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Study of Reaction Kinetics of Magnesium Sulfate Formation from Bittern and Sulfate Acid

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ABSTRACT

Bittern is a concentrated liquid obtained from the salt plant waste, and the amount is abundant. Bittern contains various minerals; this mineral occurs because it does not crystallize during the manufacture of salt. The minerals have high concentrations, among others: Magnesium (Mg), Sodium (Na), and Calcium (Ca). In general (28.5 – 30 oBe) is still contained Magnesium about 4-5% w/v. Considered the high content of Mg on Bittern is worth as the raw material for the manufacture of MgSO4. In this study, Mg(OH)2 was obtained by reacting Bittern with NaOH to obtain Mg(OH)2 deposits. The study aims to determine the reaction rate constant and activation energy of the formation of Magnesium Sulfate. The prescribed variable is Mg(OH)2 46.6 gr; NaOH 4N 3 liters; H2SO4 1N 500 ml; Drying temperature 100oC; Stirring speed of 110 rpm. As for the modified variable, temperature: 40, 45, 50, 55, 60oC and stirring time: 20, 30, 40, 50, 60 minutes. The best result for forming magnesium sulfate is at temperature 60oC and 60 minutes with reaction conversion (xA) 26.9%. The formation of magnesium sulfate followed the second-order reaction and the equation of the rate constant k = 0.00512 min-1 and the activation energy of 131.394 kJ/mol.K.

Keywords: Bittern, reaction rate constant, activation energy

Introduction

Indonesia is an archipelago with the second-longest coastline globally, covering an area of 100,000 km. Thus, Indonesia can be developed into a salt production area, especially for Eastern Indonesian waters with low rainfall, such as West Nusa Tenggara, East Nusa Tenggara, most of Eastern Java, and Madura. The ions contained in seawater are 55% sodium (Na^+); 31% chlorine (Cl^-); 4% magnesium (Mg); 8% sulfate (SO_4^{2-}); 1% calcium (Ca^{2+}) and 1% potassium (K^+). Waters at subtropical latitudes have lower salinity due to low evaporation. The open ocean has constant salinity, in the range of 34-37%, with differences in solubility due to precipitation and evaporation (Sidharta, 2016).

In Indonesia, the salt is mostly produced by evaporating the brine using sunlight directly. The evaporation process will produce NaCl precipitate and residual liquid, known as bittern. Bittern contains various compounds such as magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), magnesium chloride ($MgCl_2$), potassium chloride (KCl), and calcium chloride ($CaCl_2$). Mineral content in bittern partly includes macro and micronutrients needed by plants and plankton, such as Mg^{2+}, $K^{+,}$ and Ca^{2+}. The mineral content of bittern is very valuable and will increase its value if used as fertilizer (Sato et al., 2010).

Several earlier studies have studied the process of taking Magnesium from salt with a batch process. The extraction of magnesium salt from seawater through the crystalization process has been done by Natasha and Sulistiyono (2016). The Precursor for the separation of Magnesium

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chloride from bittern has been done by Aal et al. (2017). Selective extraction of Magnesium content from bittern using NaOH on experimental and pilot-scale (Shahjooei et al., 2019), Recovery of high purity Magnesium hydroxide from calcium-rich brines (Yousefi et al., 2016), and Separation of Magnesium Hydroxide from saltwater by addition of NaOH solution (Turek & Gnot, 1995). The manufacture of $MgSO_4$ has also been carried out by Hapsari (2008) by reacting $Mg(OH)_2$ and H_2SO_4.

The extraction of Magnesium from Bittern has various benefits, one of which is the use of Magnesium from bittern for the manufacture of struvite, as in the study by Sutiyono et al. (2016). This research aims to study the kinetics of magnesium sulfate formation $Mg(OH)_2$ from bittern and sulfate acid as raw materials. This study refers to the value of the reaction rate constant and activation energy obtained from the Arrhenius equation.

The Reaction mechanism in this research are:

1. The reaction of manufacture magnesium hydroxide $Mg^{2+} + NaOH \rightarrow Mg(OH)_2 + 2Na$
2. The reaction of manufacture magnesium sulfate $Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$

Reaction kinetics model

The reaction between magnesium hydroxide and sulfate acid is a solid-liquid heterogeneous reaction. Smith and Vannes (1981), in non-catalyzed reactions between solids and fluids, reactions at the solid surface occur by adsorption of the fluid reactants to the surface, followed by a surface reaction involving the adsorbed molecule.

Reaction mechanism

The reaction for the formation of magnesium sulfate can be written as:

$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$$

Equation of reaction can be written:

$$-ra = -\frac{dCA}{dt} = k.CA.CB$$

Where,

A = Sulfate acid (H_2SO_4)
B = Magnesium hydroxide ($Mg(OH)_2$)

C_B (Concentration of $Mg(OH)_2$) is in excess, C_B is considered constant. So, the equation becomes:

$$-ra = -\frac{dCA}{dt} = k.CA$$

Determination of order reaction

Since $CA = CAo$, the equation for the order of reaction becomes (Levenspiel,1999),

1. Zero order reaction (n=0)
$$(-XA)\,CAo = -k.t$$
2. First-order reaction (n=1)
$$ln\,(1 - XA) = -k.t$$
3. Second-order reaction (n=2)
$$\frac{XA}{CAo\,(1-XA)} = k.t$$

If the reaction rate does not depend on the concentration of the reactants, then the order of the reaction is zero. Meanwhile, if the reaction is proportional to one of the reactant concentrations, the reaction order is one. However, sometimes the order of reaction can be changed by changing the concentration of reactants, i.e., by increasing or decreasing the concentration of one or the other reactant.

Reactions that are not the first-order reaction remain the first-order reaction by increasing or decreasing the concentration of one or the other reactant, known as pseudo-first-order reactions. Therefore, the name indicates that this is not a first-order reaction.

Arrhenius equation

In the Arrhenius equation, there is the term activation energy. Activation energy is the energy needed to activate the reactants to be able to react completely. The Arrhenius equation can express the relationship between temperature and reaction rate constant as follows (Levenspiel, 1999):

$$k = k_o e^{-Ea/RT} \quad \text{or} \quad ln\, k = ln\, ko - \frac{Ea}{R}\frac{1}{T}$$

Material and Methods

Material

The material used in the manufacture of Magnesium Sulfate is Bittern, obtained from PT. Garam (Persero) in Madura.

Research variables

In this study, the variables used in the reaction for the formation of Magnesium Sulfate were the concentration of H2SO4, the water content of Mg(OH)2, and reaction time. The variables determined were Magnesium Hydroxide 46.6 g; Sodium Hydroxide 4N 3 liters; Sulfate Acid 1N 500 ml; Drying temperature 100oC, and Stirring speed 110 rpm.

Temperature : 40, 45, 50, 55, and 60 oC
Stirring time : 20, 30, 40, 50, and 60 min

Manufacture of magnesium hydroxide

Three liters of bittern were put into a glass beaker, then slowly mixed with 3 liters of 4N NaOH Solution, then stirred and allowed to form two phases. Filter the precipitate obtained and dry using the oven until dry. The resulting Mg(OH)2 was ground using porcelain and mortar until it became a solid powder.

Formation of magnesium sulfate MgSO4

500 ml of 1N H2SO4 solution is mixed with solid Mg(OH)2 46.6 g, stirred using a magnetic stirrer at speed 110 rpm, at the variable's temperature and time. The precipitate was separated from the filtrate formed from the solution of Magnesium Sulfate. Amount of Mg in the formed filtrate analyzed and calculated the conversion and reaction rate constant.

Results and Discussion

The initial content of Magnesium in the Bittern is 14.7473 mg/L. While the initial level of Magnesium in solid $Mg(OH)_2$ was 34.42%. from the experimental research, the Mg content in $MgSO_4$ formed at reaction times 20, 30, 40, 50, and 60 min are shown in Table 1.

Table 1. Effect of of temperature and reaction time on the content of $mgso_4$ formed

Time (min)	Mg Content in $MgSO_4$, mg/L				
	Temperature				
	40°C	45°C	50°C	55°C	60°C
20	1417.5	1411.1	1565.4	1652.4	2506.2
30	1436.5	1438.9	1703.5	1873.4	2796.9
40	1441.2	1488.6	1787.8	2034.1	3087.6
50	1451.8	1537.3	1856.2	2124.8	3178.3
60	1472.9	1606.1	1904.8	2415.5	3269.0

As shown in table 1, the Mg content in $MgSO_4$ formed at reaction times 20, 30, 40, 50, and 60 min; the result is directly proportional to the reaction time. As the reaction time increases, the Mg Content in $MgSO_4$ also formed increases. It indicates that increasing reaction time can increase the formation of Mg content in $MgSO_4$. Meanwhile, the Mg content in $MgSO_4$ formed at temperatures 40, 45, 50, 55 dan 60°C is also directly proportional to the reaction temperature. As the reaction temperature increases, the Mg content in $MgSO_4$ also formed increases. It indicates that increasing the reaction temperature also increases the formation of Mg content in $MgSO_4$. The highest $MgSO_4$ content was obtained at 60 min and 60°C, which was 3269.0.

The effect of the temperature and the reaction time on $MgSO_4$conversion are shown in Table 2 and figure 1.

Table 2. Effect of temperature and reaction time on the conversion of MgSO4

Time (min)	Conversion of $MgSO_4$, %mole				
	Temperature				
	40°C	45°C	50°C	55°C	60°C
20	11.67	11.61	12.88	13.60	20.63
30	11.82	11.84	14.02	15.42	23.02
40	11.86	12.25	14.71	16.74	25.41
50	11.95	12.65	15.28	17.49	26.16
60	12.12	13.22	15.68	19.88	26.90

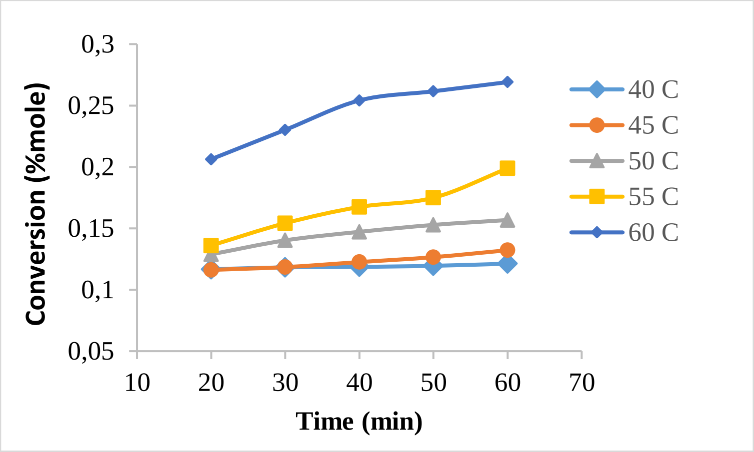

Figure 1. Relations between time reaction and conversion of various temperatures

Figure 1 shows that as the reaction time increases, the conversion also obtained increases. The increased reaction time causes the contact between the reactants to be longer, so the Magnesium sulfate obtained is also greater. As the reaction temperature increases, the conversion also obtained increases. The increased temperature can affect the reactivity of the molecules to move and interact with each other and result in collisions between molecules so that the reaction proceeds well and results in greater conversion. The highest conversion of MgSO4 was obtained at 60 min and 60oC, which was 26.90%. in the experiment of synthesis of Mg(OH)2 using the electrochemical method, the conversion of Mg in bittern was 93.22% (Amrulloh et al., 2017)

The reaction order determined by plotting the graph $X_A/Cao(1-X_A)$ Vs time and find the regression value. The Relations between $X_A/Cao(1-X_A)$ against time in various reaction temperature as shown in figure 2.

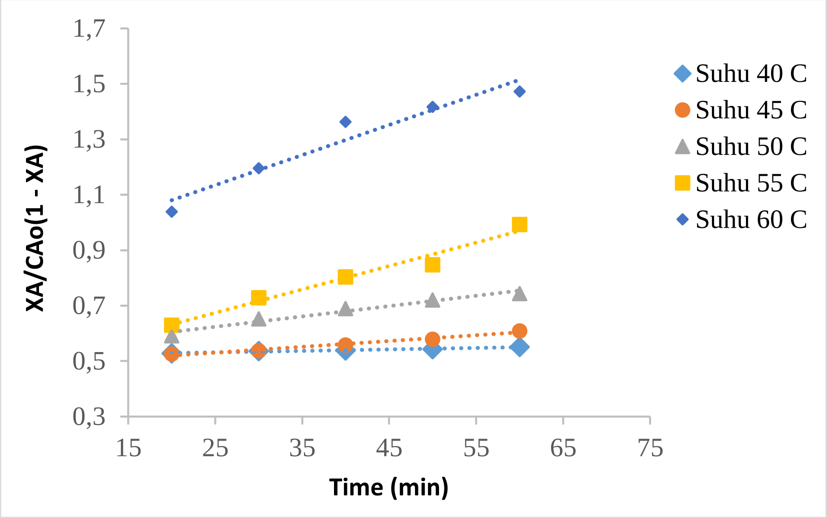

Figure 2. Relations between XA/Cao(1-XA) against time

Based on Figure 2, it can be seen that the graphic pattern that relates changes in the concentration of XA/Cao(1-XA) to time already shows a straight line pattern. Based on Figure 2, a straight line equation and the regression value (R^2) of each temperature. The average regression value (R^2) obtained from the straight-line equation is 0.96138. Compared with the regression value (R^2) on the first and zero-order, the regression value (R) on the second-order is closer to the value 1. So, the reaction for the formation of Magnesium sulfate follows a second-order reaction (n=2). However, because in the reaction for the formation of Magnesium Sulfate, there is an excess concentration of one of the reactants, it can be concluded that the reaction for the formation of Magnesium Sulfate in this study follows a pseudo-first-order reaction. In Figure 2, the reaction of order 2, the value of the reaction rate constant (k) can be determined by the slope value of the formed straight line equation, as shown in Table 3.

Table 3. Straight line equations at various temperature reaction orders 2

Temperature(°C)	**Straight Line Equations**	**k**	**R^2**
40	0.0005x + 0.5181	5×10^{-4}	0.9561
45	0.0021x + 0.4783	2.1×10^{-3}	0.9782
50	0.0037x + 0.5305	3.7×10^{-3}	0.964
55	0.0084x + 0.4631	8.4×10^{-3}	0.9713
60	0.0109x + 0.8629	1.09×10^{-2}	0.9373

After obtaining the slope value data from the straight-line equation, it can be obtained that the final value of the reaction rate constant for the formation of Magnesium Sulfate is k = 0.00512 min^{-1}.

Determination of the value of Activation Energy (Ea) refers to the equation:

$$k = k_o e^{-Ea/RT}$$

$$ln\ k = ln\ ko - \frac{Ea}{R}\frac{1}{T}$$

The value (k) is the slope value of the straight line equation. Activation Energy can be determined from the relations curve of the reaction rate constant (k) as a function of temperature by plotting a graph of the relations ln k versus 1/T, as shown in Figure 3.

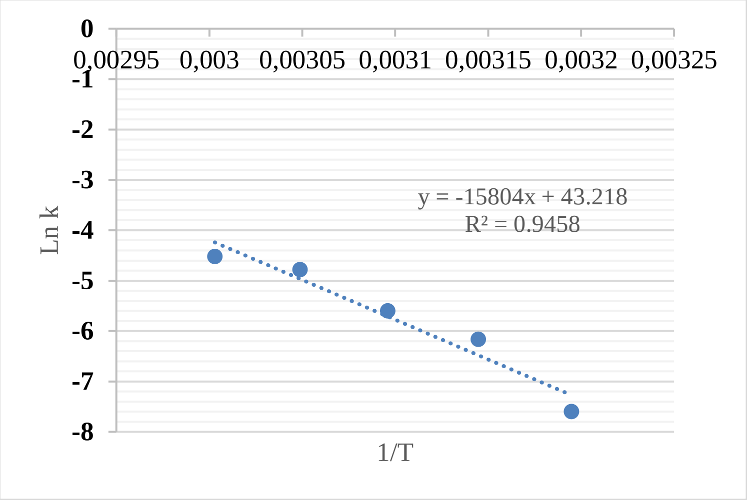

Figure 3. Relation of reaction rate constants as a function of reaction temperature order 2

Based on Figure 3, the equation of the relations line between ln l and 1/T is obtained, which is expressed by $y = -15804x + 43.218$ with R^2 value is 0.9458 (closer to the value 1) so that the slope and intercept obtained can represent the frequency factor and activation energy with the line equation

$ln\ k = -15804x + 43.218\ or\ - ln\ k = 15804x - 43.218.$

Determination of the value of Activation Energy (Ea) in forming Magnesium Sulfate according to the graph of the Arrhenius equation, the equation of the $-ln\ k = 15804x - 43.218$ is equivalent to $y = ax + b$. Therefore, the slope of the graph ln k with $1/T$ will get Ea/R as the slope and ln koas the intercept. It means $Ea = slope\ x\ R$ (ideal gas constant) so that the final value of Activation energy for the formation of magnesium sulfate is $Ea = 131.394\ kJ/mol.K$.

Conclusion

The results showed that the best operating conditions for the reaction of formation of magnesium sulfate are at 60 min and 60°C, which was 26.90%. The formation of magnesium sulfate follows a second-order reaction (n=2), or it can be a pseudo-first-order reaction. The value of the reaction rate constant for the formation of magnesium sulfate is k=0.00512 $min^{-1,}$ and

Activation Energy for the formation of magnesium sulfate obtained $Ea = 131.394\ kJ/mol.K$. Because the reactions of order 0, order 1, and order 2 are not significantly different, the discussion is not much different.

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