The Effects of Voltage and Concentration of Sodium Bicarbonate on Electrochemical Synthesis of Ethanol from Carbon Dioxide Using Brass as Cathode

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Abstract. The effects of voltage and concentration of sodium bicarbonate were investigated to determine the optimum conditions of the electrochemical synthesis process to convert carbon dioxide into ethanol. The conversion process is carried out using a sodium bicarbonate electrolyte solution in an electrochemical synthesis reactor equipped with a cathode and anode. As the cathode was used brass, while as the anode carbon was utilized. Sample of the electrochemical synthesis process was analyzed by gas chromatography to determine the content of the compounds produced. The optimum electrochemical synthesis conditions to convert carbon dioxide into ethanol are voltage and concentration of sodium bicarbonate are 3 volts and 0.4 M with ethanol concentration of 1.33%.

Keywords: carbon dioxide, electrochemical synthesis, ethanol, brass, optimum conditions.

1. Introduction
Energy is one of the major problems faced by almost all countries in the world. Given that energy is one of the main factors of economic growth of a country. Energy problems are becoming increasingly complex as energy demand from all countries in the world continues to increase to sustain economic growth that makes the inventory of conventional energy reserves less and less. The increasing need for energy is in fact also in conflict with the needs of mankind to create a clean environment and free from carbon dioxide (CO₂) pollution.

Global issues about CO₂ are also increasingly widespread talked about 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 CO\(_2\) in the air is related to the use of fossil [1].

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 CO\(_2\) 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 [2].

Due to the high potential of CO\(_2\) hazards, research is needed that can convert CO\(_2\) 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 CO\(_2\) as its base material. This is one of many ways to overcome CO\(_2\) hazard aside from minimizing its source of production.

The synthesis of other more useful compounds is a great solution for CO\(_2\) processing, as it will provide great and sustainable benefits. Also, it will also provide a dual solution i.e., reducing the amount of CO\(_2\) as well as the production of a more useful compound. Some of the methods that have been done in the synthesis of CO\(_2\)-based compounds are chemistry, radiochemistry, thermochemistry, photochemistry, biochemistry, and electrochemistry [3].

The synthesis of alcohol by using CO\(_2\) is also a hot topic. From various studies that have been done, it is known that CO\(_2\) is very potential for the synthesis of renewable energy. The products of the most potent CO\(_2\)-based synthesis of the compounds are carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH\(_2\)O), methanol (CH\(_3\)OH), oxalic acid (H\(_2\)C\(_2\)O\(_4\)), methane (CH\(_4\)), ethylene (CH\(_2\)CH\(_2\)), or ethanol C\(_2\)H\(_5\)O) [4][5].

Ways can be done to synthesis alcohol from CO\(_2\) is by electrochemistry. The synthesis of alcohol from CO\(_2\) 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 [6].

Until now, the optimization process of CO\(_2\)-based alcohol 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 used brass as cathode and carbon as anode in electrolysis process to get target product, that is ethanol.

2. Experimental Method

2.1. The Series of Electrochemical Synthesis Reactor

The series of electrochemical synthesis reactor used in this study is shown in Figure 1.
2.2. Electrode Preparation
The brass electrode plate is cut to the size of 1.5 × 4 cm, then rubbed using sandpaper until the dirt on the surface of the electrode is lost. The brass electrode plate is then washed with deionized water until clean and dried. The carbon electrode rod from the used battery was washed with deionized water until clean, then washed for 3 hours at 110 °C to remove the water content. The carbon electrode is then cooled in the desiccator.

2.3. Carbon Dioxide Conversion Process to Ethanol
In the variation of the voltage, a total of 50 mL of sodium bicarbonate 0.1 M electrolyte solution was put into an electrochemical synthesis reactor already equipped with a brass electrode plate (cathode) and a carbon (anode) electrode rod. Then the CO$_2$ gas is fed into the reactor electrochemical synthesis with a flow rate of 0.5 L/minute. The optimum voltage is studied by passing voltage with variations of 1, 3, 5 and 7 volts. Subsequently the sample solution of the electrochemical process was analyzed by gas chromatography to determine the optimum voltage to convert CO$_2$ into ethanol.

In the variation of the concentration of sodium bicarbonate electrolyte solution, respectively used 50 mL of sodium bicarbonate electrolyte solution 0.05, 0.1, 0.2, 0.4 and 0.6 M and put into an electrochemical synthesis reactor already equipped with a brass electrode plate (cathode) and a carbon electrode (anode) rod. Then the CO$_2$ gas is fed into an electrochemical synthesis reactor with a flow rate of 1 L/minute. The voltage used is the optimum voltage obtained from the voltage optimization process, flowing for 90 minutes. Subsequently the sample solution of the electrochemical synthesis process was analyzed by gas chromatography to determine the optimum concentration of sodium bicarbonate electrolyte solution 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 standard ethanol used is 1% standard ethanol which is also analyzed using gas chromatography.

3. Result and Discussion

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

Some studies of converting CO$_2$ to other compounds using 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$_2$ to alcohol [7]. Therefore, in this study used brass as the cathode which is where the process of CO$_2$ conversion into ethanol.

![Figure 2. Picture of Brass Electrode (a) Before Use and (b) After Use](image-url)
Figure 2 shows the difference between the brass electrode before and after it is used in the electrochemical synthesis process. Figure 2a is a pre-prepared brass electrode and has not been used for the electrochemical synthesis process. While Figure 2b is a brass electrode that has been used for electrochemical synthesis process for 90 min. The change in the surface of the brass electrode occurs with the formation of a black layer called sponges. The sponges are more clearly visible when the brass 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 brass electrode surface causing the deactivation or poisoning that can poison the electrocatalytic activity of the brass electrode. Also, deactivation of brass electrode can also be caused by the presence of carbon deposits attached to the brass electrode surface. The carbon is a by-product of CO₂ reduction [6].

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 (HCO₃⁻) 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 [7].

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 surface area is also larger [8]. Therefore, the carbon electrode used in this study is activated first.

3.2. Conversion of Carbon Dioxide to Ethanol

The success of the electrochemical synthesis process is strongly influenced by the voltage flow. The conversion process of CO₂ 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.

Electrochemical reduction of CO₂ into ethanol is a non-spontaneous reaction (E° = 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 CO₂ into ethanol using electrochemical synthesis method.

![Figure 3. Diagram of Concentration of Ethanol (%) at Voltage 1-7 Volts](image-url)
Figure 3 shows the concentration of ethanol (%) obtained at voltage of 1-7 volts. It is known that ethanol is only formed at a voltage of 3 volts and no ethanol is detected at other voltage streams. This shows 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 resulting ethanol concentration produced is 1.13%.

The composition and concentration of the electrolyte solution greatly influence 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 [9].

In this study used a solution of electrolytes sodium bicarbonate 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 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$_2$ to other compounds have been done [10]. 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 4 shows the concentration of ethanol (%) obtained at a concentration of electrolyte solution of sodium bicarbonate from 0.05 to 0.6 M. It is known that ethanol is formed at each variation of the concentration of the electrolyte solution of sodium bicarbonate used. The concentration of ethanol in the sample experienced a slight decrease of the electrolyte solution of sodium bicarbonate concentration of 0.05 to 0.1 M, then continued to increase until the concentration of the electrolyte solution of sodium bicarbonate 0.4 M. When the concentration of the electrolyte solution of sodium bicarbonate added to 0.6 M, a decline in the concentration of ethanol in the sample. Figure 4 shows that the optimum concentration of electrolyte solution of sodium bicarbonate is 0.4 M with ethanol concentration produced is 1.33%.

Theoretically, if the more quantity of CO$_2$ is flowing, the more CO$_2$ will be converted into ethanol so that the ethanol product that will be formed will also be more numerous. The flow rate of CO$_2$ given
should be noted as it will affect the outcome of electrochemical synthesis products. The solubility of CO$_2$ in water is only 0.033 mM. In water CO$_2$ forms equilibrium to H$_2$CO$_3$, but only 1% of CO$_2$ dissolves in the form of H$_2$CO$_3$ [9]. This allows the cause of ethanol not to form when CO$_2$ flow rate is increased. As the CO$_2$ boost rate is increased it will cause CO$_2$ bubbles in more and more electrolysis reactors. Excessive CO$_2$ gas bubbles will affect the stirring factor thus affecting the results of electrochemical synthesis.

Although the quantity of CO$_2$ that flows more and more, in fact not all CO$_2$ dissolves in sodium bicarbonate electrolyte solution to be converted to ethanol. Also, the sodium bicarbonate electrolyte solution is also a water-soluble compound and reacts with other compounds to produce CO$_2$. The reaction of sodium bicarbonate in producing CO$_2$ gas is as follows [11]:

$$NaHCO_3 + H^+ \rightarrow Na^+ + CO_2 + H_2O$$

4. Conclusion
Ethanol can be synthesis from carbon dioxide by electrochemical synthesis method using brass as cathode. The optimum electrochemical synthesis conditions are voltage and concentration of sodium bicarbonate electrolyte solution are 3 volts and 0.4 M with ethanol concentration of 1.33%.

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