The Kinetics Reaction of Phosphoric Acid Formation from Cow Bone

Caecilia Pujiastuti[1]*, Yustina Ngatilah[2], Muhammad Septianto[3], and Angelia Tantyono[4]
Chemical Engineering, University of Pembangunan Nasional "Veteran" East Java, Surabaya, Indonesia
***caeciliapujiastuti@gmail.com**

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Abstract
Phosphoric acid can be formed from bone waste, including cow bone which contains calcium phosphate. When reacted with sulfuric acid it becomes phosphoric acid. The purpose of this research was to determine the reaction constant of phosphoric acid from cow bones. The reaction constant can determine the good operating conditions in a reactor design. Starting with the cow bones that have been powdered with a size of 200 mesh, dissolved in the water until saturated. Then saturated solution 500 ml was taken and reacted with 4 N sulfuric acid 100 ml, stirring process was carried out at 200 rpm, with variable temperature were (70°C, 80°C, 90°C, 100°C, and 110°C) and time were (40, 50, 60, 70, and 80 minutes). Next, the sample was filtered, and the sediment was taken, and analysed of phosphoric acid filter and separated the sediment. Based on this research, an equation $k = 1.1627\ e^{-3742.4/T}$ *was generated. The graph in picture 5 shows that the equation followed a pseudo first order reaction.*

Keywords: *Cow Bone, Acid, Phosphoric*.

Abstrak
Asam fosfat dapat terbentuk dari sisa tulang, termasuk tulang sapi yang mengandung kalsium fosfat. Ketika direaksikan dengan asam sulfat akan menjadi asam fosfat. Tujuan penelitian ini adalah untuk mengetahui konstanta reaksi asam fosfat dari tulang sapi. Konstanta reaksi dapat menentukan kondisi operasi yang baik dalam perancangan reaktor. Diawali dengan tulang sapi yang sudah ditumbuk dengan ukuran 200 mesh, dilarutkan dalam air hingga jenuh. Kemudian larutan jenuh 500 ml diambil dan direaksikan dengan asam sulfat 4 N 100 ml, pengadukan dilakukan pada 200 rpm, dengan variabel suhu (70°C, 80°C, 90°C, 100°C, dan 110°C) dan waktu (40,50,60,70, dan 80 menit). Kemudian sampel disaring dan sedimen diambil, dan dianalisis kandungan saringan asam fosfat dan pemisahan sedimen. Berdasarkan penelitian ini, didapatkan persamaan $k = 1.1627\ e^{-3742.4/T}$*. Grafik pada Gambar 5 menunjukkan bahwa persamaan tersebut mengikuti reaksi orde satu semu .*

Kata Kunci: *Tulang Sapi, Asam, Fosfat*.

1. Introduction

One of the main products of cow slaughter are bone parts that have not been economically optimized. All this time, cow bones are only used as handicrafts, then with the development of science and technology, cow bones can be used for other needs. Currently, cow bones are waste that has accumulated a lot in Indonesia. The slaughter of the livestock is carried out almost every day and the process of taking the meat and skin are one after completing the slaughtering process. After that, the meat and skin will be distributed to local markets. Meanwhile, many of the cut bones are not reused. Moreover, cow bones contain calcium phosphate, the largest composition of bone constituents, this can be reused to minimize waste (Yusnita, 2014). Calcium in bones and primary inorganic components is found in natural cartilage of bones and teeth in both vertebrates and humans (Mao, 2016). Phosphorus and calcium are essential macro minerals; they are the most abundant mineral nutrient in the body (Samy, 2015). Calcium is at different biological absorption rates, so the balance between reactions will be better (Nelsone, 2018). Recent technologies in materials science have led to advances in metric synthesis of phosphates at the nanoscale (Oliveira, 2018). Comparisons of deposition have been carried out with different calcium and determination of the optimal conditions of the influencing factors (Atia, 2013). Calcium phosphate material is similar in composition to bone and has bioactive and osteoconductive properties. Calcium phosphate materials come in a various forms, such as cement, composites, and coatings (Al-Sanabani, 2013). The reaction of the H_3PO_4 from chicken powder and H_2SO_4 is 35%. Sembodo (2005) studied about wet process method and obtained a quasi-order reaction against Ca_3 $(PO_4)_2$ with a reaction rate constant k' = 0.0006/ minute. Meanwhile, the sulfuric acid concentration which gave the highest yield was 45%. From the results obtained in the largest concentration conversion of a concentration of H_2SO_4 within 3 hours of heating, it was amount to 61.62% (Darmawan, 2014). The phosphoric acid from chicken bones using a wet process showed the optimum results, it were obtained at a concentration of 20% HCl and a time of 120 minutes. The phosphoric acid can be made by a wet process and an electric furnace process. However, this study was using wet process, namely sulfuric acid solvent and the applied heating temperature was not too high. So, that the substance that is

deposited is gypsum (Anggraenie, 2017). The composition of organic and inorganic materials are in a ratio of about 1: 2. The material of these animals provides strength, elasticity and minerals to bone tissue. The removal of organic matter by heating does not change the general shape of the bone, but it reduces its weight by about a third, and makes it very brittle and soft. On the other hand, decalcification, although it does not affect the shape and size of the bones, it makes the bones soft and supple. Fresh dead bone has a yellowish white colour. Calcium phosphate exists in two forms, namely the amorphous phase and the crystalline phase. Depending on it, there are various phosphorus elements that can be processed (Ramadhani, 2012). Phosphate is an essential nutrient needed by plants for their growth and development. Phosphate is present in abundant amounts in the soil, but around 95-99% is in the form of undissolved phosphate so it cannot be used by plants (Raharjo, 2007). A use of phosphate substances as fertilizers was practiced unconsciously long before the isolation and discovery of phosphorus. This is because bone continued to be the main source of phosphorus and phosphoric acid until after the mid-nineteenth century, but this supply was still limited. The bones are finely ground and applied directly to the ground. However, it appears that increasing the treatment of this mineral phosphate with sulfuric acid increases the availability and efficiency of the phosphate for agricultural purposes (Renaudin, 2017). Phosphoric acid can be found in materials containing phosphorus, especially rocks and from animal bones. In their use, phosphoric acid, phosphate salts, and their derivatives have increased not only in the fertilizer industry but are also widely used in the foodstuff industry, textiles, plastics, glass, paints, and the pharmaceutical industry. In the foodstuff industry, phosphoric acid is used as a preservative and flavour agent for drinks, while the salts (sodium hydro phosphate and sodium carbonate) are used as purifiers in sugar or baking soda factories so that the cake dough expands (Falah, 2013). A good standard of phosphoric acid has physical properties in the form of a clear liquid that is quite thick and has a typical sour aroma in general. Phosphoric acid has the molecular formula H_3PO_4 or commonly referred to as the IUPAC trhydroxidophosphorus nomenclature with a molar mass of 98.00 g/mol. Phosphoric acid can be a solid or a

thick white liquid. For water solubility, it is 5.48 g/mL. With a melting point of 42.35°C and a boiling point of 158°C (Perry, 2008). Chemical reaction kinetics is the study of quantitative reaction rates including studying the measurement of reaction rates and variables at reaction rates, namely concentration, temperature, and pressure, especially for slow reactions, where reaction time affects the amount of conversion and the mechanism or stage of the reaction. Conversion is the amount of the substance that is turned into a product compared to the amount of the original reactant. To determine the reaction speed and reaction rate constants, it can be completed in a batch reactor, meaning that all the reagents are put into the reactor, and then it is proceeded. A homogeneous reaction in the liquid phase is a reaction in which all the phases of the compound react the same, it can be dissolved first until it reaches the homogeneity of a material. The saturated solution then is reacted with sulfuric acid, it is formed a homogeneous reaction. The reaction is provided in Equation (1):

$$Ca_3(PO_4)_2(l) + 3\,H_2SO_4(l) \rightarrow 2\,H_3PO_4(l) + 3CaSO_4(s) \quad (1)$$

The equation for the reaction speed is shown in Equation (2)

$$\frac{dC_A}{dt} = -k\,C_A C_B^{\,3} \quad (2)$$

Where:

C_A= Concentration $Ca_3(PO_4)_2$

C_B= Concentration of Sulfuric Acid

The concentration of sulfuric acid can be considered constant so that Equation (2) changes to:

$$\frac{dC_A}{dt} = -k'\,C_A \quad (3)$$

$$\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = -\,k' \int_0^t dt \quad (4)$$

$$\ln C_A - \ln C_{Ao} = -k't \quad (5)$$

The rate constant and activation energy are linked by the Arrhenius Equation (6)

$$k = Ae^{-Ea/RT} \quad (6)$$

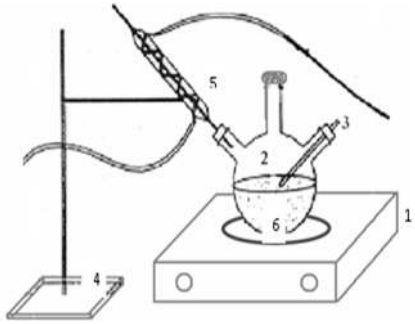
Where:

E a = Activation Energy
T = Temperature (K)
A = Frequency Factor
e = Mathematical Quantity
k = Rate Constant

The factors which affect the reaction rate has the best concentration, and the reaction rate is also better. The faster reaction will be so that the constant value of the reaction speed will also be the best. The rate constant and activation energy are calculated by the Equation 6. In general, the longer of reaction time, then the conversion obtained because the longer the reactants contact each other to produce changes (the product obtained). The stirring, there will be more opportunities for the reagents to combine with each other (Levenspiel, 1999)

2. Method

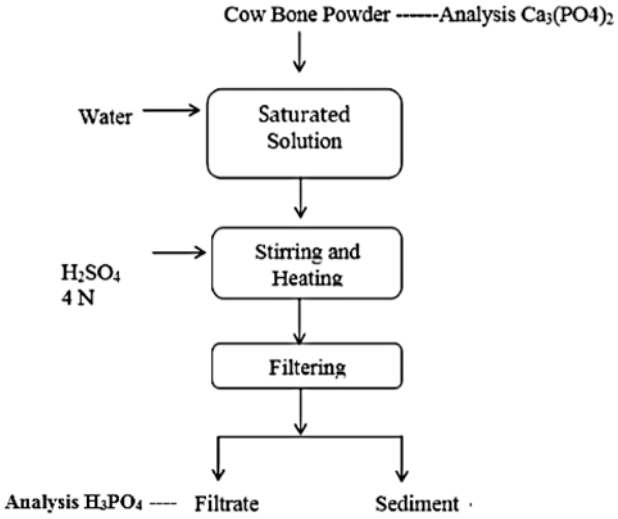
This study used cow bone powder with a size of 200 mesh which it was reached soluble a saturated state. This saturated solution was reacted with sulfuric acid so that the reaction occurred in the liquid-liquid phase (homogeneous reaction). It could be seen that amount of bone powder dissolved first until it reached the homogeneity of a material. The refined powder was sieved with a size of 200 Mesh, then a uniform particle size was obtained. The powder was dissolved in 500 ml of distilled water to form a homogeneous solution. Next, 4 N concentration of H_2SO_4 solution of 100 mL. Saturated solution was put into a three-neck flask, then added with a 100 ml H_2SO_4 solution of 4 N concentration, heated while stirring at a speed of 200 rpm, the temperature studied (70ºC, 80ºC, 90ºC, 100ºC, and 110ºC) in the time as executed (40,50,60,70, and 80 minutes). The obtained filtrate was analysed for its phosphoric acid content. The processing tools are shown in Picture 1.



where:
1. Heater
2. Three-neck Rounded Flask
3. Thermometer
4. Clamp holder and stat
5. Condenser
6. Magnetic

Picture 1. Processing Tools.

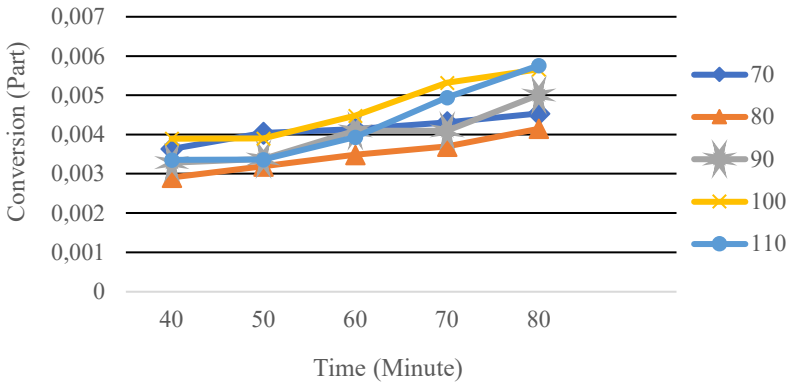
The research flow is provided in Picture 2.



Picture 2. Research Flowchart

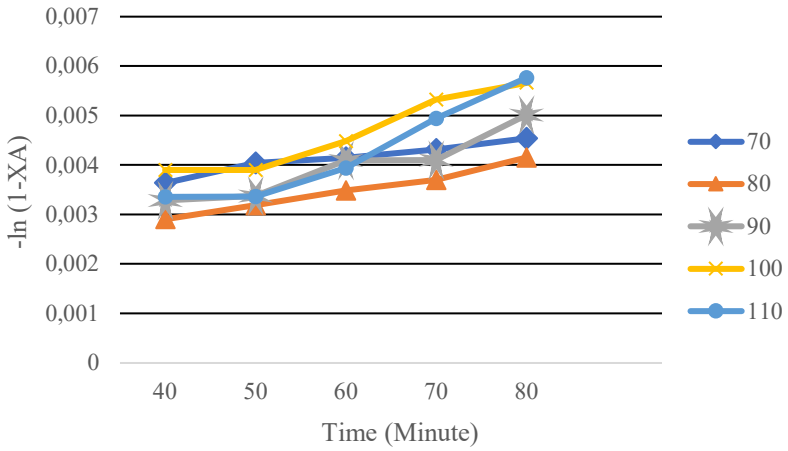
3. Result and Discussion

The powder used contained 12.88% Calcium phosphate (Industrial Research and Development Agency Surabaya, 2018). The research results obtained are shown in Picture 3.



Picture 3. Conversion (Parts) and Time (Minute) at Various Reaction Temperatures.

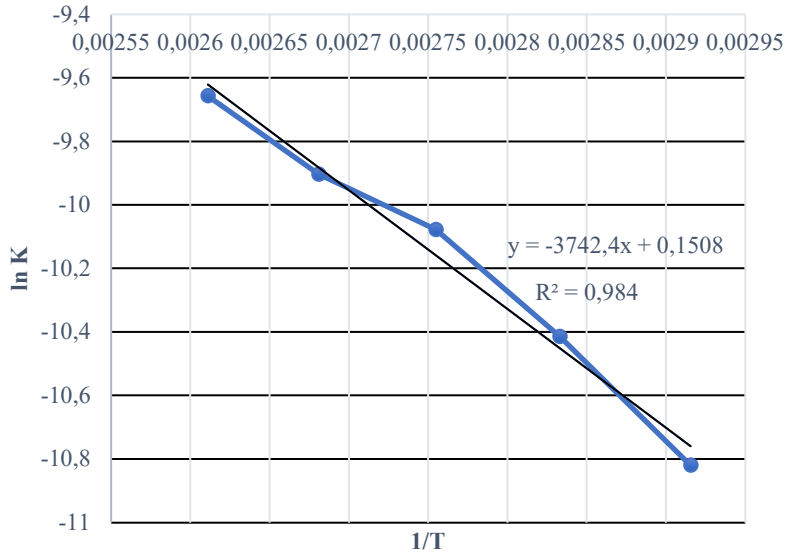
Based on Picture 3, the longer achieve of reaction time, then better conversion was obtained. So, that the long reaction time will increase the time contact between reactants, therefore, the conversion of phosphoric acid is also better. This is also applied to temperature. Due to the temperature can increase the kinetic energy of the particles, it can cause the collision frequency to be more effective (Lozano, 2013). The largest conversion obtained at a reaction time of 80 minutes and a temperature of 110ºC was 0.00576 parts. The relationship -ln (1-Xa) with time t (minutes) in the form of a graph with 70℃-110℃ intervals can be seen in Picture 4.



Picture 4. -ln (1-Xa) and Time (Minute) at Various Reaction Temperatures.

Based on Picture 4, when it reached higher temperatures, then the reaction rate constant will increase. The increasing of temperature can increase the reaction rate of the particles kinetic energy and allow more collisions to be generated. According to the collision theory, a reaction occurs when molecules collide with a sufficiently large amount of energy, which is usually called the activation energy and is related to the Equation 6.

According to Picture 5, it is obtained the relation between ln k vs 1/T, based Equation 6, $k = k_0 e^{-Ea/RT}$ (Levenspiel, 1999). The slope of y= -3742.4x + 0.1508. With exponent 0.1508 =1.1627, the symbol (x) has the equal position with the symbol (T) temperature. So, the picture above rate constant is $k = 1.1627\ e^{-3742.4\ /\ T}$. The activation energy can be obtained by dividing the gas constant (R) obtained is -3742.4:1.987= -1883.44 with a value of $R^2 = 0.984$ and because the R^2 close to the value 1, so the graph follows the pseudo first order graph (Levenspiel, 1999).



Picture 5. ln k vs 1 / T

4. Conclusion

Based on the research results, it could be concluded that the best of time and temperature were obtained from the best conversion reaction. The reaction of phosphoric acid formation followed a pseudo first order reaction with a rate constant k = 1.1627 e $^{-3742.4 / T}$. The conversion obtained was very small and the largest was only 0.00576 parts. The more parts were gotten, the better achieved process between contact reactions. This showed that research could be applied in a batch reactor with the wet process method.

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