 5.7 and 8.2 for the samples before illumination and after 16 h and 24 h illuminations, respectively. These results show that the aromatic ring degrades faster than the aliphatic chain. In this regard it has been reported that permanganate oxidizes predominantly aliphatic side chain (in neutral and alkaline media) [4,7] whereas O_3 degrades mainly aromatic moieties [4]. It should be noted that both ozonation and photocatalytic process are oxidation by OH radical.

In GPC a peak is centered around 2630 of molecular weight (Fig. 7). By illumination the peak shifted toward lower molecular weight, indicating that lignin molecule was depolymerized by illumination. However the comparison of chromatograms before and after illumination suggests that some portions of lignin molecules were polymerized in the beginning of degradation. By the further illumination lignin degraded successively to lower molecular weight. On the other hand decrease in the peak area demonstrates the transformation of aromatic ring occurring simultaneously with the depolymerization.

As aliphatic intermediates formic acid, acetic acid, glycolic acid, formaldehyde and a trace of glyoxylic acids ($< 10^{-5} \text{ mol l}^{-1}$) were detected. They were formed from the early stage of degradation. Acetic acid, formic acid and formaldehyde were in the highest concentration

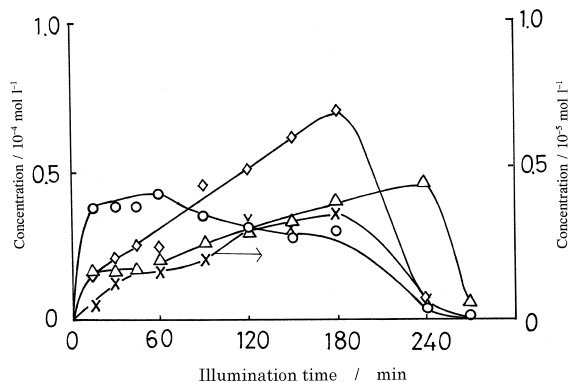


Fig. 8. Formation of aliphatic compounds. Lignin: 0.01%, TiO_2 3.3 g l^{-1} . \circ Formic acid, \triangle acetic acid, \times glycolic acid, \diamond formaldehyde.

throughout the degradation (Fig. 8). Total of TOCs from acetic acid, formic acid and formaldehyde accounted for about 6 and 15% of remaining TOC after 60 and 180 min, respectively. Since formaldehyde can be oxidized to formic acid, it is considered that lignin is eventually converted to CO₂ mainly via acetic and formic acids [11].

4. Conclusion

Lignin was adsorbed to TiO₂ quickly, and the subsequent illumination resulted in the desorption and degradation simultaneously. In the degradation process lignin was depolymerized successively and aromatic ring was opened, which produced oxygenated compounds such as carboxylate and aldehyde. The prolonged illumination led to the complete mineralization.

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