Process Production Simulation Of Sodium Hydroxide From Seawater

Eduardus Budi Nursanto[1, 2*], Ananda Cahya Chairunnisa[1)]

[1] Chemical Engineering Department, Universitas Pertamina, Jakarta, Indonesia
[2] Downstream Chemical Industry, Universitas Pertamina, Jakarta, Indonesia

*) *Corresponding author*: eduardus.bn@universitaspertamina.ac.id

Abstract

Sodium hydroxide (NaOH) is a chemical compound that widely used for chemical industry, oil and gas industry , and water treatment. The Chlor-alkali process is one of the processes to produce NaOH via electrolyzer membrane, with seawater as a feedstock. The electrolysis reaction that takes place in the electrolyzer membrane will produce products such as NaOH, Cl_2 gas, and H_2 gas. Based on the process simulation using Aspen Plus, the NaOH concentration of 35 wt% was obtained according to the Chlor-alkali process using membranes. In addition, the energy consumption in the NaOH production process from seawater is 2218.33 kWh/ton NaOH and the current efficiency is 96.66%. The electrolyzer membrane used is equipped with an anode of titanium, a cathode of nickel, and the membrane is made of perfluorocarboxylate polymer.Based on techno-economy analysis, the return on investment value (ROI) is 6.88%.

Abstrak

Sodium Hidroksida (NaOH) adalah senyawa kimia yang banyak digunakan oleh industri kimia, industri minyak dan gas bumi, dan pengolahan air. Proses Klor-Alkali adalah salah satu proses untuk memproduksi NaOH dengan metode elektrolisis dan menggunakan bahan baku air laut. Reaksi elektrolisis yang terjadi di membran elektroliser. Berdasarkan proses simulasi dengan menggunakan Aspen Plus, konsentrasi NaOH sebesar 35% dapat diperoleh dengan menggunakan klor-alkali proses dengan menggunakan membran. Elektroliser membran yang digunakan menggunakan titanium sebagai anode, nikel sebagai katode dan menggunakan membran yang berbahan baku polimer perfluorocarboxylate. Berdasarkan tekno-ekonomi analisis didapatkan bahwa nilai dari return on investment (ROI) adalah 6.88%.

Keyword: *process simulation, NaOH production, Chlor-alkali process, techno economy analysis*
.

INTRODUCTION

The increasing demand for freshwater has led to a water crisis in some area. This crisis led to an increase usage of seawater desalination to use as drinking water. By considering energy consumption and production costs, the dominant seawater desalination technology used today is reverse osmosis (RO). However, most seawater desalination processes produce large amounts of concentrated brine, that will be discharged back into the sea. The consequences of this disposal triggered a negative impact, such as damage to marine ecosystems and pollution of liquid waste [1].

Reusing saltwater to produce useful and commercially valuable chemicals is a sustainable action. However, this approach is rarely applied because there are various impurities in the water which cause the need for complex separation and purification. Despite the complex process, this approach can reduce factory production costs and make clean water more affordable. The use of concentrated brine, resulting in conversion of NaCl contained in brine into NaOH or commonly called caustic soda. [2]

As much as 99.5% of global production of caustic soda uses a chlor-alkali electrolysis process. In this process a salt solution or NaCl is decomposed by electrolysis under direct current to produce chlorine, hydrogen and sodium hydroxide solution. There are three types of this chlor-alkali process such as, Mercury Cell, Diaphragm Cell, and Membrane Cell. Currently, the chlor-alkali process using cell membranes is widely used compared to the other two processes because it has several advantages including low energy consumption, low cost of capital investment, less expensive cell operation and high purity caustic soda.

By considering the quality of chlorine, caustic soda products, equipment costs, operating costs and energy consumption mentioned above, we choose chlor-alkali membrane process. In this research, we build process simulation for production of sodium hydroxide from seawater by using ASPEN PLUS software.

EXPERIMENTAL SECTION

The software for the process simulation of NaOH production from seawater is ASPEN PLUS. The important parameter for process simulation is property method.

The Electrolyte wizard is useful for determining property methods, chemical reactions and simulation approaches that may arise from components that have been entered. In this process simulation, because the components are electrolyte compounds. Furthermore, ionic reactions and interactions occur from these compounds, ENRTL-RK was chosen as the property method, where ENRTL (Electrolyte non-random two-liquid) models the non-ideal electrolyte liquid phase and RK (Redlich - Kwong) models the equation of state for the gas phase. This model is quite flexible because it is suitable for application at low to medium pressures and the simulation approach used is true component.

Assumptions made during modelling:

a. Seawater is modelled as a NaCl solution, the impurities on sea water consist of Ca^{2+}, Mg^{2+}, bromide (Br^-) and sulphate ions (SO_4^{2-}).
b. Streams are well mixed without gradients of temperature, pressure, and concentration.
c. In each flow, chemical equilibrium of aqueous phase reactions including dissociation of electrolyte and salt deposition can be achieved at each flow. This balance is predicted automatically by Aspen Plus
d. The resulting efficiency at the anode and cathode refers to the journal data

RESULT AND DISCUSSION

Figure 1 shows block flow diagram of NaOH production by using chlor alkali membrane. Seawater as feed into the nanofiltration unit. Nanofiltration unit functions is to remove sulphate ions and other ions such as Ca^{2+} and Mg^{2+} contained in the feed. Ion rejection is 95.7% for sulphate ions, Ca^{2+} ions 38.3, Mg^{2+} ions 40.1% [1]. Furthermore, seawater must have a concentration up to its saturation limit before entering the electrolysis membrane unit to ensure the efficiency of the process, so an electrodialysis unit can well perform [2]. However, there are limitation for electrodialysis, the concentration of salt in seawater that comes out of concentrated stream should not be higher than 20 wt. % because it increases the energy consumption [3]. The concentrated flow pass through the evaporation unit to get a saturated brine 27 wt.%. After the concentration reaches the desired saturation, sea water enters chemical softening process to precipitate Ca^{2+} and Mg^{2+} ions, such as calcium and magnesium salts with the help of Na_2CO_3 40 wt. % and NaOH 35 wt. %. The precipitate formed will be removed using a centrifuge. Before it enters the membrane electrolyser, brine 27 wt. % was added with HCl 37 wt. %. HCl is act as an acidifier to prevent pH of brine less than 2 [4]. Brine enters the membrane electrolyser with a temperature of 88°C and a pressure of 1.09 bar. At the anode, chloride is oxidized to chlorine gas and partially dissolved in the anolyte. The side reaction that occurs at the anode is the oxidation of water to produce oxygen. At the cathode, water is reduced to hydrogen to produce hydroxide ions. Na^+ ions will migrate from the anode to the cathode to combine with OH- ions to form NaOH with a concentration of 35 wt. % which will be split to be recycled back to the cathode and added with make-up water. The following is a reaction that occurs at the anode and cathode:

$$Anode: 2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cathode: 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

$$Overall: 2NaCl + 2H_2O \xrightarrow{elektrolysis} 2NaOH + H_2 + Cl_2 \quad (3)$$

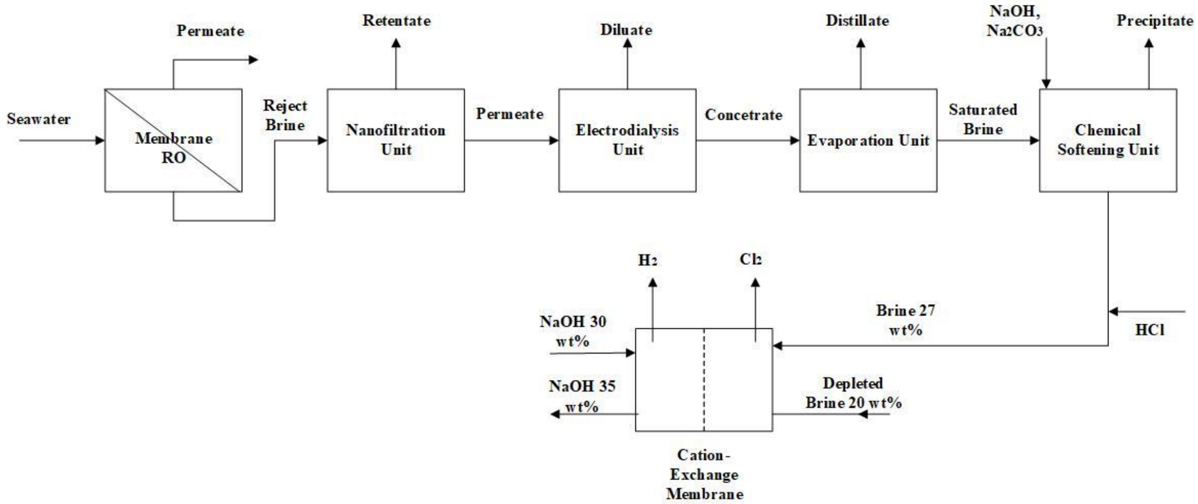

Figure 1. Block flow diagram of production NaOH from seawater via chlor-alkali membrane

Process optimization is carried out to obtain optimum operating conditions for the membrane electrolyser. The parameters used to optimize the production of NaOH are reactor conversion, brine pH and make-up water. Figure 2 shows the process simulation by using ASPEN PLUS software.

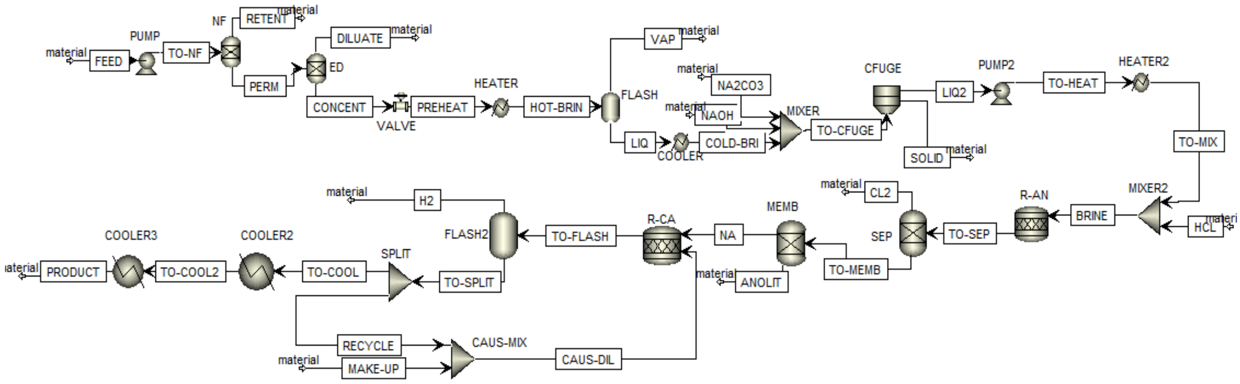

Figure 2. Process simulation of NaOH production from seawater via chlor-alkali membrane process

The conversion of NaCl also affects the concentration of NaCl in the anolyte as shown in the Figure 3. From Figure 3, the conversion of NaCl to the production of NaOH and Cl_2 is linear. The higher conversion of NaCl, the production of NaOH and Cl_2 also increases, but the concentration of NaCl in the anolyte decreases to 16 wt.% where it must be avoided to maintain a stable condition [1]. operation. Therefore, the NaCl conversion is varied so that the NaCl concentration in the anolyte reached 20 wt.% and 73.2% NaCl conversion was obtained.

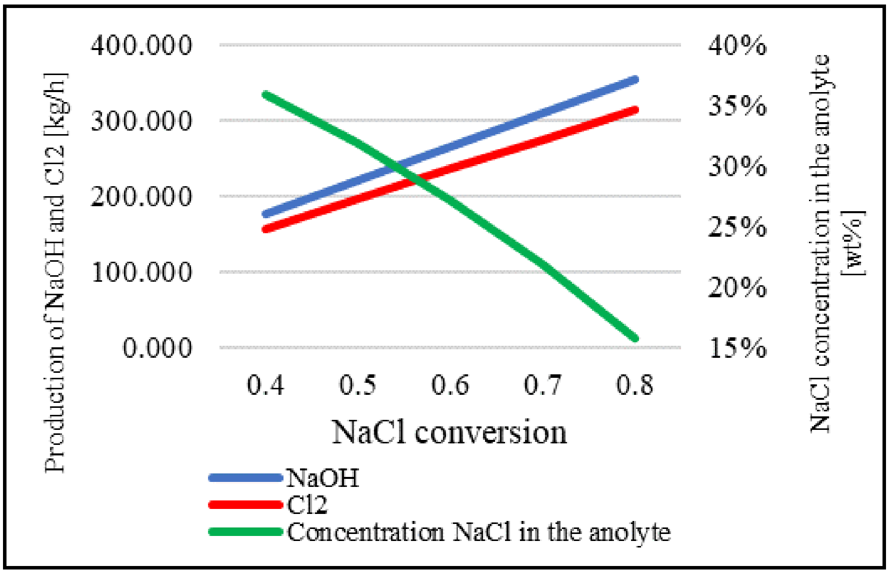

Figure. 3 Correlation between Conversion of NaCl (to NaOH and Cl_2) and Concentration of NaCl in the Anolyte

Furthermore, to obtain a product concentration of 35 wt.% NaOH, the flowrate variation of make-up water added during recycling was carried out using the design spec. From the design spec in ASPES PLUS software, make-up water flowrate is 61.5043 kg/hour.
In this simulation, the anode efficiency is determined by the following equation:

$$\xi^p = \frac{\dot{n}Cl_2}{\dot{n}H_2} \quad (1)$$

The flow rate of the moles of hydrogen gas formed at the cathode is carried out and an anode efficiency is 48.34%. To measure the efficiency of the cathode, the following equation is used

$$\eta = \frac{\dot{n}Na^+}{\dot{n}H_2} \quad (2)$$

The flow rate of moles of Na^+ that passed through the membrane is varied and the cathode efficiency was obtained at 96.66%. The low anode efficiency is caused by the simulation of mole of Cl_2 which is a fixed variable. Meanwhile, mole of H_2 is a manipulated variable, resulting is low anode efficiency.

To monitor the performance of the cell, the electrical power consumed during the process of producing one tonne of NaOH must be considered. The following equation is used to calculate energy consumption in the chlor-alkali process [4].

$$P = \frac{U}{F \times CE} \quad (3)$$

Where:
P = Power (kWh/ton NaOH)
U = Cell Voltage (Volts)
F = Faraday's constant for NaOH (1.4923 kg/k.Ah)
CE = Current Efficiency of NaOH (%)

From the simulation results obtained energy consumption of 2218.33 kWh/ton NaOH while the experimental results (from reference) of the resulting energy consumption of 2930 kWh/ton [1]. The energy consumption of the simulation results is lower than the experimental results because the efficiency of NaOH produced in the simulation is higher than the experiment.

The annual income from sales of the product can be listed below

Table I. Annual Plant Income

Product	Income	
NaOH	Rp	49,898,444,451
Cl_2	Rp	40,379,817,341
H_2	Rp	7,682,326
Total Income	Rp	90,285,944,118

Table 2. Plant Components

Component	Amount
Direct Plant Cost	Rp 378,015,889,604
Indirect Plant Cost	Rp 13,529,972,721
Working Capital	Rp 41,580,763,309
Total Capital Investment	Rp 433,126,625,634
Total Production Cost	Rp 50,530,260,152.52

The return on investment from the NaOH production process is 6.88% after tax. The minimum return on investment (ROI) for the chemical industry category is 11% with low risk [5-6], while the calculation of the ROI value obtained is below the minimum limit. It can be concluded that based on the ROI value, this NaOH production project does not meet the requirements since it has high total capital investment.

Pay out time from the NaOH production process takes 11 years to return the capital that has been spent. The maximum pay out time (POT) before tax for low risk chemical industry is 5 years [5]. Then, the internal rate of return of the project is calculated by iterate the value of discount rate until the net present value of all cash flows equal to zero. The internal rate of return of the project calculated to be 15% when compared to the Minimum Attractive Rate of Return (MARR) obtained from bank loan deposits, which is 3.56%, it can be concluded that the NaOH production project from seawater is economically justified.

Based on this economic analysis, it can be concluded that the NaOH production project from seawater is worth investing in if the production capacity is increased. The initial investment cost for this project is quite expensive because of the membrane price.

CONCLUSION

Based on the simulation of the NaOH production process from seawater using ASPEN Plus, the product obtained is 929.526 kg/hour with a NaOH product concentration of 35 wt.%. For the economic analysis on the NaOH production project from seawater, the ROI value of 6.88% and the IRR value of 15% can be declared economically justified. However it would be better if the production capacity was increased because the initial investment cost for this project was quite expensive. The expensive part on this system is the price of the membrane

ACKNOWLEDGEMENT

Authors is fully supported from Universitas Pertamina, Indonesia.

REFERENCES

[1] Du, F., Warsinger, D. M., Urmi, T. I., Thiel, G. P., Kumar, A., & Lienhard V, J. H. (2018). Sodium Hydroxide Production from Seawater Desalination Brine: Process Design and Energy Efficiency. Environmental Science & Technology, 52(10), 5949–5958. https://doi.org/10.1021/acs.est.8b01195

[2] Casas Garriga, S. (2011). Valorization of brines in the chlor-alkali industry. Integration of precipitation and membrane processes [Ph.D. Thesis, Universitat Politècnica de Catalunya]. In TDX (Tesis Doctorals en Xarxa). http://www.tdx.cat/handle/10803/131052

[3] Nayar, K. G., Fernandes, J., McGovern, R. K., Dominguez, K. P., McCance, A., Al-Anzi, B. S., & Lienhard, J. H.
(2019). Cost and energy requirements of hybrid brine concentration systems for salt production. Desalination,
456, 97–20. https://doi.org/10.1016/j.desal.2018.11.018

[4] O'Brien, T. F., Bommaraju, T. V., & Hine, F. (2005). Handbook of Chlor-Alkali Technology: Volume I: Fundamentals, Volume II: Brine Treatment and Cell Operation, Volume III: Facility Design and Product Handling, Volume IV: Operations, Volume V: Corrosion, Environmental Issues, and Future Developments. Springer US. https://doi.org/10.1007/b113786

[5] Aries, R. S., & Newton, R. D. (1955). Chemical Engineering Cost Estimation. Chemonomics.

[6] Sullivan, W. G., Wicks, E. M., & Luxhoj, J. T. (2006). *Engineering Economy.* Upper Saddle River, N.J: Pearson/Prentice Hall.