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Abstract. Research on conversion of carbon dioxide into ethanol has been done. The conversion process is carried out in a sodium bicarbonate electrolyte solution in an electrochemical synthesis reactor. As cathode was used Cu-Zn, while as anode carbon was utilized. Variations of voltage, concentration of sodium bicarbonate electrolyte solution and time of electrolysis were performed to determine the optimum conditions to convert carbon dioxide into ethanol. Sample of the electrochemical synthesis process was analyzed by gas chromatography. From the result, it is found that the optimum conditions of the electrochemical synthesis process of carbon dioxide conversion into ethanol are voltage, concentration of sodium bicarbonate electrolyte solution and time of electrolysis are 3 volts, 0.4 M and 90 minutes with the ethanol concentration of 10.44%.

1. Introduction

According to the Badan Pusat Statistika Indonesia, the number of motor vehicles in Indonesia is increasing rapidly every year. In 2014, the number of motor vehicles in Indonesia reached 114,209,266 units [1]. Increasing the number of motor vehicles is also the cause of increasing energy needs that in fact conflict with the needs of mankind to create a clean environment and free carbon dioxide (CO2) pollution.

In 2016, Indonesia is ranked sixth as the world's largest CO2 emitting country [2]. Global issues about CO2 are increasingly being discussed and studied along with the increasing number and impact on the world climate. This increase is triggered by the accelerated growth in CO2-producing energy consumption worldwide, carbon-based energy resource crisis and low energy efficiency in existing technology. According to the Intergovernmental Panel on Climate Change (IPCC), three-quarters of the increase in CO2 in the air is related to the use of fossil-based fuels [3].

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...
Due to the high potential of CO₂ hazards, research is needed that can convert CO₂ into other safer forms of compounds, moreover compounds that can be utilized for the welfare of mankind. Currently there are many studies that try to produce a compound by using CO₂ as its base material. This is one of many ways to overcome CO₂ hazard aside from minimizing its source of production.

The synthesis of other more useful compounds is a great solution for CO₂ processing, as it will provide great and sustainable benefits. In addition, it will also provide a dual solution, i.e. reducing the amount of CO₂ as well as the production of a more useful compound. Some of the methods that have been done in the synthesis of CO₂-based compounds are chemistry, radiochemistry, thermochemistry, photochemistry, biochemistry and electrochemistry [5].

The synthesis of ethanol by using CO₂ is also a hot topic. From various studies that have been done, it is known that CO₂ is very potential for the synthesis of renewable energy. The products of the most potent CO₂-based synthesis of the compounds are carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH₂O), methanol (CH₃OH), oxalic acid (H₂C₂O₄), methane (CH₄), ethylene (CH₂CH₂) or ethanol (C₂H₅OH) [6][7].

Ways can be done to synthesis ethanol from CO₂ is by electrochemistry. The synthesis of ethanol from CO₂ electrochemically has two major advantages over the other way. The first advantage is the selectivity of the product produced on each electrode. Second, the tools and materials used are simple and economical because they do not require high vacuum or temperature conditions [8].

The successful conversion of CO₂ into ethanol by electrochemical synthesis method is influenced by the type of metal on the electrode. The electro-catalytic properties of metals used as electrodes will not only affect the percent conversion of CO₂, but also their distribution to the resulting compounds. In addition, the electrochemical synthesis results also depend on several things such as the reaction potential, the type of electrolyte solution, the pH and the reaction conditions such as pressure and temperature [9].

Some research on converting CO₂ to other compounds with electrochemical synthesis method shows that the type of electrode and its preparation techniques greatly affect the results to be obtained. Methanol has been produced from CO₂ conversion by a combined method between electrochemistry and photo-electrochemistry using pyridium that acts as an electro-catalyst [10]. Acetate and methane have resulted from CO₂ conversion by electrochemical synthesis method of mixed and pure microbial culture using graphite and stainless steel as cathode [11]. Different types of electrochemical reduction of CO₂ and its results in fuel cells, metal electrodes and molecular catalysts have also been studied [12].

Until now, the optimization process of CO₂-based ethanol synthesis is still very necessary to do. Efficiency in the process and the intended product should still be improved, so that a more effective and selective method is obtained. In this study, it is proposed the use of Cu-Zn as cathode and carbon as anode in electrolysis process to get target product, that is ethanol.

A mixture of copper and platinum has greater catalytic activity than pure copper to convert CO₂ into ethanol [13]. Therefore, in this study used Cu-Zn as a cathode which is where the process of CO₂ conversion into ethanol. Carbon is an inert electrode that does not react when used as anode in the electrochemical synthesis process. Therefore, in this study used carbon as anode which is where the water oxidation reaction takes place. The inert carbon properties cause carbon not to be damaged during use in the electrochemical synthesis process. Since carbon is inert and the bicarbonate anion (HCO₃⁻) does not undergo oxidation in the water solvent, instead the water undergoes oxidation and becomes a source of protons and electrons [14]. This will support the process of ethanol formation at the cathode, because the mechanism of reaction of ethanol formation at the cathode involves protons and electron transfer [13].
2. Methods

2.1. The series of electrochemical synthesis reactor

The series of electrochemical synthesis reactor used in this study is shown in Figure 1.

![Figure 1. The Series of Electrochemical Synthesis Reactor](image)

2.2. Determination of the characteristics and element content of Cu-Zn electrode

The Cu-Zn electrode plate is cut to the size of 1.5 × 4 cm and rubbed using sandpaper until the dirt on the surface of the electrode is lost. Then the Cu-Zn electrode plate was washed using deionized water until clean and dried by wiping with a tissue. The Cu-Zn electrode plate is then analyzed by Scanning Electron Microscope-Electron Dispersive Spectrometer.

2.3. Electrode preparation

The Cu-Zn electrode plate is cut to the size of 1.5 × 4 cm and rubbed using sandpaper until the dirt on the surface of the electrode is lost. Then the Cu-Zn electrode plate was washed using deionized water until clean and dried by wiping with a tissue. The carbon electrode rod from the used battery was washed using deionized water until clean, then dried by oven for 3 hours at 110 °C to remove the water content. The carbon electrode is then cooled in the desiccator.

2.4. Carbon dioxide conversion process to ethanol

Conversion of CO$_2$ into ethanol in an electrochemical synthesis reactor is done by varying the voltage, concentration of sodium bicarbonate electrolyte solution and time of electrolysis to obtain the optimum conditions to convert CO$_2$ into ethanol.

On the variation of voltage, 50 mL of sodium bicarbonate electrolyte 0.1 M solution is incorporated into an electrochemical synthesis reactor already equipped with a brass electrode plate (cathode) and a carbon electrode rod (anode). Then the CO$_2$ gas flowed into the electrochemical synthesis reactor with a flow rate of 1 L/minute. The optimum voltage is studied by flowing voltages with variations of 1, 3, 5 and 7 volts. The electrochemical synthesis process is carried out for 90 minutes. Subsequently the sample solution of the electrochemical synthesis process was analyzed by gas chromatography to determine the optimum voltage to convert CO$_2$ into ethanol.

On the variation of the concentration of sodium bicarbonate electrolyte solution, each of 50 mL of sodium bicarbonate electrolyte 0.05, 0.1, 0.2, 0.4 and 0.6 M solution was taken and incorporated into an electrochemical synthesis reactor equipped with a brass Electrode plate (cathode) and a carbon electrode rod (anode). Then the CO$_2$ gas flowed into the electrochemical synthesis reactor with a flow rate of 1 L/minute. Then the voltage is also fed into the electrochemical synthesis reactor of the optimum voltage. The electrochemical synthesis process is carried out for 90 minutes. Subsequently the sample solution of the electrochemical synthesis process was analyzed by gas chromatography. The optimum concentration of sodium bicarbonate electrolyte solution is studied from the variations that produce the most ethanol.

At the variation of time of electrolysis, 50 mL of sodium bicarbonate electrolyte solution with optimum concentration is incorporated into an electrochemical synthesis reactor already equipped with a brass electrode plate (cathode) and a carbon electrode rod (anode). Then the CO$_2$ gas flowed into the
The electrochemical synthesis reactor with a flow rate of 1 L/minute. Then the voltage is also fed into the electrochemical synthesis reactor of the optimum voltage. The optimum time of electrolysis is studied by varying it to 60, 90, 120, 150 and 180 minutes. Subsequently the sample solution of the electrochemical synthesis process was analyzed by gas chromatography to determine the optimum time of electrolysis to convert CO$_2$ into ethanol.

The chromatogram obtained from each sample is compared with standard ethanol chromatogram so that it can be known that the compound composition is formed qualitatively and quantitatively. The concentration of standard ethanol used was 1% which was also analyzed by using the same gas chromatography.

3. Results and discussion

3.1. Determination of the characteristics and element content of The Cu-Zn electrode

In this study, the Cu-Zn electrode plate was analyzed by scanning electron microscope-electron dispersive spectrometer to determine the morphological structure and elemental content in it qualitatively and quantitatively.

![Figure 2. Morphological Structure of The Cu-Zn Electrode (a) Magnification x 1,000 and (b) Magnification x 5,000](image)

Figure 2 shows the morphological structure of the Cu-Zn electrode analysis using scanning electron microscope. Figure 2a shows the morphological structure of the Cu-Zn electrode at magnification x 1,000. Figure 2b shows the morphological structure of the Cu-Zn electrode at magnification x 5,000. It is known that the Cu-Zn electrode has a rough morphological structure. This is the result of the sanding process when the Cu-Zn electrode plate is cleaned from the impurities on the surface.

![Figure 3. Electron Dispersive Spectrometer Spectrum of The Cu-Zn Electrode](image)
Figure 3 shows the element content of the Cu-Zn electrode qualitatively. It is known that the Cu-Zn electrode consists of copper (Cu), zinc (Zn), carbon (C) and oxygen (O). Quantitatively, the content of each of these elements can be seen in Table 1.

Table 1. The Element Content of The Cu-Zn Electrode

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol of Element</th>
<th>Atomic Number</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>29</td>
<td>59.77</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>30</td>
<td>34.45</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>12</td>
<td>4.65</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>8</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Table 1 shows the element content of the Cu-Zn electrode. It is known that the element content of the Cu-Zn electrode is copper (59.77%), zinc (34.45%), carbon (4.65%) and oxygen (1.12%). If the content of copper and zinc contained in the Cu-Zn electrode are known, then the type of the Cu-Zn electrode can also be determined. The Cu-Zn electrode used in this study is an alpha (α) type with face centered cubic crystal structure. This type of the Cu-Zn electrode is also called the yellow alfa Cu-Zn or brass [15].

3.2. Observations on the electrode

Before use the Cu-Zn electrode plate is rubbed using sandpaper paper until the dirt on the surface of the electrode is lost then washed using the deionized water. This preparation aims to clean the surface of the electrode of impurities of metal or metal oxide covering the active side of the Cu-Zn electrode. If the active side of the Cu-Zn electrode is good, it will increase the efficiency of the formation of the compound in the electrochemical synthesis process.

Some studies of conversion CO$_2$ into other compounds by electrochemical synthesis method show that the type of electrode and its preparation techniques greatly affect the results to be obtained. One of the electrodes commonly used to convert CO$_2$ into ethanol is copper or a mixture of copper with other metals. A mixture of copper and other metals has greater catalytic activity than pure copper in converting CO$_2$ into ethanol [13]. Therefore, in this study used Cu-Zn as the cathode which is where the process of CO$_2$ conversion into ethanol.

Figure 4 shows the difference between the Cu-Zn electrode before and after it is used in the electrochemical synthesis process. Figure 4a is a pre-prepared Cu-Zn electrode and has not been used for the electrochemical synthesis process. While Figure 4b is a Cu-Zn electrode that has been used for electrochemical synthesis process for 90 minutes. The change in the surface of the Cu-Zn electrode occurs with the formation of a black layer called sponges. The sponges are more clearly visible when Cu-Zn electrode is dried in the air.

The formation of the sponge layer is caused by the impurity metal present in the electrolyte solution attached to the Cu-Zn electrode surface causing the deactivation or poisoning that can poison the electro-catalytic activity of the Cu-Zn electrode. In addition, deactivation of Cu-Zn electrode can also be caused
by the presence of carbon deposits attached to the Cu-Zn electrode surface. The carbon is a by-product of CO$_2$ reduction [8].

Carbon is an inert electrode, so it does not react when used as anode in the electrochemical synthesis process. Therefore, in this study used carbon as anode which is where the water oxidation reaction takes place. The inert carbon properties cause carbon not to be damaged during use in the electrochemical synthesis process. Since carbon is inert and the bicarbonate anion (HCO$_3^-$) does not undergo oxidation in the water solvent, instead the water undergoes oxidation and becomes a source of protons and electrons. This will support the process of ethanol formation at the cathode, because the mechanism of reaction of ethanol formation at the cathode involves protons and electron transfer [13].

Activated carbon electrode can increase the quantity of ethanol to be obtained and the optimum time required in the electrochemical synthesis process is also less. The activated carbon electrode has a larger pore size, so the touch surface area is also larger [16]. Therefore, the carbon electrode used in this study is activated first.

### 3.3. Conversion of carbon dioxide to ethanol

The success of the electrochemical synthesis process is strongly influenced by the voltage flow. The conversion process of CO$_2$ into ethanol will occur perfectly if the applied voltage is appropriate, so that the desired target product will be formed. The reaction that occurs at the cathode (reduction reaction) will produce a different product when the voltage flow is also different. In this study, the applied voltage varied into 1, 3, 5 and 7 volts, then studied the optimum voltage to produce ethanol.

Reduction of CO$_2$ into ethanol is a non-spontaneous reaction ($E^0 =$ negative), where an outside source of voltage from the power supply is required. The electrochemical synthesis process carried out in this study uses a fixed voltage, so that the current conditions are stable or remain unnoticed. This will make it easier to determine the optimum voltage to convert CO$_2$ into ethanol by electrochemical synthesis method.

![Figure 5. Diagram of Concentration of Ethanol (%) on Voltage of 1-7 Volts](image)

Figure 5 shows the concentration of ethanol (%) obtained on voltage of 1-7 volts. It is known that the voltage required to convert CO$_2$ into ethanol is very specific. So, it can be determined that the optimum voltage is 3 volts with the ethanol concentration of 1.13%.

The composition and concentration of the electrolyte solution greatly influences the results to be obtained in the electrochemical synthesis process. In this study used sodium bicarbonate as an electrolyte solution. The basis of this election is that sodium bicarbonate containing a small alkali metal cation is hydrophilic, so it is not adsorbed on the electrode surface due to its hydration environment and can increase the evolution of hydrogen. This will increase the efficiency of current in the electrochemical synthesis process (CO$_2$ reduction reaction) in the cathode [14].

In this study used sodium bicarbonate electrolyte solution with low concentrations or dilute. The concentration of the sodium bicarbonate electrolyte solution used varied to 0.05, 0.1, 0.2, 0.4 and 0.6 M, then we studied the optimum concentration of sodium bicarbonate electrolyte solution to produce ethanol.
Previous studies that have used sodium bicarbonate as an electrolyte solution to convert CO$_2$ into ethanol have been done [17]. Their results show that if the lower concentration of sodium bicarbonate electrolyte solution is used, the higher the applied voltage. This is due to the conductivity force of an electrolyte solution influenced by the quantity of ions present in the solution. When the electrolyte solution is used, the more concentrated, the more ions are in the solution so that the higher the conductivity and the smaller the voltage difference.

![Figure 6. Diagram Concentration of Ethanol (%) on Concentrations of Sodium Bicarbonate Electrolyte Solution of 0.005-0.6 M](image)

Figure 6 shows the ethanol concentration (%) obtained on concentration of sodium bicarbonate electrolyte solution of 0.05-0.6 M. It is known that ethanol is formed on each variation of the concentration of sodium bicarbonate electrolyte solution used. The concentration of ethanol in the sample experienced a slight decrease of concentration of sodium bicarbonate electrolyte solution of 0.05 to 0.1 M, then continued to increase until concentration of sodium bicarbonate electrolyte solution of 0.4 M. When the concentration of sodium bicarbonate electrolyte solution added to 0.6 M, a decline in the concentration of ethanol in the sample. Figure 6 shows that the optimum concentration of sodium bicarbonate electrolyte solution is 0.4 M with ethanol concentration of 1.33%.

Ethanol will be formed after the electrochemical synthesis process is done until the optimum time is reached. If the electrochemical synthesis process continues with a longer time, it will be able to cause the already formed ethanol is lost or turned into another compound. In addition, some researchers claim that metal electrodes can be deactivated which can poison their electro-catalytic activity after being used for a period of time [14]. In this study, the time of electrolysis varied to 60, 90, 120, 150 and 180 minutes to determine the optimum time to convert CO$_2$ into ethanol.

![Figure 7. Concentration of Ethanol (%) at Time of Electrolysis of 60-180 Minutes](image)
Figure 7 shows the concentration of ethanol (%) obtained at time of electrolysis of 60-180 minutes. It is known that the ethanol concentration in the sample continues to increase until time of electrolysis of 90 minutes, then continues to decrease until time of electrolysis of 180 minutes when the electrochemical synthesis process is continued. The optimum time of electrolysis is studied from the variations that produce the most ethanol. Figure 7 shows that the optimum time of electrolysis is 90 minutes with the ethanol concentration of 10.44%.

3.4. Ethanol formation process on cu-zn electrode
Until now the mechanism of the reaction of ethanol formation on the cathode that occurs during the electrochemical synthesis process is not known with certainty. However, the most proposed reaction pathway in this study is as described by [13].

Figure 8. Reaction Pathway for The Formation of Ethanol in Electrochemical Synthesis

Figure 8 it is explained that the mechanism of reaction of ethanol formation at the cathode involves protons and electron transfer to form COOH on the cathode surface in the first few steps. Then COOH is hydrogenated so as to release H2O and adsorb CO*. The adsorbed CO2 species can then be dimerized and the hydrogenation becomes *CH3CHO. This intermediate product subsequently undergoes a reduction reaction to form ethanol [13].

4. Conclusion
Carbon dioxide can be converted into ethanol by electrochemical synthesis method using Cu-Zn electrode. The optimum electrochemical synthesis conditions to convert carbon dioxide into ethanol are potential, concentration of sodium bicarbonate electrolyte solution and time of electrolysis are 3 volts, 0.4 M and 90 minutes with the ethanol concentration of 10.44%.

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