ORIGINAL ARTICLE

CrossMark

Vanillin production from native softwood lignin in the presence of tetrabutylammonium ion

Misaki Maeda[1] · Takashi Hosoya[1] · Koichi Yoshioka[1] · Hisashi Miyafuji[1] · Hiroyuki Ohno[2] · Tatsuhiko Yamada[3]

Abstract

Vanillin is one of the industrially important compounds that can be produced from lignin. This study presents production of vanillin and vanillic acid (oxidized form of vanillin) through aerobic oxidation of Japanese cedar (*Cryptomeria japonica*) at 120 °C for 72 h in aqueous alkali solutions with several Bu_4N^+ and OH^- concentrations (1.25, 2.50, and 3.75 mol/L), where Bu_4N^+ is an enhancer of the vanillin formation reported in our previous study. The concentrations of Bu_4N^+ and OH^- were adjusted by the additions of Bu_4NCl and solid NaOH into the base medium $Bu_4NOH·30H_2O$, which forms 1.25 mol/L aqueous solution of Bu_4NOH at the elevated temperature. Vanillin and vanillic acid were produced with the maximum yields of 21.0 and 1.7 wt% (lignin-base), respectively, at the 1.25 mol/L Bu_4N^+ and 3.75 mol/L OH^- concentrations. This vanillin yield is close to that obtained by the alkaline nitrobenzene oxidation (26.5 wt%), indicating significantly high selectivity of our lignin degradation with Bu_4N^+ toward vanillin formation. We also proposed a novel $Bu_4NOH·30H_2O$-free reaction medium, where $Bu_4NOH·30H_2O$ as the base medium were substituted with an aqueous solution of Bu_4NCl and NaOH to avoid using expensive $Bu_4NOH·30H_2O$. The treatment of the Japanese cedar with this alternative medium exhibited the moderately decreased vanillin yield of 14.6 wt%, which is, however, much higher than the vanillin yield obtained with a simple 1.25 mol/L NaOH solution.

Keywords Lignin · Aerobic oxidation · Vanillin · Quaternary ammonium · Alkali

Introduction

Chemical conversion of lignin, an aromatic polymer consisting 20–35% of lignocellulose, into industrially valuable compounds is one of the hottest topics in the research field of biorefinery. Among various candidate products to be produced from lignin, vanillin is a highly promising compound because of versatility in its uses not only as a fragrance but also as a starting material of pharmaceuticals and synthetic polymers [1–3]. Vanillin is almost ubiquitous in the product mixture from various biomass conversion processes [4–14], which suggests that vanillin is located at one of the major minima on the potential energy map of lignin degradation. This idea also justifies vanillin production from lignin and related raw materials.

Industrial vanillin production from lignin has been carried out since the 1950s by aerobic oxidation of sodium lignosulfonate (waste from sulfite pulping) in the presence of NaOH [15, 16]. Until the 1990s this method was the most dominant for worldwide vanillin production. However, in spite that the lignin-based process efficiently utilizes renewable wastes [17, 18], most of the present industrial vanillin production relies on petrol-derived chemicals, mostly guaiacol produced from phenol [19].

This ironical switching of the raw materials in vanillin production is attributed to complicated wastewater management required for the lignin-based process and tedious purification procedure originated essentially from low yield of vanillin from lignosulfonate, usually ~5% [16, 20].

✉ Hisashi Miyafuji
miyafuji@kpu.ac.jp

[1] Graduate School of life and Environmental Sciences, Kyoto prefectural University, Kyoto, Japan

[2] Graduate School of engineering department, Tokyo University of Agriculture and Technology, Koganei, Japan

[3] Forestry and Forest Products Research Institute, Tsukuba, Japan

Considering the alternatives, if the above problems are fixed by further improvement of the process—for instance, if the yield of vanillin is improved to compensate the disadvantages—it is still possible that the lignin-based method recapture the dominant position for the world vanillin supply. Needless to mention, in view of the current global environmental issues, the vanillin production from renewable resource is much more favorable than those relying on fossil resources.

Alkaline nitrobenzene oxidation (AN oxidation) is currently the most selective method to convert lignin into vanillin and its related compounds [21, 22]. However, considering the toxic nature of nitrobenzene and its reduced products, it is not realistic to put this method into industrial application, although the yield obtained with AN oxidation can be a good reference to measure the performance of a newly developed lignin conversion method. To this end, we have been developing a nitrobenzene-free method for vanillin production that gives the target compound with higher yield than the current NaOH-based process.

Our previous study have revealed that various lignin samples produce low molecular weight (MW) compounds, mainly vanillin and vanillic acid, with high selectivity through aerobic oxidation at 120 °C in the 1.25 mol/L aqueous solution of tetrabutylammonium hydroxide (Bu_4NOH), which is formed through melting of solid $Bu_4NOH \cdot 30H_2O$ at the elevated temperature [23]. As the aqueous solution of NaOH with the same OH^- concentration as that of the Bu_4NOH aq shows only much lower selectivity toward the low MW compounds, it is most likely that the Bu_4N^+ cation enhance their formation through the aerobic oxidation. Unlike the AN oxidation, the active oxidant in our reaction system is gaseous O_2, which is of course not toxic and does not leave any harmful compounds after its consumption.

According to the above information, it is easy to expect that the selectivity toward the low MW compounds is greatly influenced by the Bu_4N^+ and OH^- concentrations. It is especially important to clarify what improvement will be made when their concentrations are increased to more than 1.25 mol/L. However, control of the concentrations is not trivial since intensive removal of crystal water from $Bu_4NOH \cdot 30H_2O$ results in degradation of Bu_4N^+. This consideration led us to the idea that the concentrations of Bu_4N^+ and OH^- are increased by the addition of a Bu_4N salt (Bu_4NX) and NaOH to $Bu_4NOH \cdot 30H_2O$. With such addition, the $Bu_4NOH \cdot 30H_2O$-based reaction solution is destined to contain the salt NaX as an artifact. The first part of this study investigates the effects of the NaX with Cl^-, Br^-, and SO_4^{2-} being selected as the anionic part. We will then discuss our major results on the effects of the concentrations of Bu_4N^+ and OH^- with Bu_4NCl being selected as the Bu_4N^+ source. The final part of this study propose a new reaction medium composed only of Bu_4NCl and NaOH, which

medium exhibits high performance for the lignin conversion without an expensive reagent $Bu_4NOH \cdot 30H_2O$.

Experimental

Materials

$Bu_4NOH \cdot 30H_2O$ ($\geq 98\%$) was purchased from Sigma-Aldrich Co. Bu_4NCl, NaOH (solid), NaCl, NaBr, and Na_2SO_4 were provided from Wako pure chemical Co. Milled wood lignin was prepared according to the literature [24]. The particle size of the Japanese cedar (*Cryptomeria japonica*) wood flour was 90–180 μm.

Preparation of reaction media

Solid $Bu_4NOH \cdot 30H_2O$ was first liquefied at 30 °C to give a 1.25 M aqueous solution of Bu_4NOH. To the Bu_4NOH solution were put additives [NaCl (145 mg, 2.5 mmol), NaBr (257.5 mg, 2.5 mmol), Na_2SO_4 (355 mg, 2.5 mmol), Bu_4NCl (693.8–1387.5 mg, 2.5–5.0 mmol), and NaOH (100–200 mg, 2.5–5.0 mmol)]. The resulting mixture was then stirred for 4 h to form a homogeneous solution, which was directly used as the reaction medium for lignin degradation. In case only Bu_4NCl and NaOH were used as the reaction medium, 100–300 mg (2.5–7.5 mmol) of NaOH was added to a 1.25–3.75 M aqueous solution of Bu_4NCl and the solution was stirred for 4 h in the same manner as that presented above.

Degradation of lignin samples and analysis of the reaction mixture

Lignin sample (14 mg) and 2.0 mL of a reaction medium prepared from the above method were put in a 25 mL glass tube. After the tube was tightly sealed, the reaction solution was heated up to 120 °C in an oil bath and stirred for 72 h. After the tube was cooled with cold water, 800 μL of the 2.0 g/L 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene/ethanol solution was added as an internal standard. 100 μL of the resulting reaction mixture was taken and put into 900 μL of acetonitrile containing 1.5% acetic acid. The solution was filtrated and used as a sample for HPLC analysis.

The HPLC analysis was carried out with HPLC system (Shimadzu, Ltd., Kyoto, Japan) equipped with pump (LC-10AD), 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.

Results and discussion

Effects of inorganic salt

The major purpose of this paper is to carry out degradation of lignin with increased concentrations of Bu_4N^+ and OH^- by adding Bu_4NX and NaOH to the 1.25 M aqueous solution of Bu_4NOH, namely $Bu_4NOH \cdot 30H_2O$ in liquid form. As mentioned above, NaX destined to exist in the Bu_4NX–NaOH-added system may affect the degradation of lignin and decrease the product yields. To this end, we first investigated the effects of NaCl, NaBr and Na_2SO_4 on the degradation of the milled wood lignin prepared from Japanese cedar (*Cryptomeria japonica*). The milled wood lignin is a lignin sample supposedly retaining the original lignin structure in the wood.

A control experiment without the addition of the sodium salts was carried out at 120 °C for 72 h under air, for which conditions were proposed as the optimum ones in our previous report [23]. As presented in the HPLC chromatogram in Fig. 1 the mixture obtained after degradation contained vanillin, vanillic acid, acetoguaiacone, *p*-hydroxybenzaldehyde, and guaiacol with several minor unidentified compounds, which is in accordance with the results in our previous study. Further quantification showed that the yields of vanillin, vanillic acid, acetoguaiacone, and *p*-hydroxybenzaldehyde were 10.5, 2.5, 0.49 and 0.38 wt%, respectively, indicating
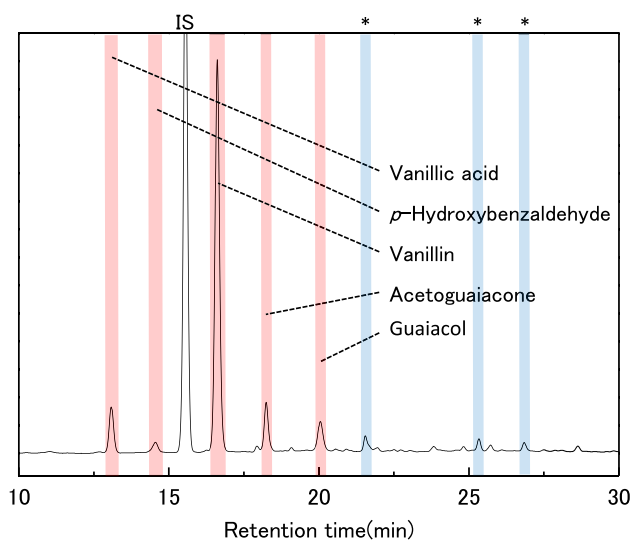
that the low molecular weight products are composed most of vanillin and vanillic acid. We will thus focus on these two compounds, vanillin and vanillic acid, hereafter.

We then degraded the milled wood lignin with the addition of NaCl, NaBr, and Na_2SO_4. The concentration of the salt was taken to be the same as that of Bu_4N^+, 1.25 mol/L. As shown in Fig. 2, in the NaCl-added system, the yield of vanillin decreased to 9.2 wt% from 10.5 wt% with a slight increase in the yield of vanillic acid (2.5 wt% → 2.6 wt%). The total yield of vanillin and vanillic acid was accordingly decreased by 1.1 wt% by the NaCl addition. In the NaBr-added system, although the total yield (11.8 wt%) of vanillin and vanillic acid was similar to that of the NaCl-added system, the formation of vanillin became more dominant over that of vanillic acid. In general, halide anions have reducibility and its ability becomes stronger in heavier anions. Thus, this trading-off behavior observed between vanillic acid and vanillin is explained by relatively strong reducibility of Br^-. In the Na_2SO_4-added system, the yields of both vanillin and vanillic acid decreased from 10.5 and 2.5% to 10.1 and 1.2%, resulting in the 1.7% decrease in their total yield, which decrease was the largest of the three salt-added systems.

The above results indicate that the yields of vanillin and vanillic acid are decreased by the addition of the sodium salts, but the decrease is more moderate in NaCl and NaBr than in Na_2SO_4. As NaBr changes the ratio of vanillin and vanillic acid (see above)—although the detailed mechanisms for the influence of these sodium salts are not clear at present—it can be said that NaCl has the smallest influence on the lignin degradation. From these considerations, we concluded that Cl^- should be adapted as the anionic part of the Bu_4N salt to increase the Bu_4N^+ concentration of the 1.25 M Bu_4NOH aq. In the next section, we make concrete discussion on the influence of the Bu_4NCl and NaOH additions on the lignin degradation.

Fig. 1 HPLC chromatogram of the reaction mixture obtained from the degradation of the milled wood lignin in the 1.25 mol/L Bu_4NOH aq at 120 °C for 72 h. IS: Internal standard (1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene). Unidentified peaks are shown with an asterisk
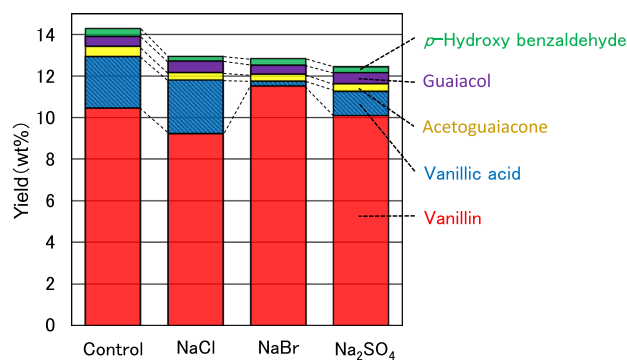

Fig. 2 Yield of major products from the milled wood lignin after the degradation in the 1.25 mol/L Bu_4NOH aq at 120 °C for 72 h with NaCl, NaBr, and Na_2SO_4. The concentrations of the Cl^-, Br^-, and SO_4^{2-} were taken to be the same as that of Bu_4N^+ (1.25 mol/L). See Table S1 in Supporting information for detailed yields of the identified compounds

Bu₄NCl- and NaOH-added systems

Degradation of lignin was carried out under the additions Bu_4NCl and NaOH to the 1.25 M Bu_4NOH solution. In this case, we employed the wood flour as a potential raw material. Figure 3a summarizes the yields of vanillin and vanillic acid in the systems in which solid NaOH was added to the 1.25 M Bu_4NOH solution to increase the OH^- concentration. The yields of vanillin and vanillic acid considerably increased along with the addition of NaOH and reached 7.2 and 0.6 wt%, respectively, at the OH^- concentration of 3.75 mol/L. Note that the increase in the yield of vanillin was much more remarkable than that of vanillic acid: the yield of vanillin increased from 3.9 to 7.2% upon going from the OH^- concentration of 1.25–3.75 mol/L, whereas the yield of vanillic acid remained relatively stable (0.5–0.6%). This suggests that vanillic acid is produced by a reaction pathway different from that of vanillin and the vanillin-forming pathway is more sensitive to the OH^- concentration, but further investigation is required for details. It is also noted that treatment of vanillin in the 1.25 M Bu_4NOH solution at 120 °C for 72 h under air resulted in almost quantitative recovery of vanillin, which suggests that vanillin is considerably stable under the conditions employed and not likely to be a precursor of vanillic acid.

As shown in Fig. 3a–c, when the Bu_4N^+ concentration was increased from 1.25 to 3.75 mol/ L by adding Bu_4NCl with the OH^- concentration being fixed at 1.25 mol/L, the total yield of vanillin and vanillic acid increased from 4.4 to 5.8 wt%. This increase in the yield was less remarkable than that caused by the increase in the OH^- concentration. There are three possible explanations for this result, as far as we think of. The first is that the increase in the Cl^- concentration by the addition of Bu_4NCl suppressed the formation of vanillin and vanillic acid. In the previous section, we have shown that the addition of NaCl moderately reduces

the yield of vanillin, which also supports this possibility. The second is that the effect of the viscosity of the reaction solution increased by the Bu_4NCl addition. Aqueous solutions of Bu_4NOH exhibit viscosity much higher than that of water [25] and the Bu_4NCl addition is expected to further increase the viscosity of the reaction solutions. Our previous report has shown that oxygen supply to the reaction solution is indispensable for the production of vanillin and vanillic acid (Yamamoto et al., 2016 [23]). The increased viscosity of the reaction solution should inhibit the stirring of the reaction solution, resulting in oxygen deprivation of the reaction system. The last possibility is that the increase in the Bu_4N^+ concentration is not as effective as that in the OH^- concentration from the view point of fundamental mechanisms of the lignin degradation in the present reaction system, although the detailed mechanisms has not been clear yet. Further investigation to elucidate the molecular role of Bu_4N^+ will provide clearer views for these three hypotheses.

When the OH^- concentration was increased with the Bu_4N^+ concentration being fixed at 2.50 mol/L (Fig. 3b), the significant increase in the yields of vanillin and vanillic acid was not observed unlike the case with the Bu_4N^+ concentration of 1.25 mol/L (Fig. 3a). Furthermore, when the Bu_4N^+ concentration was 3.75 mol/L, the increase in the OH^- concentration resulted in a decrease in the yields of vanillin and vanillic acid (Fig. 3c). We would be able to explain these results in similar ways to those presented above. That is, the increased Cl^- concentration causes the decrease in the yields; the increase in the OH^- concentration becomes ineffective for improving the yields in higher Bu_4N^+ concentrations due to presently unknown mechanistic reasons.

From the above results it was revealed that the formation of vanillin and vanillic acid proceeds most efficiently when the concentrations of OH^- and Bu_4N^+ were set to be 3.75 and 1.25 mol/L, respectively, although the detailed

Fig. 3 Yields of vanillin and vanillic acid after the degradation in several Bu_4NOH-based reaction media at 120 °C for 72 h. a) The concentrations of Bu_4N^+ and OH^- were changed by the addition of Bu_4NCl and NaOH, respectively. See Table S2 in Supporting information for detailed yields of the vanillin and vanillic acid
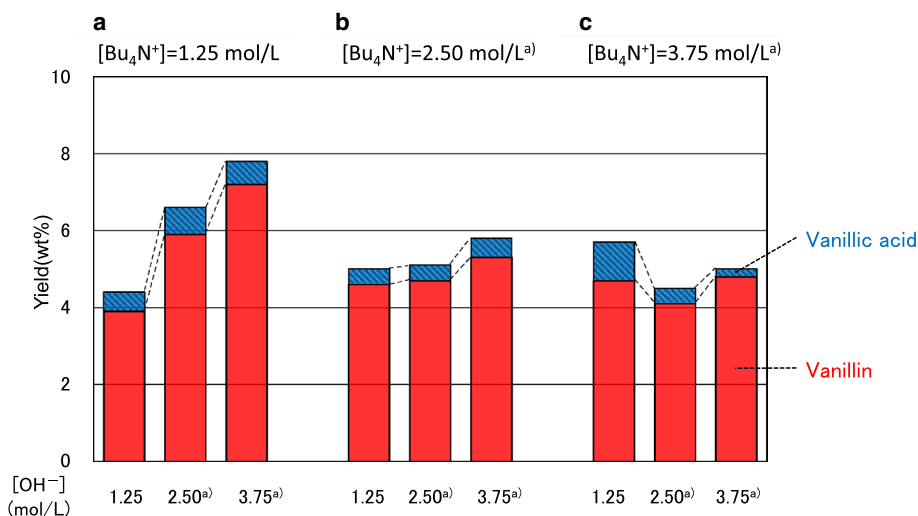
mechanisms underlying this phenomena are unknown at the moment. Under these ion concentrations, the yields of vanillin and vanillic acid were 7.2 and 0.6%, respectively. As the Klason lignin content of the wood was 34.3%, the yields of vanillin and vanillic acid were 21.0 and 1.7%, based on the lignin amount in the wood, which indicates high selectivity of the lignin conversion in our Bu_4NOH-NaOH system. It is also noted that the yields of vanillin and vanillic acid achieved in our reaction system is close to those reported for the alkaline nitrobenzene oxidation (vanillin: 9.1 wt% and vanillic acid: 0.4 wt%) [23], which is currently the most highly selective lignin degradation method.

Bu_4NCl–NaOH (Bu_4NOH-free) systems

The Bu_4NOH-based solutions used so far have excellent performance for selective lignin degradation, as a result of the positive effects exhibited by the Bu_4N^+ cation under alkaline conditions. This led us to the idea that Bu_4NCl may be used as a source of Bu_4N^+ instead of $Bu_4NOH \cdot 30H_2O$, which is a relatively expensive reagent. In this section, we propose a new reaction system employing an aqueous solution composed of only Bu_4NCl and NaOH without $Bu_4NOH \cdot 30H_2O$. The Bu_4N^+ concentration of this Bu_4NCl–NaOH system alternative for the Bu_4NOH one was set to be 1.25 mol/L, in which the total maximum yield of vanillin and vanillic acid was achieved in the previous section (Fig. 3a).

Figure 4 shows the yields of vanillin and vanillic acid obtained in the Bu_4NCl–NaOH system. In the Bu_4NCl–NaOH system with the different OH^- concentrations of 1.25 and 3.75 mol/L, the total yields of vanillin and vanillic acid were 3.7 wt% (vanillin: 3.2 wt%, vanillic acid:0.5 wt%) and 5.2 wt% (vanillin: 5.1 wt%, vanillic acid:0.1 wt%), respectively. These yields were lower than those in the case of the corresponding Bu_4NOH-based system with the same Bu_4N^+ and OH^- concentrations (Fig. 2). One of the possible causes of this decrease in the yield is that, as already presented above, Cl^- masked the positive effect of Bu_4N^+, by which the yields of the compounds were decreased.

Our previous study showed that, when the wood flour was degraded in a simple alkaline solution, 1.25 mol/L NaOH aq, vanillin and vanillic acid were produced with the yields of 1.1 and 0.83 wt%, as shown in Fig. 4. In the alternative Bu_4NCl–NaOH system—although the yields were lower than those in the Bu_4NOH-based system (see above)—they are still much higher than those in the NaOH system. These results suggest that, considering Bu_4NCl is much less expensive than $Bu_4NOH \cdot 30H_2O$, the aqueous solutions consisting only of Bu_4NCl and NaOH have significant ability for selective lignin conversion, although further efforts to improve the yields are necessary to employ this system as a substitute for $Bu_4NOH \cdot 30H_2O$-based system.
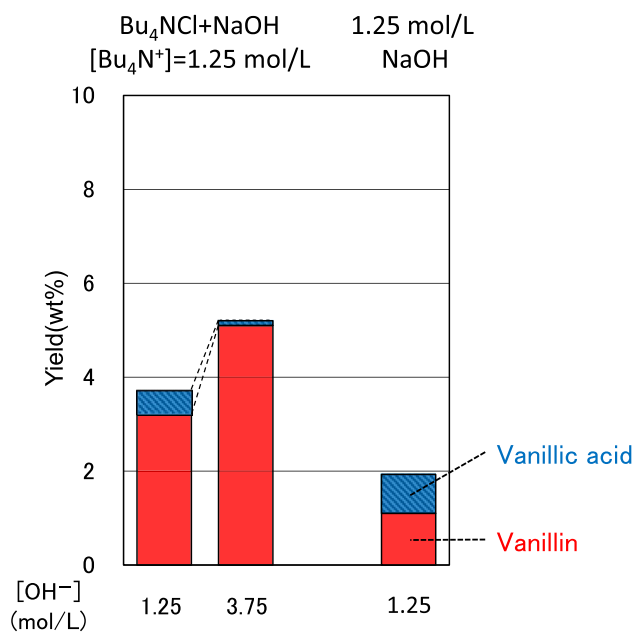

Fig. 4 Yields of vanillin and vanillic acid after the degradation of the wood flour in the aqueous solutions of Bu_4NCl (1.25 mol/L) and NaOH (1.25 and 3.75 mol/L) at 120 °C for 72 h, as compared with those after the degradation in the 1.25 mol/L NaOH aq under the same conditions [23]. See Table S2 in Supporting information for detailed yields of the vanillin and vanillic acid

Conclusions

Our preliminary investigation on the effects of the sodium salts on the degradation behavior of the milled wood lignin suggested that NaCl have the smallest influence on the lignin degradation in the Bu_4NOH aq. We thus selected Bu_4NCl as the additive for the Bu_4NOH aq to increase the concentration of Bu_4N^+. The experiments with various concentrations of Bu_4N^+ and OH^- indicated that vanillin and vanillic acid were obtained with the maximum yields (7.2 and 0.6 wt%, respectively) at the $[Bu_4N^+] = 1.25$ mol/L and $[OH^-] = 3.75$ mol/L. These yields are similar to those exhibited by the alkaline nitrobenzene oxidation, which is the most selective method for vanillin formation from lignin at present and frequently employed as an analytical method for chemical properties of lignin. This indicates excellent selectivity achieved in our lignin degradation method with the Bu_4NOH aq and the additives. In addition, it was shown that the aqueous solutions of Bu_4NCl and NaOH can be substituted for $Bu_4NOH \cdot 30H_2O$ which is an expensive reaction medium.

References

1. Brianna MU, Andrea MK (2016) Strategies for the conversion of lignin to high-value polymeric materials: review and perspective. Chem Rev 116:2275–2306

2. Audrey L, Etienne G, Stéphane C, Stéphane G, Henri C (2016) From lignin-derived aromatic compounds to novel biobased polymers. Macromol Rapid Comm 37:9–28

3. Francisco G, Dobado AJ (2010) Lignin as renewable raw material. Chem Sus Chem 3:1227–1235

4. Jiang G, Nowakowski JD, Bridgwater VA (2010) Effect of the temperature on the composition of lignin pyrolysis products. Energy Fuels 24:4470–4475

5. Kang S, Li X, Fan J, Chang J (2013) Hydrothermal conversion of lignin. Renew Sust Energ Rev 27:546–558

6. Borges da Silva EA, Zabkova M, Araujo JD, Cateto CA, Barreiro MF, Belgacem MN, Rodrigues AE (2009) An integrated process to produce vanillin and lignin-based polyurethanes from kraft lignin. Chem Eng Res Des 87:1276–1292

7. Jose DPA, Carlos AG, Alirio ER (2009) Structured packed bubble column reactor for continuous production of vanillin from kraft lignin oxidation. Catal Today 147:330–335

8. Jose DPA, Carlos AG, Alirio ER (2010) Vanillin production from lignin oxidation in a batch reactor. Chem Eng Res Des 88:1024–1032

9. Paula CRP, Carina EC, Alirio ER (2013) Oxidation of lignin from *eucalyptus globulus* pulping liquors to produce syringaldehyde and vanillin. Ind Eng Chem Res 52:4421–4428

10. Mathias LA, Rodrigues EA (1995) Production of vanillin by oxidation of pine kraft lignins with oxygen. Holzofrsch 49:273–278

11. Claire F, Alvaro M, Alirio R (1996) Kinetic of vanillin production from kraft lignin oxidation. Ind Eng Chem Res 35:28–36

12. Guozzhan J, Daniel JN, Anthony VB (2010) Effect of the temperature on the composition of lignin pyrolysis products. Energy Fuels 24:4470–4475

13. Shimin K, Xianglan L, Juan F, Jie C (2013) Hydrothermal conversion of lignin. Renew Sust Energ Rev 27:546–558

14. Ogawa S, Miyafuji H (2015) Reaction behavior of milled wood lignin in an ionic liquid, 1-ethyl-3-methylimidazolium chloride. J Wood Sci 61:285–291

15. Forss GK, Talka TE, Fremer KE (1986) Isolation of vanillin from alkaline oxidized spent sulfite liquor. Ind Eng Chem Prod Res Dev 25:103–108

16. Hocking MB (1997) Vanillin: synthetic flavoring from spent sulfite liquor. J Chem Edu 74:1055–1059

17. Tomlinson G 2nd, Hibbert H (1936) Studies on lignin and related compounds. XXIV. The formation of vanillin from waste sulfite liquor. J Am Chem Soc 58:345–348

18. Tomlinson G 2nd, Hibbert H (1936) Studies on lignin and related compounds. XXIV. Mechanism of vanillin formation from spruce lignin sulfonic acids in relation to lignin structure. J Am Chem Soc 58:348–353

19. Triumph Venture Capitals Limited (2004) Part three-Aroma chemicals derived from petrochemical feedstocks. In: Study into the establishment of an aroma and fragrance fine chemicals value chain in South Africa, Triumph Venture Capitals Limited, South Africa

20. Vidal JP (2006) Vanillin. In: Kirk-Othmer encyclopedia of chemical technology. Wiley, Hoboken. https://doi.org/10.1002/04712 38961.2201140905191615.a01.pub2

21. Chang HM, Allan GG (1971) Oxidation. In: Sarkanen KV, Ludwig CH (eds) Lignins: occurrence, formation, structure, and reactions. Wiley Interscience, New York, pp 433–485

22. Schultz TP, Templeton MC (1986) Proposed mechanism for the nitrobenzene oxidation of lignin. Holzforsch 40:93–97

23. Yamamoto K, Hosoya T, Yoshioka K, Miyafuji H, Ohno H, Yamada T (2017) Tetrabutylammonium hydroxide 30-hydrate as novel reaction medium for lignin conversion. ACS Sus Chem Eng 5:10111–10115

24. Björkman A (1956) Studied on finely divided wood. part1. Extraction of lignin with neutral solvents. Svensk Papperstidn 59:477–485

25. Safdar R, Omar AZ, Ismail LB, Bari A, Lal B (2015) Measurement and correlation of physical properties of aqueous solutions of tetrabutylammonium hydroxide, piperazine and their aqueous blends. Chin J Chem Eng 23:1811–1818