Preliminary study of electrooxidation isoeugenol into vanillin using platinum and boron-doped diamond electrode

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Abstract. Vanillin was synthesized from isoeugenol through an electrochemical method using Pt and BDD electrodes using chronoamperometry technique in a one-compartment electrochemical cell. The oxidation at C-C bond termination was expected to occur to form an aldehyde group. The oxidation potential of isoeugenol at Pt and BDD electrodes were fixed at +0.61 V and +0.96 V, respectively. The oxidation results were confirmed by GC, GC-MS, and FTIR. Thin layer chromatography result showed that vanillin could be produced at Pt and BDD electrodes with the yield percentage of 2.9 % and 1.33 %, respectively.

Keywords: Isoeugenol, synthesis of vanillin, electrooxidation, BDD and Pt electrode

1. Introduction
Isoeugenol is one of compounds that contained in clove oil (Syzygium Aromaticum) approximately 5-15 % In Indonesia, the clove production is the largest in the world with a total production of about 98700 tons per year. One of isoeugenol derivate compounds is vanillin (4-hydroxy-3-methoxybenzaldehyde) [1]. The amount of vanillin demand reaches 15,000 tons per year and only 1 % is obtained from the extract of vanilla seeds (Vanilla planifolia) [2]. Vanillin is widely known as scent in perfume and flavoring in food. Moreover, it also acts as an additive to cover the bad taste in food by carrying out oxidative degradation of other compounds in food and has antioxidant activity [3].

Recently, The synthesis of an organic compound by electrochemical method without the addition of catalyst has attracted the attention of researchers [4-8] that usually using catalyst before. Einaga et al. has successfully synthesized (±) -licarin A from isoeugenol in a methanol solvent using BDD electrodes [5]. The yield percentage obtained by using BDD electrodes is relatively greater than using Pt, Ni and GC (Glassy Carbon) electrodes [8-13]. Previously, Parpot et.al. has also carried out Kraft-Lignin electrooxidation into vanillin with Pt, Ni, and Cu electrodes with % yield less than 10 % [6, 13].

In this study, the synthesis of vanillin from isoeugenol was studied by electrochemical method. The double bond in isoeugenol was expected to be broken by direct oxidation to form an aldehyde group. Boron-doped diamond (BDD) and Pt electrodes were used as the working electrodes as it was reported that BDD electrodes have a wide potential window in aqueous solutions as well as resistant to corrosion and have high mechanical strength thus allowing BDD to be used in the synthesis of organic compounds [4, 5, 14]. On the other hand, Pt electrodes are inert and quite stable, but also known for electrocatalysis in many types of reactions. Mubarok et al. reported the oxidation of vanillin at
Pt electrode [8]. In this work, % area in thin layer chromatography (TLC) was used to indicate the success of the conversion. Validation was performed by FTIR and GC-MS.

2. Materials and method
Electrochemical cell was prepared with Ag/AgCl electrode, spiral Pt electrode and Pt or BDD electrode as the reference, counter and working electrodes, respectively. A mixture solution of 2 mL of 0.1 M isoeugenol solution, 2 mL of tetrabutyl ammonium perchlorate (TBAP) salt in 0.1 M methanol, and 0.4 mL distilled water was added into the electrochemical cell in the absence and in the presence of isoeugenol. The cell was measured with cyclic voltammetry method in the potential range from -2.0 V to +2.0 V. The scan rate was varied at 50–250 mV / s, while isoeugenol concentrations were varied from 0.1 M to 0.5 M. The electrolysis was conducted at +0.61 V for Pt electrode and +0.96 V for BDD electrode for 3 h [5, 8]. The product was characterized by FTIR and GC-MS.

3. Results and discussion
3.1. Electrochemical study of isoeugenol with BDD and Pt as working electrode
In electrochemical behavior study of isoeugenol, 0.1 M TBAP solution with and without isoeugenol addition was measured with cyclic voltammetry method at scan rate 100 mV / s and range from -2000–2000 mV (figure 1a).

The oxidation peak of Pt was observed at a potential around -1000 mV and 82 mV that referred to the reaction below:

\[
Pt + 2H_2O \rightarrow Pt(OH)_2 + 2H^+ + 2e^- 
\]

At the potential of -500 mV, electrode was reduced back to the Pt form. On the other hand, the addition of isoeugenol observed an oxidation peak at +0.41 V, suggested an oxidation reaction occurred at the potential. This potential will be used for the next experiment using Pt electrodes. Furthermore, the isoeugenol addition also increased the current of H2 and O2 evolution reactions.

![Figure 1](image-url)

**Figure 1.** Cyclic voltammograms of (a) TBAP in 0.1 M methanol in the absence and in the presence of isoeugenol (b) at various scan rates between 50–200 mV/s.
The influence of various scan rate was also measured. The oxidation peak of isoeugenol only appears at the scan rate of 100 mV as shown in (figure 1b) probably because of the low kinetic rates of the reactions.

Increasing the isoeugenol concentrations was expected to increase its current response, however, the cyclic voltammograms (figure 2) show that the increasing of isoeugenol concentrations did not increase the current responses significantly, indicating the limitation of the surface area of the electrode.

In the case of the electrochemical study at BDD electrode (figure 3), an oxidation peak at +0.76 V was observed in the presence of isoeugenol in the system. Therefore, this potential was used for the next experiments. This potential is much higher than that at the Pt electrode, which is normally occurred when comparing metal and carbon electrodes. The lack of empty orbital in the carbon electrode was proposed to be the reason.

Furthermore, the influence of the scan rate variation was studied. Figure 4 shows that the increase of scan rate increases the currents as the diffusion layer that formed on the electrode surface becomes more thinner. This would make mass transfer from and to the electrode surface more easier and increase the current response. The relation between the current response and the square root of scan rate was linear, indicated the mass transfer from the bulk solution to the electrode surface was controlled by the diffusion rate.

![Figure 2.](image1.png)

**Figure 2.** Cyclic voltammogram of isoeugenol in TBAP / methanol at various concentration between 0.01–0.05 M.

![Figure 3.](image2.png)

**Figure 3.** Cyclic voltammogram of (a) TBAP / methanol and (b) isoeugenol in TBAP / methanol at BDD electrode.
3.2. Electrolysis of isoeugenol at constant potential in single compartment

The oxidation of isoeugenol was performed in various concentrations of isoeugenol (0.1–0.5 M) in 0.1 M methanol-water solution. The % area of the generated vanillin was calculated by the testing using thin-layer-chromatography (TLC) with n-hexane and ethyl acetic (9:1) as the mobile phase. Figure 5 shows 2 spots at $R_f = 0.12$ and 0.53. The $R_f$ value at 0.12 was almost similar with the $R_f$ of vanillin standard ($R_f = 0.10$), while $R_f$ at 0.53 was similar to $R_f$ of isoeugenol.

Furthermore, table 1 shows the % area of vanillin generated at TLC, indicating the increase of isoeugenol concentration from 0.1 M to 0.3 M increased the oxidation of isoeugenol to vanillin at Pt electrodes. However, the higher concentration of isoeugenol decreased vanillin production probably due to that formation of isoeugenol layer on the electrode surface that prevents water to transfer onto the electrode surface.

At the BDD electrode, the higher isoeugenol concentrations did not produce vanillin. One of the reason is due to the low reaction rate of oxidation reaction of isoeugenol that was “poisoning” the electrode. The oxidation reaction was also performed in various concentrations of TBAP in 0.1 M methanol. Table 2 shows the produced vanillin increased with the increasing of TBAP concentrations,
especially at the BDD electrodes. This probably occurs due to the increasing ion concentrations of electrodes increased the mobility of isoeugenol to the surface of the electrodes.

Pt electrode produces more vanillin than BDD electrode. The better electrocatalytic properties of Pt electrode was caused due to several things:

- The oxidation potential on the Pt electrode was more negative than the BDD electrode which means isoeugenol would be more oxidized on the Pt electrode.
- The orbital electron of Pt was empty that could be easier to be filled by an electron from the oxidation of isoeugenol. While BDD electrode consist C atom that all its orbital had been used to form tetrahedral structure.

3.3. Confirmation of the oxidation results

The chronoamperometric solution of isoeugenol at the optimum condition (0.1 M isoeugenol and 0.3 M TBAP) was characterized using GC-MS. At retention time of 13.953, the peak appeared at m/z = 152, indicated vanillin compound. with % area was 2.88 %, while the 6th and 7th peak at m/z 164 was indicated the peak of isoeugenol with % area approximately 73.90 %. The 11th peak at m/z 328 was indicated the peak of isoeugenol dimer with % area was 1.08 %. The dimer formation began with radical oxygen formation of hydroxyl group. The radical was then resonance in all parts of isoeugenol (in the benzene ring and allyl group). The two radicals from the isoeugenol compound were then reacted and formed a stable dimer compound.

The FTIR spectra of chronoamperometric solution at the optimum condition was also performed (figure 6a), showing peaks appeared at 3445 cm\(^{-1}\), 2948 cm\(^{-1}\), 2836 cm\(^{-1}\) and 1654 cm\(^{-1}\), which were related to O-H stretching, C-H \(sp^3\) stretching, C-H stretching and C=O stretching, respectively. In addition to that, the peak at 1449 cm\(^{-1}\), 1276 cm\(^{-1}\) and 1419 cm\(^{-1}\) were also observed related to C=C-C stretching, C-O stretching and C-H vinyl bending, respectively. The effect of conjugation at \(\pi\) bond of aromatic ring and hydrogen bond in methanol solvent would shift the frequency of C=O stretching to the lower frequency [15] The fragmentation of synthesized vanillin with chronoamperometry method is shown in figure 6b.

Gas chromatogram of the synthesized vanillin is shown in figure 6c. The 5th peak was appeared at retention time of 13.953 min with m/z is 152 that indicated vanillin was successfully synthesized with % area is 2.88 %. This synthesized product was too little compared to the volume of solution (55 mL).

| Isoeugenol concentration | Retention time (Rt) | % area | BDD % area |
|-------------------------|--------------------|-------|------------|
| Pt                      | BDD                |       |            |
| 0.1 M                   | 1.633              | 1.615 | 1.80 %     | 0.32 %    |
| 0.3 M                   | 1.634              | -     | 2.90 %     | -         |
| 0.5 M                   | 1.645              | -     | 0.03 %     | -         |

| TBAP concentration | Retention time (Rt) | % area | BDD % area |
|--------------------|--------------------|-------|------------|
| Pt                 | BDD                |       |            |
| 0.1 M              | 1.633              | 1.615 | 1.80 %     | 0.32 %    |
| 0.3 M              | 1.634              | 1.634 | 2.90 %     | 0.65 %    |
| 0.5 M              | 1.645              | 1.62  | 0.03 %     | 1.33 %    |
4. Conclusion
The oxidation of isoeugenol performed at +0.41 V and +0.76 V (Vs. Ag / AgCl) in 0.1 M methanol containing of water and of tetrabutyl ammonium perchlorate at Pt and BDD electrode, respectively, produced vanillin about 2.9 % at the Pt electrode as the working electrode, while it was 1.33 % at BDD electrode.

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