Electrochemical Synthesis of Ethanol from Carbon Dioxide Using Copper and Carbon-Polyvinyl Chloride (C-PVC) Electrode

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Abstract. There is a significant number of unpublished research by university lecturers and students about Gorontalo’s local medicinal plants that have contributed to the insufficiency of information to the society regarding the benefits of local medicinal plants. Moreover, the public lacks digital backup and documentation of the medicinal plants referred. This research aims to create a web database of Gorontalo’s local medicinal plant, by comprising waterfall method of software engineering approach. The waterfall method involves four steps. The first step is system requirement analysis through preliminary study and observation based on field study and library research. The second is system design, by context diagram and system architecture designs, i.e., use case diagram, class diagram, activity diagram, and database design. The third is coding using PHP programming language by OOP (object oriented programming) concept and MVC (model view controller) architecture. The last step is system test using the black-box testing method. The result shows that the web application designed is able to operate properly.

1. Introduction
Carbon dioxide (CO2) is a very abundant constituent component of the atmosphere. Since the industrial revolution, atmospheric CO2 gas levels have increased to 379 ppm. The abundance of CO2 gas is one of the major contributors of greenhouse gas activity in the Earth’s atmosphere. The carbon dioxide gas comes from nature by 10% and from fossil fuels and industrial processes by 64% [1].

A high CO2 concentration will lead to a rise in global temperatures and climate change (global warming). Climate change will result in natural disasters (floods, extreme temperature rise, various diseases, and landslides), seasonal changes, and changes in wind direction, pollution and ecosystems. High CO2 potential in air and very harmful effects, then research to convert into useful compounds is very necessary to do. Techniques to convert must have characteristics that are efficient, do not produce waste, efficient and easy to operate.

The recent global climate change is caused by the disturbance of the energy balance between the earth and the atmosphere. The balance is influenced, among others, by the increase of charcoal gases or carbon dioxide (CO2), methane (CH4) and nitrogen dioxide (NO2), better known as greenhouse gases. Current greenhouse gas concentrations have reached levels that danger the climate change and the balance of ecosystems [2].
Concerns over world climate change are contained in the Kyoto Protocol document and the United Nations Framework Convention on Climate Change (UNFCCC) which emphasizes the importance of reducing CO2 emissions and their absorption from the atmosphere. Similarly, the United Nations Conference on Environment and Development (UNCED) in 1992 in Rio Janeiro, Brazil, which produced two general declarations, one of which also emphasized efforts to reduce global climate change [3].

Several methods have been done convert CO2 to chemicals compounds such as ethanol, methanol, propanol and butanol and ethylene. CO2 conversion can be done using radiochemical, chemical, thermos chemical, photochemical, biochemical and electrochemical methods [4-11]. The conversion of CO2 by electrochemical method by reduction has two main advantages over the other way: the selectivity of the product produced at the cathode and the material used is simple and economical because it does not require high vacuum or temperature conditions [12].

Some literature states that the electrochemical reduction of CO2 is highly dependent on the electrodes used, the reaction conditions, the composition, the concentration and the pH of the electrolyte solution [13]. A study to develop the electrochemical reduction of CO2 has been done using Cu electrode and electrolyte solution of KHCO3 0.5 M method produced by CH4 and C2H2 products [14]. Electrochemical reduction of CO2 with a 0.65 M NaHCO3 electrolyte solution has produced 42.5% efficiency for CH4 formation [14]. Electrochemical reduction by using Cu electrode to produce a propanol and ethanol compound [15]. The research has been done by researcher have many weaknesses, especially on the efficiency of process and the resulting product. The research to electrochemical reduction of CO2 to more useful product needs to be done. One useful product that can be produced is ethanol. Ethanol has many uses compared to other alcohol compounds were used as biofuel and intermediate compounds in biodiesel feeding.

In this paper, the presents work of the electrochemical synthesis of ethanol from carbon dioxide using carbon-polyvinyl chloride (C-PVC) electrode. The researchers proposed an electrochemical reduction method using a copper cathode (Cu) as a reducing agent, carbon anode (C) as an oxidizing agent and a solution of NaHCO3 as an electrolyte solution. Cu electrode has high selectivity to electrochemical reduction of CO2 to ethanol [5]. Electrochemical reduction of CO2 is carried out in electrochemical cells made of glass. The concentration of electrolyte solution of NaHCO3 influences the concentration of ethanol produced, where the more dilute NaHCO3 solution the greater the concentration of ethanol produced.

2. Methods

2.1. Instrumentations and materials research
The instruments used in this research are electrolysis cells equipped with current source, power supply SP-303E, Magnetic Stirrer ST-2B and Gas Chromatography Buck Scientific Model 910. The materials used in this research are CO2 gas with 100% purity, carbon (C) from Merck, copper (Cu) plate, sodium hydrogen carbonate (NaHCO3) Merck and distilled water.

2.2. Electrode preparation
The electrodes used in this study were copper and carbon-PVC electrodes. Carbon-Polyvinyl Chloride electrode was prepared by carbon powder and PVC in 4 mL tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100°C for 3 h. The mixture was placed in stainless steel mould and pressed at10 ton/cm2.

2.3. Effect of electrolysis time on ethanol concentration
An electrolyte solution of 0.1 M NaHCO3 of 50 mL was introduced to the reactor, then in the CO2 gas bubble and electrolyzed for 150 min with a 30 minutes interval taken by the product. The potential used is 3 volts and the flow volume is 1.5 mL/cm3. The electrolysis results were analysed by gas chromatography and the best time to obtain high concentrations of ethanol was found. A schematic
diagram of the electrolysis cell for electrochemical reduction of CO2 to ethanol can be seen at Figure 1.

![Electrolysis Cell Diagram](image)

**Figure 1.** A schematic diagram of the electrolysis cell for electrochemical reduction of CO2 to ethanol

2.4. Effect of potential on ethanol concentration
In this study potential is used with variations of 1, 3, 5 and 7 volts. A NaHCO3 0.1 M electrolyte solution of 50 mL was introduced into the electrolysis cell with CO2 gas using flow rate of 1.5 mL/cm3 and the optimum time. The results obtained were analysed by gas chromatography and were found to be the best potential to produce ethanol with the highest concentration.

2.5. Effect of gas flow rate of CO2 on ethanol concentration
In this study used volume of CO2 gas with a variation of flow rate are 0.5, 1, 1.5 and 2 mL/cm3. A 50 mL NaHCO3 0.1 M electrolyte solution was introduced into the electrolysis cell with each CO2 gas flow volume, time and optimum potential. The results obtained were analysed using gas chromatography and were found to be the best potential to produce ethanol with the highest concentration.

2.6. Effect of concentration of electrolyte solution on ethanol concentration
The electrolytes used in this study were NaHCO3. The NaHCO3 solution was prepared with a concentration of 0.05; 0.1; 0.15 and 0.2 M in a 50 mL volumetric flask. Each of the NaHCO3 solutions with various concentrations was introduced to the reactor then in the CO2 gas bubble while electrolyzed. The time, potential and volume of the flow rate used are the optimization results in the previous optimization experiments. The results were analysed using gas chromatography by spiking method, and then determination of the best concentration to get ethanol with the highest concentration.

3. Results and discussion
Figure 2 shown is the characterization of carbon-PVC electrode using Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). Figure 2A shown is the characterization of carbon PVC material at cross section and surface. Carbon-PVC has high homogeneity and pores. Homogeneity and pores are very important in materials for electrodes. PVC is used as a binder, because carbon is available in powder. PVC can strengthen the bonds between the carbons atom, but the amount of PVC should be as small as possible because PVC is an insulator. The amount of PVC used should be able to increase the strength of the material, maintaining the nature of the carbon conductor. A high amount of PVC will cause C-PVC material as an insulator and low PVC amount will cause the material is not strong and easy to erosion. Carbon will be released from the bond so that the C-PVC electrode is unstable. The best composition to make C-PVC is the maximum 5% PVC and the amount of carbon as much as 95%.
Figure 2B shown is the spectra EDX the C-PVC material. Based on the EDX spectra it is shown that C-PVC contains C, Al, Si and S. C-PVC atoms having a very high C atomic content of nearly 99% and Al, Si and S atoms have low levels.

Figure 2. Image of SEM of C-PVC material at cross section with magnification 10.000x (A) and spectra EDX (B)
Figure 3. Chromatogram of the result of analysis using Gas Chromatography (GC) the pure ethanol 0.5% (A) and electrolysis of CO2 in 50 mL NaHCO3 0.1 M with potential 3 V and electrolysis time 30 (B), 60 (C) 90 (D) 120 (E) and 150 minute (F).

The electrochemical reduction of CO2 in sodium hydrogen carbonate (NaHCO3) has been result of solution. This solution has analysis using Gas Chromatography (GC) Buck Scientific Model 910. Result of analysis can be seen at Figure 3. Operational parameters of the GC are manufacturer from Buck Scientific Model Number 910, Carbowax 20 m 6 ft long column, detector temperature 155 oC, TCD as a detector, column/oven temperature 121oC and pressure at10 PSI using Helium gas as mobile phase.

Figure 3 shown is result of the analysis using gas chromatography at the electrolysis product. Figure 3 shown is ethanol standard with concentration 0.5% (pro analysis grade). The chromatogram of CO2 electrolysis result in NaHCO3 with C-PVC electrode is shown in Figure 3B-3F. The chromatogram from Figure 3 can be used for qualitative and quantitative analysis. Qualitative and quantitative analysis can be used retention time and percent area. In this research has been using percent area ethanol standard 0.5% for determination of concentration of ethanol at product electrolysis. The quantitative product analysis, a comparison of standard solutions is called a single standard method. Figure 3 show the result of electrochemical reduction of CO2 on Cu electrode surface is ethanol with single compound. Based on chromatogram at Figure 3 shown is single peak, because Cu electrode has high selectivity to ethanol product. This result supported by Song et al. [5] is electrochemical reduction of CO2 on Cu electrode is
single compounds. Figure 4 shows the electrochemical reduction of CO2 on Cu electrode have results is ethanol.

**Figure 4.** The mechanism of electrochemical reduction of CO2 to ethanol on the Cu electrode surface (modified from Song et al. [5])

**Figure 5.** The concentration of ethanol from the variation of electrolysis time of CO2 in 50 mL NaHCO3 0.1 M using C-PVC with non-activated carbon (A) activated carbon (B)

Figure 5A shown the result of concentration of ethanol is the effect of electrolysis time using non-activated carbon electrode to electrochemical reduction of CO2. Based on the Figure 5A can be seen that the longer electrolysis time the higher ethanol concentration is obtained and then decreased at electrolysis 150 minutes. Electrolysis time at 120 minutes, the highest ethanol concentration is 0.36%. Figure 5B shown the result of concentration of ethanol is the effect of electrolysis time to electrochemical reduction using activated carbon. Based on the Figure 5B is that the increase in ethanol concentration at variations of time 30 and 60 minutes, while at other time variations decrease. At the time of electrolysis 60 minutes obtained ethanol concentration as high as 1.01%. The results differ greatly with the results obtained in the non-activated C electrode, which in the activated carbon electrode
requires faster time to produce maximum ethanol concentrations and greater yields. This happens because the activated carbon has larger pores so the touch surface area with CO2 is getting bigger.

**Figure 6.** The concentration of ethanol from the potential variation (Volt) of the electrolysis of CO2 in 50 mL NaHCO3 0.1 M using C-PVC electrode

Based on Figure 6 the result of concentration of ethanol on the potential variation on electrochemical reduction of CO2 can be concluded from concentration of ethanol on potential variation. The Figure 6 shows is that only at potential 3 volts can produce ethanol, where in other potential supply not identified ethanol. This happens because the electrochemical reduction process of CO2 to ethanol is very specific and only occurs at E° = 3 volts. If the potential supply is too small or too large it will form products other than ethanol. Thus, the optimum potential for maximum ethanol is 3 volts. There are several possible products that can be produced from CO2 electrochemical reduction process, as follows [16]:

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\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow \text{HCOO}^- + \text{OH}^- & E^o &= -0.43 \text{ Volt} \\
\text{CO}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow \text{CO} + 2\text{OH}^- & E^o &= -0.52 \text{ Volt} \\
\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- & \rightarrow \text{CH}_4 + 8\text{OH}^- & E^o &= -0.25 \text{ Volt} \\
2\text{CO}_2 + 8\text{H}_2\text{O} + 12e^- & \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^- & E^o &= -0.34 \text{ Volt} \\
2\text{CO}_2 + 9\text{H}_2\text{O} + 12e^- & \rightarrow \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- & E^o &= -0.33 \text{ Volt} \\
2\text{CO}_2 + 13\text{H}_2\text{O} + 18e^- & \rightarrow \text{C}_3\text{H}_7\text{OH} + 18\text{OH}^- & E^o &= -0.32 \text{ Volt} \\
2\text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- + \text{H}_2 & E^o &= -0.41 \text{ Volt}
\end{align*}
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**Figure 7.** The concentration of ethanol from the variation of the flow rate of CO2 of the electrolysis of CO2 in 50 mL NaHCO3 0.1 M using C-PVC electrode
Figure 8. The concentration of ethanol on the variation of concentration of NaHCO$_3$ of the electrolysis of CO$_2$ in 50 mL NaHCO$_3$ 0.1 M using C-PVC electrode

Figure 7 shown is the effect of the flow rate of CO$_2$ on electrochemical reduction CO$_2$. Based on the Figure 7 shows that the greater the flow rate of CO$_2$ gas the concentration of ethanol obtained will be greater. The result of CO$_2$ electrochemical reduction chromatogram on NaHCO$_3$ can be concluded on Figure 8 which shows the ethanol on the concentration variation of NaHCO$_3$ solution. Based on the Figure 8 shows that the lower the concentration of NaHCO$_3$ the higher the ethanol concentration. At the concentration of NaHCO$_3$ 0.05 M obtained the highest ethanol concentration of 0.39%. This is because in dilute NaHCO$_3$ solution the OH$^-$ release on the electrode surface cannot be neutralized and causes an increase in pH at the electrode surface. This increase in pH leads to an increase in reduced H$^+$ reduction and CO$_2$ reduction would be more likely to occur. The CH$_4$ increase was always followed by increased hydrogen production in concentrated KHCO$_3$ solution, while alcohol was more likely to form in dilute KHCO$_3$ solution [17].

4. Conclusion

According to the results of research that has been done, it can be concluded as electrolysis time affects ethanol concentration of electrochemical reduction of CO$_2$, where the optimum time to conduct the experiment is 60 minutes with ethanol concentration produced at 1.01%. Potential affects product specifications resulting from electrochemical reduction of CO$_2$, where to produce optimum potential ethanol is 3 volts with ethanol concentration of 0.14%. The CO$_2$ gas flow rate affects the ethanol concentration obtained, where by a large CO$_2$ gas flow rate, the greater the ethanol concentration. The concentration of electrolyte solution of NaHCO$_3$ influences the concentration of ethanol, where the more dilute NaHCO$_3$ solution the greater the ethanol concentration.

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