Makara Journal of Technology

Volume 17 | Issue 2 Article 2

8-2-2013

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Recommended Citation

Saksono, Nelson; Abqari, Fakhrian; and Bismo, Setijo (2013) "The Plasma Electrolysis Phenomenon in a Two-Compartment Reactor for Chlor-Alkali Production," *Makara Journal of Technology*: Vol. 17: Iss. 2, Article 2.
DOI: 10.7454/mst.v17i2.1929
Available at: https://scholarhub.ui.ac.id/mjt/vol17/iss2/2

Makara Seri Teknologi, 2013, 17(2): 59-63
DOI: 10.7454/mst.v17i2.1929

The Plasma Electrolysis Phenomenon in A Two-Compartment Reactor for Chlor-Alkali Production

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Abstract

Chlor-alkali is one of the most important processes in the chemical industry. It produces chlorine and caustic soda, which become the main feedstock of daily products. The aim of this study is to report the phenomenon of plasma electrolysis and how it can be used in chlor-alkali production for more efficient energy consumption. When the plasma is formed, the current fluctuates and gradually declines. Plasma electrolysis begins with the process of electrolysis itself. Due to Joule heating, gas bubbles are formed and a sheath is made on both electrodes, resulting in the plasma field. Plasma electrolysis can be identified by its radical production. The higher the voltage and concentration, the greater the production of radicals. In 10 minutes or less, the number of OH radicals produced can reach 4 ppm at 400 V and 0.1 M. This amount is relatively small and is caused by other reactions consuming OH radicals to form other radicals such as chlorine. The energy consumption of plasma electrolysis in this study can reach 16 kJ/mmol Cl_2 at 0.5 M NaCl solution.

Abstrak

Fenomena Elektrolisis Plasma dalam Reaktor Dua-Ruang pada Produksi Klor-Alkali. Klor-alkali merupakan salah satu proses penting dalam industri kimia. Proses ini menghasilkan gas klor dan soda api yang merupakan bahan baku utama dari banyak produk yang digunakan sehari-hari. Tujuan utama penelitian ini adalah menjelaskan fenomena elektrolisis plasma yang dapat digunakan dalam produksi klor-alkali dengan konsumsi energi yang lebih efisien. Saat pembentukan plasma, arus listrik berfluktuasi dan secara bertahap menurun. Proses elektrolisis plasma dimulai dengan proses elektrolisis terlebih dahulu. Sebagai akibat pemanasan Joule maka terbentuk gelembung gas yang membentuk selubung pada kedua elektroda dan menghasilkan plasma. Karakteristik elektrolisis plasma ditunjukkan dengan terbentuknya produk radikal. Produksi radikal meningkat dengan bertambahnya tegangan dan konsentrasi. Selama 10 menit proses, OH radikal yang dihasilkan mencapai 4 ppm pada 400 V dan 0,1 M. Hasil ini relatif kecil, hal ini disebabkan oleh reaksi lain yang mengkonsumsi radikal OH membentuk radikal lain seperti klorin. Konsumsi energi elektrolisis plasma dalam penelitian ini mencapai 16 kJ/mmol Cl_2 pada larutan 0,5 M NaCl.

Keywords: chlor-alkali, current, plasma electrolysis, radical formation, voltage

1. Introduction

The chlor-alkali process is one of the most important industrial processes for producing chlorine and caustic soda, which become the main feedstock of daily products such as medicine, detergent, plastic, deodorant, insecticide, disinfectant, etc. However, the process of electrolysis consumes so much electricity that it represents almost 70% of the total production cost of the industry [1]. Electricity cannot be replaced or substituted by other materials due to its function in the process of electrolysis. Hence, the process needs to be intensified in order to reduce the amount of electricity consumed. In this case, plasma technology can be implemented. The existence of plasma in electrolysis will result in an increase in productivity and its characteristics will cause electricity consumption to be lower. Previous research about the production of hydrogen from water using plasma electrolysis found that it was more efficient compared to the Faraday law of conventional electrolysis [2-3].

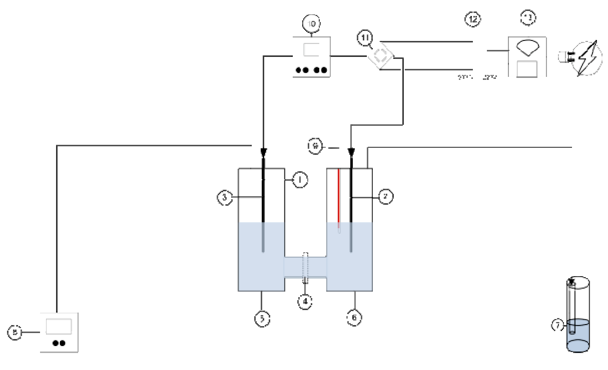
The reactor design influences the activity of plasma when the process occurs. In the application of plasma electrolysis, the reactor with one compartment in which the anode and the cathode are located in the same chamber results in stable plasma activity [2,4]. However, this design has limitations when the process is run with a high concentration of NaCl solution and requires a higher voltage to get more chlorine gas. The

DOI: 10.7454/mst.v17i2.1929

high concentration increases the conductivity of the solution. This results in a higher electric current and consumes more energy as more chlorine gas is produced. The aim of this study is to report the phenomenon of plasma electrolysis that can be used in Chlor-alkali production with more efficient energy consumption. The existence of plasma signals the radicalization process and may increase the reactivity of species in the solution so that the electric current and power consumption can be reduced.

2. Methods

The design of the reactor is shown in Fig. 1. The reactor has two compartments: one compartment is equipped with a graphite anode and the other is equipped with a stainless steel cathode. The reactor is a batch system made from an acrylic housing filter connected to the globe valve. The electric source is connected to a 3-kVA-slide regulator that is then connected to a 4x transformer. A diode bridge is used to rectify the electric current. The current is measured and noted from an ampere-meter Yuhua A830L. The reactor design is also filled with chlorine and hydrogen gas. The chlorine gas produced is then passed into a KI 2% solution and hydrogen gas is passed into a hydrogen analyzer. The KI solution attracts the chlorine gas and both react to form iodine that results in an orange color in the KI solution. Then, the solution is titrated by $Na_2S_2O_3$ 0.01 N. This study analyzes the formation of plasma by varying NaCl concentrations from 0.05 M to 0.5 M within a voltage range of 500–700 V. Furthermore, an examination of energy consumption is conducted by measuring the amount of chlorine gas produced.



1. Reactor
2. Anode (Graphite)
3. Cathode (Stainless Steel)
4. Connector
5. NaCl Solution (Catholyte)
6. NaCl Solution (Anolite)
7. Bubbler of KI Solution
8. Hydrogen Analyzer
9. Thermometer
10. Ampere-meter
11. Diode “Bridge”
12. Transformer
13. Slide Regulator

Fig. 1. Plasma Electrolysis for Chloralkali Production System

3. Results and Discussion

Plasma electrolysis phenomena. The influence of plasma formation in the electrolysis process can be identified by changes in the current. Fig. 2 shows the changes in electric current when plasma is formed. When the plasma is formed, the current fluctuates and gradually declines.

The process of plasma electrolysis begins with the process of electrolysis. Due to Joule heating, gas bubbles are formed and vapor sheaths are created on both electrodes [5-6]. The formation of gas bubbles triggers a collision between gas bubbles and creates an electrical charge so that energy can be scattered and plasma can form [7]. Based on the theory of hydrodynamic instability, gas sheaths begin to concentrate when the current’s density reaches the critical value, followed by a reduction in surface tension [5]. The gas sheath reduces the electric current’s conductivity (high resistance) of gas. As a result, when electric currents pass through the gas, the electric current fluctuates and declines.

According to energy consumption, plasma electrolysis is lower than electrolysis. This is caused by its lower power, which may produce more chlorine due to its unconventional radicalization process. Radicals are formed by the excitation of electrons in ionic substances. High-energy collisions inside the solution will cause the electrons to become excited. The existence of radicals will increase the amount of chlorine produced because it results in a faster reaction. The energy consumption of plasma electrolysis in this study reached 16 kJ/mmol Cl_2 at 0.5 M NaCl solution. Meanwhile, it reached 2,585 kJ/mmol Cl_2 by electrolysis in the same condition. This result shows that plasma electrolysis made the process about 165 times more efficient.

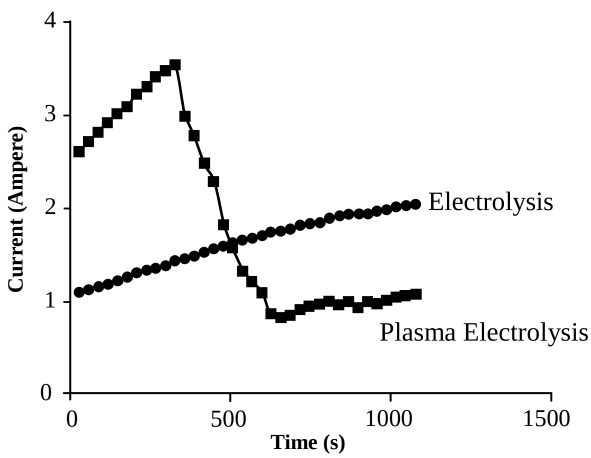


Fig. 2. Electric Current Changes in 500 V Voltages for Electrolysis and the Plasma Electrolysis Condition of a NaCl Solution

Voltage-current characteristic. As shown in Fig. 3, plasma in a two-compartment reactor is formed in voltages above 500. The V-I curve has the typical characteristics of plasma electrolysis [2,4,8]. The first region is the one in which conventional electrolysis occurs (V_A–V_B). This region is shown by an increase in the current when the voltage increases. Jin et al. (2010) stated that this region is called the Ohmic region, and that it is where gas bubbles start to form. Bubble formation is influenced by the hydrodynamic instability of the solution. Based on the Helmholtz-Taylor theory of instability, when current density is closed to its critical value, the boundary between liquid and gas (which supports the formation of the gas sheath) will be broken [6]. The second area is the region where plasma starts to form, which is shown by the decrease of the fluctuating current (V_B–V_C). The plasma formed was caused by energy dissipation due to the collision of electric charges with saturated gas [7]. Energy dissipation caused a temperature increase due to the Joule heating effect. Gas was ionized and electrons were excited, forming the spark of plasma. This region is called the limiting current region or the current saturation region. The voltage in B is called the breakdown voltage from all regions. The breakdown voltage is a voltage value in which the highest current occurs before it fluctuates due to plasma formation.

One of the parameters influenced by the activity of plasma is the distance between electrodes. In a two-compartment reactor, there is about a 15 cm distance between the anode and the cathode. It causes a lower electric current due to the higher resistance of the solution [9]. Although energy consumption was lower, the effect of Joule heating on the solution was lower. This caused the formation of the gas sheath to take longer because of the local solvent vaporization around the electrodes. It also made it more difficult for the plasma to form. In this study, the condition was set at a high voltage in order to make the electric current higher. This, in turn, caused higher Joule heating, so plasma was easily formed.

Fig. 3 shows that the higher solution concentration resulted in a lower breakdown voltage. The higher conductivity caused plasma to form at a lower voltage. The higher conductivity caused a higher current in the same voltage. Therefore, energy dissipation was higher and made gas sheath formation faster.

Reaction mechanism. The increase in productivity is influenced by the increase of chlorine gas production. This is caused by the activity of radical species that can increase the production of chlorine gas. In the process of electrolysis, the reaction is only an ionic reaction. Otherwise, in plasma electrolysis, the existence of radicals helps the reaction occur faster. Radicals are formed due to energy dissipation, which excites the electrons. In this study, the radicalization process can be separated into two processes: water and NaCl-splitting. Due to the Joule heating effect, Gao (2008) stated that an early step in plasma electrolysis reactions is caused by the gas phase of an H_2O reaction, as follows [10]:

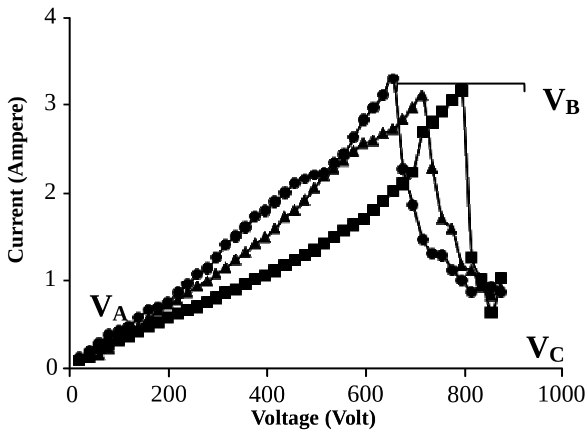


Fig. 3. Current-voltage Characteristic Curve at 70–80 °C in NaCl Solution: 0.1 (■), 0.15 (▲), and 0.2 (●)

$H_2O_{gas} \rightarrow H_2O^{+}_{gas} + e^{*}$
$H_2O^{+}_{gas} + H_2O \rightarrow \bullet OH + H_3O^{+}$

The reaction is then continued by the following radical reaction [3-4]:

$4OH^{-} \rightarrow 4\bullet OH + 4e^{*}$
$4H^{+} + 4OH^{-} \rightarrow 4\bullet H + 4\bullet OH$
$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet$
$2HO_2\bullet \rightarrow H_2O_2 + O_2$
$HO_2\bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2$
$2\bullet H + 2\bullet H \rightarrow 2H_2$
$4\bullet OH \rightarrow 2H_2 + 2O_2$

The formation of radicals can be identified by the formation of OH radicals in the form of H_2O_2. Fig. 4 shows the increased concentration of H_2O_2 as the voltage and solution concentrations increased. The higher voltage and concentration show that plasma formation became more stable, which resulted in more radical species formation (such as OH radicals). However, a previous study conducted by Jin *et al.* (2010) showed that the concentration of H_2O_2 in a NaCl solution was lower than in solutions such as Na_2SO_4, KOH [4]. This was caused by other reactions that can occur and that may consume OH radicals to form other radicals. In a NaCl solution, Cl^- can be changed into Cl radicals. Two chlorine radicals can react with each other to form Cl_2 molecules. Furthermore, HClO is also formed in the solution that may consume H_2O_2. By following this radicalization process, chlorine gas can be produced in two ways: by the reaction of two chlorine radicals or by the reaction of two chlorine ions. The radical reactions in chlorine species are shown as

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follows:

$Cl^- \rightarrow Cl\bullet + e^*$
$\bullet OH + Cl^- \rightarrow Cl\bullet + OH^-$
$Cl\bullet + Cl\bullet \rightarrow Cl_2$
$Cl_2 + H_2O \rightarrow HCl + HClO$
$2HClO + H_2O_2 \rightarrow 2Cl^- + O_2 + 2H^+$

Besides chlorine gas, caustic soda (NaOH) is also produced due to the reaction between OH^- and Na^+ ions by an ionic reaction mechanism in the cathode region. After the decomposition of NaCl, Na^+ ions moved into the cathode region with other ions in the anode region due to plasma formation. In the cathode region, Na^+ reacted with hydroxyl ions to form NaOH. The formation of NaOH increased the solution's pH due to its strong base characteristics, as shown in Fig. 5.

Side reactions occured and formed other products such as hypochlorite ions and chlorate ions. In the reaction mechanism of the plasma electrolysis process, HClO forms in the solution and reacts with H_2O_2, resulting in H^+ and $2Cl^-$ ions. The reactions of side products are listed as follows:

$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$
(hypochlorite formation)
$3NaOCl \rightarrow NaClO_3 + 2\ NaCl$
(chlorate formation)
$NaCl + H_2O \rightarrow NaOCl + H_2$
(hypochlorite formation)
$Cl_2 + H_2O \rightarrow HCl + HClO$
(hydrogen chloride formation)
$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$
(chlorate formation)
$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$
(chlorate formation)

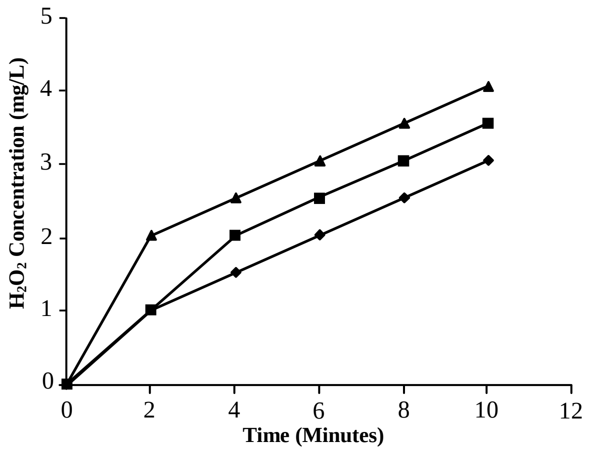

Fig. 4. H_2O_2 Concentration in Plasma Electrolysis of a 0.1 M NaCl Solution. 200 V (♦), 300 V (■), and 400 V (▲)

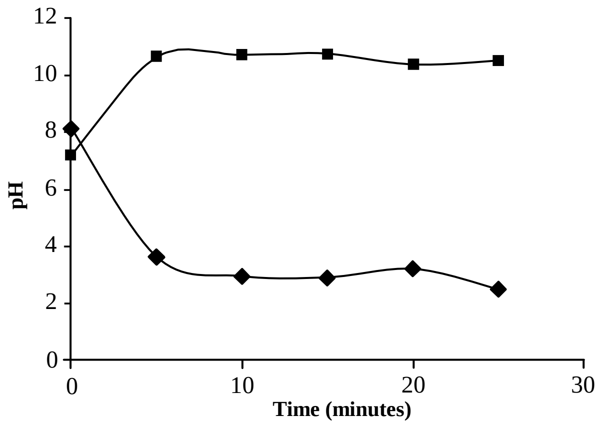

Fig. 5. Final Solution pH in 0.5 M NaCl at 70–80 °C. Anolyte pH (♦), Catholyte pH (■)

4. Conclusions

The application of plasma electrolysis can be implemented in the production of Chlor-alkali. At the time of plasma formation, the electric current fluctuated and gradually declined. Furthermore, the radicalization process produced active species that could make the reaction mechanism unusual. It also led to faster gas product formation, which enhanced the overall system of the process. Thus, it can reduce the amount of energy consumption up to 165 times compared to electrolysis.

Acknowledgements

The Directorate General of Higher Education, Ministry of Education Republic of Indonesia and Directorate of Research and Community Service Universitas Indonesia supported this work by the funding scheme BOPTN, contract no.: 2802/H2.R12/HKP.05.00/2013.

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