Original Article

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# Production of Vanillin and Vanillic Acid by Aerobic Oxidation of Polyethylene Glycol (PEG)-modified Glycol Lignin in Tetrabutylammonium Hydroxide

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**Abstract**

Aerobic oxidation of lignin in reaction media containing $Bu_4NOH$ facilitates efficient production of vanillin (4-hydroxy-3-methoxybenzaldehyde) and vanillic acid (4-hydroxy-3-methoxybenzoic acid). This study presents production of these compounds from polyethylene glycol (PEG)-modified glycol lignin (PEG-lignin) from Japanese cedar (*Cryptomeria japonica*). A $Bu_4NOH$-based reaction medium was prepared by the addition of NaOH(s) to 1.25 mol/L $Bu_4NOH$ aq. Degradation of the PEG-lignin (14 mg) in 2.0 mL of the medium at 120 $^{o}$C under $O_2$ in a sealed test tube produced vanillin and vanillic acid with 9.1 and 2.6 wt% yields, respectively, based on the Klason lignin amount of the PEG-lignin. The total yield of vanillin and vanillic acid reached 79.6 % of that in the corresponding alkaline nitrobenzene oxidation (14.7 wt%), indicating high performance of the medium. Bench-scale aerobic oxidation of the PEG-lignin (100 g /1.0 L) under $O_2$ pressurized at 0.7 MPa gave the products with their maximum yields similar to those in the above lab-scale experiment. Further increase in the $O_2$ pressure to 2.5 MPa significantly shortened the reaction time to achieve the maximum product yield. This pressure increase did not affect the vanillin yield, but suppressed the formation of $O_2$-sensitive vanillic acid, by which selective vanillin production was achieved.

***Keywords**:  Alkali; Conversion; Depolymerization; Ionic liquid; Quaternary ammonium*

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## INTRODUCTION

Vanillin (3-methoxy-4-hydroxybenzaldehyde) is one of the target compounds to be produced from softwood lignin. The compound is a platform chemical in industry, which is a source of several medicine, polymer material, etc [1-4)]. Aerobic oxidation of lignosulfonate, a major component of waste water from sulfite pulping, is a way to produce lignin-based vanillin [3-8)]. This vanillin production is usually carried out in alkaline media such as NaOH under compressed air at 170-180 $^{o}$C in the presence of Cu(II)-based catalysts. However, management of waste water containing sulfur compounds is a major draw-back of this biomass-based vanillin production process [3)]. Worldwide decrease in the sulfite puling process also makes this type of vanillin production less commercially attractive.

Our previous studies have reported that selective vanillin production can be made by aerobic oxidation of several softwood lignin samples at 120 $^{o}$C in the presence of tetrabutylammonium ion $Bu_4N^+$ and $OH^-$ [9-11)], where the employed medium $Bu_4NOH$ is a precursor of various $Bu_4N^+$-based ionic liquids. For example, when Japanese cedar (*Cryptomeria japonica*) wood flour is oxidized in 1.25 mol/L $Bu_4NOH$ aq. at 120 $^{o}$C under $O_2$, vanillin is produced in 23.2 wt%, based on the Klason lignin amount of the wood [11)]. This vanillin yield is comparable to that obtained in the alkaline nitrobenzene (AN) oxidation (27.2 wt%), indicating high performance of the aerobic oxidation in $Bu_4NOH$ for vanillin production. This high efficiency achieved with the $Bu_4NOH$-based medium has been attributed to stabilization of a vanillin precursor formed at the end of lignin polymer by positive interaction between $Bu_4N^+$ and the aldehyde group of the precursor [11)]. The aerobic oxidation also produces vanillic acid (3-

hydroxy-4-hydroxybenzoic acid), the oxidized form of vanillin, as the second major product, where vanillic acid is also expected as a source of biomass-based polymer materials 12).

The $Bu_4NOH$-based oxidation method has several advantages over the process with lignosulfonate and simple alkali: this method employs reaction temperature (120 °C) that is significantly lower than that of the lignosulfonate process (~170 °C); the process can utilize non-sulfur containing row materials such as wood flour and soda-lignin as well as lignosulfonate. Also, the use of molecular oxygen as an ideal non-toxic oxidation reagent in this process should be emphasized.

Polyethylene glycol (PEG)-modified glycol lignin (PEG-lignin hereafter) is produced by solvolysis of native lignin in PEG in the presence of a catalytic amount of sulfuric acid 13-16). PEG-lignin from Japanese cedar wood shows viscous thermal flow properties, which enables its application as various lignin-derived plastic materials 17-19). The present paper shows another option of using PEG-lignin as useful monomer chemicals. Our idea in this article is to produce vanillin from PEG-lignin with the $Bu_4NOH$-based method being employed. The PEG-lignin production process - as it goes for any material production processes - cannot avoid formation of some amount of the products that do not meet quality standard from the view point of their material use, but almost chemically identical to the required PEG-lignin. The production of vanillin, a compound with significant usefulness, from such by-produced PEG-lignin is beneficial to make overall PEG-lignin production process more commercially efficient.

On the basis of the above considerations, this article presents production of vanillin and vanillic acid by aerobic oxidation of PEG-lignin in our $Bu_4NOH$-based medium, first in a small lab-scale (14 mg of the sample/2.0 mL of the medium) system that has been previously applied to several lignin samples 9-11). We will discuss difference in the vanillin and vanillic acid formation behaviors between PEG-lignin and native lignin in Japanese cedar and clarify several properties specific for PEG-lignin as a raw material for the aerobic oxidation. Next issue to be handled in this paper is scaling-up of the reaction system, looking ahead at industrial application of the process. In this topic, we carry out the aerobic oxidation of PEG-lignin in a 5.0 L bench-scale reactor under pressured $O_2$ atmosphere, with increased amounts of the starting material and the medium (100 g and 1.0 L, respectively).

## EXPERIMENTAL

### Materials

1.5 mol/L $Bu_4NOH$ aq. was purchased from the Sigma-Aldrich Co. The solution was diluted to 1.25 mol/L with distilled water and used as the reaction solution. PEG-lignin was prepared by solvolysis of Japanese cedar wood with PEG-200 in the presence of sulfuric acid, accroding to the procedure presented in the literature 16). The Klason lignin content and the PEG/lignin ratio of the PEG-lignin was 81.7 and 22.3 wt%, respectively 16).

### Lab-scale Experiment

The PEG-lignin (14-200 mg) was placed in a 10 mL glass tube. After adding the reaction medium (2.0 mL of 1.25 mol/L $Bu_4NOH$ aq. containing 200 mg of NaOH), the tube was flushed with $O_2$ and immediately sealed. This medium will be called $Bu_4NOH$-based reaction medium, hereafter. The PEG-lignin was completely solubilized into the $Bu_4NOH$-based reaction medium with a dark-colored homogeneous solution being eventually formed. The tube was then heated at 120 °C in an oil bath with stirring. These reaction conditions were similar to those optimized for the aerobic oxidation of Japanese cedar wood 11). After the reaction solution was stirred for a certain time, the tube was cooled with cold water and an ethanol solution of an internal standard (1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene, 2.0 g/L, 800 μL) was added to the resulting solution. A sample (50 μL) of the reaction mixture was taken and added to acetonitrile (450 μL) containing 1.5% acetic acid. The solution was filtered and used directly for high-performance liquid chromatography (HPLC) analysis.

The HPLC analysis was carried out with HPLC system (Shimadzu, Ltd., Kyoto, Japan) equipped with pump (LC10AD), column oven (CTO-10A), and ultraviolet–visible detector (SPD-10A) set at 280 nm. Analytical conditions were a Cadenza CD-C18 (Imtakt, Co., Kyoto, Japan) column, a flow rate of 0.8 mL/min, a 1.5% acetic acid aq/acetonitrile eluent (90/10 → 45/55 0–30 min, 45/55 →

0/100 30–35 min, 0/100 35–40 min, 0/100 → 90/10 40–45 min, 90/10 45–60 min) after passing through the degasser (DGU-14A, Shimadzu, Ltd., Kyoto, Japan), and a column temperature of 30 °C.

## Bench-scale Experiment

The PEG-lignin (100 g) was mixed with 1.0 L of 1.25 mol/L $Bu_4NOH$ aq. containing 100 g of NaOH (the $Bu_4NOH$-based medium). The resulting mixture was then put in a high pressure reaction vessel illustrated in Fig. 1. After closing the vessel, $O_2$ was introduced via the valve A in Fig. 1 and the inside was pressurized at 0.7–2.5 MPa. The reaction solution was stirred at 300 rpm with the mixer and the inside temperature was elevated to 80–120 °C. We defined the reaction time zero as the time the inside temperature reached the target temperature; it usually took 20 to 30 min after the heating was started. During the reaction around 10 mL of the reaction solution was taken by carefully opening the valve B in Fig. 1 at certain reaction times. The ethanol solution (800 μL) of the internal standard was then added to 1.0 mL of the sample and the resulting solution was analyzed with HPLC with the same manner presented above.

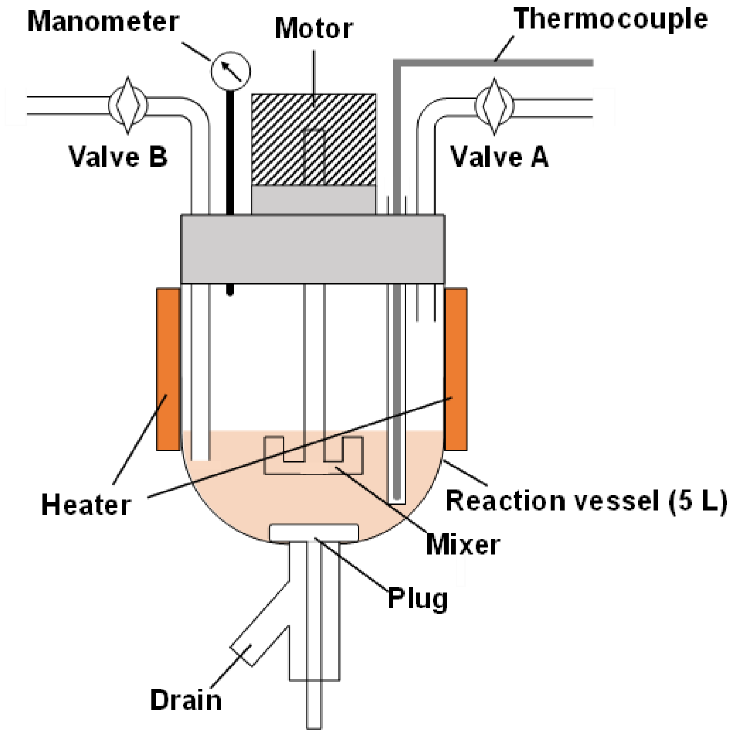

**Fig. 1.** High pressure 5.0 L reactor for the bench-scale experiments.

The pressure in the vessel was reverted back to atmospheric by opening the valve A. After the reaction solution was cooled to room temperature, all solution in the reaction vessel was taken away from the drain in Fig. 1. We usually observed two separated phases for the resulting solution probably due to the insufficient solubility of NaOH to the $Bu_4NOH$ aq.: one of the phases was dark-colored with the other being nearly colorless and their volume ratio was around 9:1. We sampled 1.0 mL of both phases and analyzed them with HPLC, finding that the minor colorless phase contained only trace of HPLC-detectable products. Thus, we do not take the products in the minor phase into consideration for overall discussion in this article.

## RESULTS AND DISCUSSION

### Property of PEG-lignin as a Source for Aerobic Oxidation

To investigate the performance of the Bu$_4$NOH-based reaction medium for vanillin production from the PEG-lignin, we first carried out the aerobic oxidation of a small amount (14 mg) of the PEG-lignin in the lab-scale reactor (10 mL test tube) under the conditions similar to those previously employed for Japanese cedar wood: 2.0 mL of the Bu$_4$NOH-based reaction medium/ 120 °C/ $O_2$ 11). Fig. 2 shows a typical HPLC chromatogram of a resulting reaction mixture. Vanillin and vanillic acid were produced from the PEG-lignin as the major low molecular weight products from the PEG-lignin along with relatively minor amounts of *p*-hydroxybenzaldehyde, acetoguaiacone, and guaiacol; vanillic acid appears as a seemingly small peak in Fig. 2 due to its low absorbance at 280 nm.

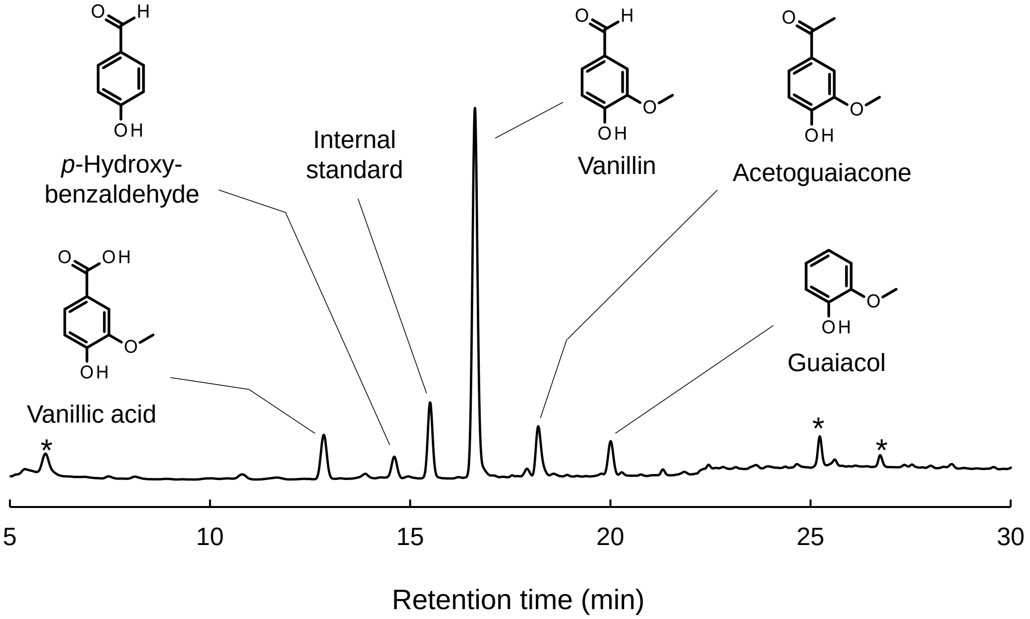

**Fig. 2.** HPLC chromatogram of the reaction mixture obtained after the aerobic oxidation of the PEG-lignin (14 mg) in the Bu$_4$NOH-based medium (2.0 mL) at 120 °C under air (detector: UV$_{280nm}$). Unidentified peaks are indicated with asterisk.

As shown in Fig. 3A, the yields of the major products, vanillin and vanillic acid, reached maximum at 6 h and their yields were 9.1 and 2.6 wt%, respectively, on the basis of the Klason lignin amount of the PEG-lignin. Table 1 compares these yields to those obtained in the AN oxidation of the same sample (entry 1 and 4). It becomes clear that the total yield of vanillin and vanillic acid (11.7 wt%) obtained after the aerobic oxidation in the Bu$_4$NOH-based medium reached 79.6 % of that after the corresponding AN oxidation (14.7 wt%). We therefore concluded that the aerobic oxidation in the Bu$_4$NOH-based medium produced these compounds, especially vanillin, with significant efficiency from the PEG-lignin.

Table 1 also compares the yields of vanillin and vanillic acid from the PEG-lignin (14 mg) to those from Japanese cedar (14 mg) reported previously (entry 1 and 5) 11). The aerobic oxidation of the PEG-lignin obviously formed vanillin with lower yields than that of Japanese cedar. For vanillic acid, on the other hand, the maximum yield (2.6 wt%, entry 1) was higher in the PEG-lignin than in Japanese cedar (1.2 wt%, entry 5). We have previously suggested that vanillin and vanillic acid are produced via different pathways: oxidation of vanillin into vanillic acid is not a major pathway at least under the conditions employed in our studies 11). It would be thus stated that some modification of the reaction pathway has been made by the changes of the sample from Japanese cedar to the PEG-lignin, although detailed mechanistic background is unclear at present.

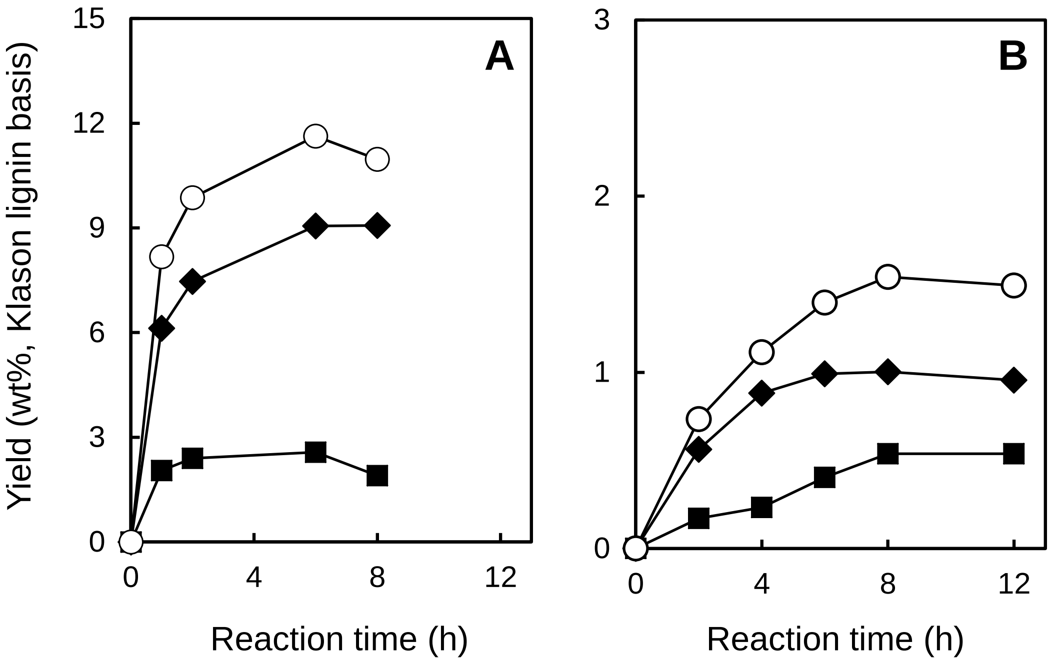

**Fig. 3.** Changes in the yields of vanillin (◆), vanillc acid (■), and their total yield (○) during the lab-scale aerobic oxidation of 14 mg (A) and 200 mg (B) of the PEG-lignin in 2.0 mL of the $Bu_4NOH$-based reaction medium at 120 °C under $O_2$.

**Table 1.** The yields (wt%, Klason lignin basis [a)]) of vanillin and vanillic acid after the aerobic oxidation of the PEG-lignin and Japanese cedar in the $Bu_4NOH$-based medium (2.0 mL) under $O_2$ at 120 °C, along with the results of alkaline nitrobenzene (AN) oxidation of the PEG-lignin.

| Entry | Sample | Sample (mg) /medium (mL) | Oxidant /reaction time [b)] | Yield (wt%) | | |
|---|---|---|---|---|---|---|
| | | | | Vanillin | Vanillic acid | Total |
| 1 | PEG-Lignin | 14/ 2.0 | $O_2$/ 6 h | 9.1 | 2.6 | 11.7 |
| 2 | PEG-Lignin | 200/ 2.0 | $O_2$/ 8 h | 1.0 | 0.54 | 1.5 |
| 3 | PEG-Lignin | 20/ 0.2 | $O_2$/ 8 h | 1.5 | 0.50 | 2.0 |
| 4 | PEG-Lignin | 14/ 2.0 | Nitrobenzene/ 2.5 h [c)] | 12.1 | 2.6 | 14.7 |
| 5 | Japanese cedar [11)] | 14/ 2.0 | $O_2$/ 4 h | 23.2 | 1.2 | 24.4 |
| 6 | Japanese cedar [11)] | 14/ 2.0 | Nitrobenzene/ 2.5 h | 27.2 | 1.2 | 29.4 |

[a)] The Klason lignin contents were 81.7 and 32.4 wt% for the PEG-lignin [16)] and Japanese cedar [11)], respectively. [b)] The results of the aerobic oxidation in the $Bu_4NOH$-based medium are those at the reaction time the total yield of vanillin and vanillic acid became maximum. [c)] AN oxidation was carried out under the conditions of the sample (14 mg)/ 2.0 M NaOH aq. (2.0 mL)/ nitrobenzene (50 μL)/ 170 °C.

Solvolysis of native lignin in wood by PEG leads to the introduction of PEG chains mainly to the α-positions of the lignin polymer [16)]. In fact, 2D HSQC NMR analyses of the PEG-lignin suggested that β-O-4 units in the PEG-lignin were derivatized with a PEG chain at the α-position and do not possess free α-OH groups. The presence of such PEG moiety would be a reason for the above differences. The PEG moieties introduced to the non-phenolic units of lignin are especially persisting under alkaline conditions and expected to be a major reason for the above modification of the reactivity.

Additional aerobic oxidation experiments with α-substituted lignin model compounds, especially β-O-4 models, will provide mechanical supports for the role of the α-PEG groups in the PEG-lignin. In the AN oxidation substitution of $C_\alpha$-OH with an alkoxy group usually ends up in decrease in the yield of the benzaldehydes [20)]. This explains the relatively low yield of vanillin in the AN oxidation of the PEG-lignin (12.1 wt%, entry 4 in Table 1). The above lower yield of vanillin from the PEG-lignin in the aerobic oxidation could also be explained from the same reason, but further systematic investigation on the mechanisms in the AN oxidation and the aerobic oxidation is necessary to clarify the details. It is also noted that the PEG-lignin employed in this study have not undertaken intensive acid condensations during its production from the raw material [16)], and hence the low yield of vanillin is not attributed to the presence of the condensed structures in the PEG-lignin.

In addition to the different yields, the PEG-lignin took longer reaction time (6 h) than Japanese cedar (4 h) to achieve the maximum total yields of vanillin and vanillic acid, according to Table 1 (entry 1 and 5). The observations about the yields and the reaction times suggest that the PEG-lignin is a more difficult starting material than native lignin in the original wood, at least when vanillin is set as the target compound. However, it should be emphasized that the product yield from the PEG-lignin is still significantly higher than that in the current vanillin production from lignosulfonate, which is usually around 5 % [3,6-8)]. Also, our method employs a much lower temperature (120 $^{o}$C) and does not necessitate metal catalysts. It is thus concluded that our $Bu_4NOH$-based process is worth being applied to the vanillin and vanillic acid production from the PEG-lignin.

To render the reaction system more practical from industrial perspective, we then carried out the aerobic oxidation of the PEG-lignin with the concentration of the sample being increased from 14 mg/ 2.0 mL to 200 mg/ 2.0 mL. As shown in Fig. 3B, however, the increase in the concentration ended up in drastic decrease in the product yields (see also entry 1 and 2 in Table 1). One of the possible reasons for this decrease is that in such concentrated solution reaction pathways other than those forming the desired products became more significant. For instance, bimolecular alkaline condensation, i.e. formation of diphenylethane structures [21)], would be enhanced with the increase in the sample concentration, although the HPLC analysis of the reaction mixture did not indicate the presence of such condensed products. Products derived from the condensations, supposedly dimers and trimers, are not usually detected as major products even under the conditions bimolecular reactions are enhanced. This is probably because condensations generally occur among aromatic units in the lignin polymer, resulting in the formation of HPLC-undetectable compounds with rather high molecular weights.

It is also possible that the $O_2$ amount relative to the PEG-lignin became insufficient with the increase in the concentration, which led to the low product yield; note that we here employed tightly sealed reaction system (see experimental section). To check the possibility of the $O_2$ shortage, we carried out the aerobic oxidation of 20 mg of PEG-lignin in 0.2 mL of the reaction solution, where the volume of the reaction solution was decreased from 2.0 mL with the sample concentration and the volume of the reactor (10 mL) being fixed. As listed in entry 3 in Table 1, the aerobic oxidation under $O_2$ in this smaller reaction scale gave vanillin and vanillic acid in 1.5 and 0.50 wt%, respectively, which were moderately greater than those obtained in the 200 mg/ 2.0 mL system. As one of the major differences between the 200 mg/ 2.0 mL and the 20 mg/ 0.2 mL systems is the amount of oxygen relative to PEG-lignin, we concluded that the decrease in the product yields caused by the increase in the concentration was partially due to the depravation of $O_2$ to fully oxidize the PEG-lignin to the final products.

## Bench-scale Aerobic Oxidation of PEG-lignin

The considerations in the previous section led us to the idea that vanillin was expected to be produced in significant yields even in the concentrated system, when the reaction was carried out under pressurized $O_2$. To this end, we performed the aerobic oxidation of the PEG-lignin (100 g) in the $Bu_4NOH$-based medium (1.0 L) under $O_2$ pressurized at 0.7 MPa with the bench-scale reaction system in Fig. 1 being employed. As shown in Fig. 4A, the maximum product yield was obtained at the reaction time of 3 h. This reaction time was significantly shorter than that in the case of the lab-scale experiment (6 h, Fig. 3A). Furthermore, the maximum vanillin yield achieved in the bench-scale experiment (8.7 wt% as listed in entry 1 in Table 2) was different by only 0.4 wt% from that obtained in the lab-scale reaction system (9.1 wt%, entry 1 in Table 1) with the 14 mg/ 2.0 mL sample concertation. Hence, the introduction of the sufficient amount of $O_2$ to the system by the pressurization drastically improved the vanillin yields and the scaling-up of the reaction system has little influence on the performance of our reaction system at least in terms of vanillin production. We also carried out the experiments at lower temperatures of 80 and 100 °C, expecting that the pressurization may cause the decrease in the optimum reaction temperature. However, as listed in entry 2 and 3 in Table 2, the decrease in the temperature resulted in the decrease in the product yields as long as a realistic reaction time of 3 h was employed.

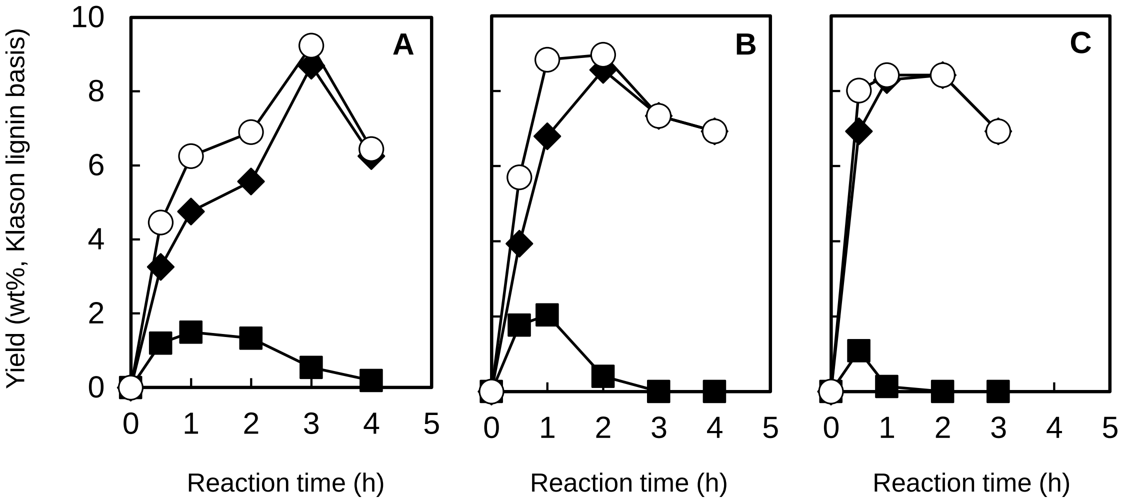

**Fig. 4.** Changes in the yields of vanillin (◆), vanillc acid (■), and their total yield (○) during the bench-scale aerobic oxidation of 100 g of the PEG-lignin in 1.0 L of the $Bu_4NOH$-based reaction medium at 120 °C under $O_2$ pressurized at 0.7 MPa (A), 1.5MPa (B), and 2.5 MPa (C).

**Table 2.** The yields (wt%, Klason-lignin [a)] basis) of vanillin and vanillic acid after the bench-scale aerobic oxidation of the PEG-lignin (100 g) in the $Bu_4NOH$-based medium (1.0 L) under pressurized $O_2$.

| Entry | Temperature (°C) | Reaction time (h) | Pressure (MPa) | Yield (wt%) | | |
|---|---|---|---|---|---|---|
| | | | | Vanillin | Vanillic acid | Total |
| 1 | 120 | 3.0 | 0.7 | 8.7 | 0.54 | 9.2 |
| 2 | 100 | 3.0 | 0.7 | 4.5 | 0.93 | 5.4 |
| 3 | 80 | 3.0 | 0.7 | 2.5 | 0.81 | 3.3 |
| 4 [b)] | 120 | 2.0 | 1.5 | 8.6 | 0.41 | 9.0 |
| 5 [b)] | 120 | 2.0 | 2.5 | 8.4 | ND [c)] | 8.4 |

[a)] The Klason lignin contents of the PEG-lignin was 81.7 wt% [16)]. [b)] The maximum vanillin yields are shown along with the corresponding conditions in the case of the experiments at 1.5 and 2.5 MPa. [c)] ND means "not detected".

The formation of vanillic acid, as compared to that of vanillin, became much faster in the case of the bench-scale experiment under pressurized $O_2$: the maximum yield (1.5 wt%) was obtained at 1 h and 0.7 MPa while 3 h was needed to achieve the maximum vanillin yield (Fig. 4A). As the lab-scale experiment showed almost simultaneous formation of vanillin and vanillic acid (Fig. 3), the formation of vanillic acid was more significantly influenced by the pressurization of $O_2$ than that of vanillin. This observation further supports our previous suggestion that these two compounds are produced in different reaction pathways [11)]. At reaction times longer than 1 h, gradual degradation of vanillic acid was observed and the yield became almost zero at 4 h (Fig. 4A). Vanillic acid is more sensitive towards $O_2$ than vanillin and degrades into guaiacol by decarboxylation. This is probably one of the reasons for this disappearance of vanillic acid. These results suggest that it is not easy for the aerobic oxidation of the

PEG-lignin under pressurized $O_2$ to produce both vanillin and vanillic acid with their potential maximum yields. This seems to be a drawback of the $O_2$ pressurization, but when viewed from the opposite side, selective production of these two compounds would be possible by careful selection of the reaction conditions, especially the $O_2$ pressure.

According to this idea, we made systematic investigations about the influence of the $O_2$ pressure with the reaction temperature being fixed at 120 $^oC$. At 0.7 MPa, as discussed above and clearly shown in Fig. 4A, the product yield got maximum at 3 h. This reaction time became shorter with the increase in the $O_2$ pressure to 2.5 MPa: the reaction times required for the maximum total product yield were 2 h at 1.5 MPa and 1 h at 2.5 MPa, according to Fig. 4. It is also indicated that the maximum yields of vanillin were almost constant no matter which pressure was employed: they were 8.7, 8.6, and 8.4 wt% at 0.7, 1.5, and 2.5 MPa, respectively (entry 1, 4, and 5 in Table 2). It is thus stated that, as long as vanillin is focused, increase in the $O_2$ pressure effectively shortens the reaction time without decrease in the yield.

For vanillic acid, on the other hand, the increase in the $O_2$ pressure from 0.7 to 1.5 MPa moderately lifted up the yield from 1.5 to 2.0 wt% with the required reaction time being unchanged, but further increase in the pressure to 2.5 MPa resulted in the decreased yield of 1.1 % (Fig. 4). Also, the degradation of vanillic acid was enhanced by the increase in the pressure. These results are consistent with the above $O_2$-sensitive chemical nature of vanillic acid. This difficult nature of vanillic acid, however, renders selective vanillin production feasible. The aerobic oxidation at 2.5 MPa for 2 h gave vanillin in 8.4 wt% yield without forming detectable amount of vanillic acid (Fig. 4C and entry 5 in Table 2). In other words, after the almost complete degradation of vanillic acid in 1 h, vanillin, which was more tolerant to further degradation, survived until 2 h. It is thus stated that vanillin is a more realistic target compound in our process. This consideration would be also supported by the experimental fact that our aerobic oxidation always produces more vanillin than vanillic acid by nature.

## CONCLUSIONS

1. The aerobic oxidation of the PEG-lignin in the $Bu_4NOH$-based medium gave vanillin and vanillic acid with the yields comparable to those in the corresponding AN oxidation, indicating high performance of the reaction medium.
2. The PEG-lignin produced vanillin in lower yields than Japanese cedar in both alkaline aerobic and nitrobenzene oxidations, probably due to the presence of the PEG moiety at the $\alpha$-position. This indicates that, when being seen from the side of the vanillin production as a sub-process, moderate (or not very intensive) introduction of PEG to the native lignin is recommended during the chief PEG-lignin production process. Solvolysis under mild conditions will produce PEG-lignin that is suitable for vanillin production.
3. As long as sufficient amount of $O_2$ is supplied to the system, the lab-scale (2 mL) and bench-scale (1.0 L) experiments gave the products with similar yields. Pressurization of $O_2$ was very effective when the oxidation is carried out in large scale.
4. Selective vanillin production can be achieved by taking advantage of the faster degradation of vanillic acid than vanillin at high $O_2$ pressures.

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