G-Tech : Jurnal Teknologi Terapan
Vol. 9, No. 1, 2025, p. 40-48
E-ISSN: 2623-064X | P-ISSN: 2580-8737

Study of Crystallization Process of Potassium Chloride (KCl) Solution with Ethanol Solution

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Article Information

Article History

Received : October 11, 2024
Revised : November 11, 2024
Accepted : January 02, 2025

***Keywords*:**

Evaporation
Crystallization
Antisolvent Crystallization
KCl Fertilizer

ABSTRACT

This study develops a method for producing KCl fertilizer from KCl waste generated during the industrial production of calcium oxide, with KCl concentrations in the wastewater ranging from 7-10%. The main objective of this research was to investigate the effect of ethanol concentration and crystallization time on pore diameter, KCl content, and the amount of product produced. The study was conducted in two stages: evaporation and crystallization. In the evaporation stage, the KCl waste was heated until it reached a saturated solution. In the crystallization stage, ethanol solution was added as an antisolvent to accelerate the crystallization process.KCl analysis results showed that increasing ethanol concentration and crystallization time led to higher K and Cl content in the final product. The highest K content was 79.55%, and the highest Cl content was 16.88%, achieved with 90% ethanol concentration and a crystallization time of 100 minutes. BET analysis indicated that as ethanol concentration increased, the resulting product size grew larger, leading to smaller pore diameters. At high ethanol concentrations, the KCl crystals formed lacked pores. SEM-EDX analysis revealed that the KCl crystals not only contained K and Cl but also other elements such as C, O, and Ca.

INTRODUCTION

The calcium oxide (CaO) industry is aimed at producing calcium oxide (CaO). In its production process, this industry uses raw materials such as blood clam shells, which are reacted with hydrochloric acid (HCl) and then mixed with potassium hydroxide (KOH). Based on the production process, the calcium oxide (CaO) industry generates wastewater containing potassium chloride (KCl) with concentrations of 7-10%. Given the composition of the wastewater, this study proposes a process to utilize this wastewater to produce a product, namely crystallization. Crystallization occurs when a solution exceeds its solubility limit. This process is one of the most important in industry because it produces solid crystal products with high purity and facilitates storage and transportation. One important property of crystals to consider is the individual crystal size and the uniformity of their size (McCabe, 1985). The management of KCl (potassium chloride) waste into fertilizer is crucial for environmental sustainability, particularly in the context of processing industrial waste from CaO that contains KCl. KCl waste, often generated in processes like calcium oxide (CaO) production, poses a risk of environmental contamination if not properly managed. One of the negative impacts of KCl waste is the accumulation of excess salts in soil and water, which can degrade soil quality and disrupt aquatic ecosystems.By converting

KCl waste into potassium fertilizer, this research presents an environmentally friendly solution that also benefits the agricultural sector. Potassium is an essential nutrient for plant growth, and transforming KCl waste into fertilizer can enhance the availability of potassium for plants while reducing dependence on imported chemical fertilizers. This approach also supports sustainable agriculture by decreasing waste and minimizing environmental pollution.Thus, this research can mitigate the environmental impact of industrial waste disposal by repurposing KCl in CaO waste. With the right technology, KCl in this waste stream can be processed into a safer and more effective potassium fertilizer, which not only reduces pollution but also enhances the sustainability of agricultural production. This approach aligns with the principles of a circular economy, where industrial waste is converted into valuable products, reducing pollution and promoting environmentally friendly agricultural practices.Overall, the relevance of this research is significant in the context of industrial waste management and environmental conservation, providing practical and sustainable solutions for turning KCl waste into a useful resource.

The process of producing KCl fertilizer is highly significant for the sustainability of the fertilizer industry, particularly in efforts to reduce environmental impact and improve resource efficiency. Crystallization processes, whether through cooling or evaporation, have great potential in producing potassium fertilizer from industrial waste, such as KCl found in the byproducts of calcium oxide (CaO) production. By converting KCl waste into a useful fertilizer for plants, this research not only helps reduce the accumulation of harmful waste but also supports the production of more environmentally friendly fertilizers. There are several methods for the production of KCl fertilizer itself. Crystallization occurs through several methods, including cooling, evaporation (evaporative), and antisolvent methods. The cooling crystallization method is carried out under low-temperature operational conditions. Cooling crystallization is easy to apply and can produce high-quality crystals. This method is used for crystallizing potassium chloride (KCl) from a saturated KCl solution by dissolving a specific amount of KCl in distilled water (Kardum, 2005). Evaporative crystallization involves continuously heating a solution to obtain crystals. Evaporative crystallization is commonly used in salt production, where salt is typically produced through the evaporation of seawater with the help of sunlight (Umam, 2019). Evaporation can be used for the purpose of separating solvents from more concentrated solutions. Furthermore, this concentrated solution is usually processed for crystallization. In designing the evaporation process (concentration) to obtain a certain solution concentration, operating conditions greatly affect the desired results. The evaporation of an evaporator can be calculated by knowing the absolute pressure that occurs in the evaporation chamber. Where the evaporation temperature is the temperature of saturated vapor at absolute pressure in the evaporation chamber. And the concentrated solution will show an increase in its boiling point, resulting in a higher boiling point temperature compared to pure water (Ismiyati, 2020).

Antisolvent crystallization is an effective separation and purification method because it involves the addition of a solvent such as methanol as the antisolvent. The use of an antisolvent in this crystallization process reduces the solubility of the solute in the solution, leading to faster crystal formation. The energy required for antisolvent crystallization is much lower compared to evaporative crystallization. Generally, antisolvents contain hydrophilic stabilizing agents (i.e., surfactants) that are absorbed onto the crystal surface to hinder further crystal growth (Marco, 2010).

Crystallization using an antisolvent is an effective separation and purification method to produce nano-sized particles, as it involves adding a solution of a compound as the antisolvent. The use of an antisolvent reduces the solubility of the solute in the solution, causing crystallization to occur rapidly (Christianty, 2015). According to research by Tarigan (2016), in antisolvent crystallization, the antisolvent is added to the main solution, reducing the solubility of the solute and creating a supersaturated condition. The type of antisolvent affects the crystal size and distribution. Maximum solubility occurs when methanol is used as the antisolvent. Research by Hervelly (2016) shows that ethanol concentration affects the mass of crystals produced. The higher the ethanol concentration, the more crystals are produced. Factors affecting crystallization also influence the mass of crystals formed. The supersaturation of the parent solution is a key factor in the crystallization process. Under this condition, crystals begin to form, and in antisolvent crystallization, supersaturation is achieved by changing the solvent composition.

KCl fertilizer is an inorganic fertilizer that is needed by plants in large quantities. Potassium chloride (KCl) is a type of potassium fertilizer, with a nutrient content of 60% K2O, adding potassium to the soil can increase the amount of available potassium, potassium is important in stimulating growth and facilitating photosynthesis. The main function of potassium (K) is to help form proteins and carbohydrates. Potassium also plays a role in strengthening the plant body (Zulkifli, 2018). The nutrients contained in KCl fertilizer are potassium nutrients that can be absorbed by plants in the form of K2O compounds. KCl fertilizer in the soil will first break down into K2O compounds and Cl++ ions before the absorption process. K2O is beneficial for growth and strengthening plant resistance to disease, while Cl++ ions are actually detrimental to plants if given in excess (Nurhalim, 2019). KCl fertilizer has the advantage of improving the quality and production of plants, helping plants to be more resistant to pests and diseases. Giving the right dose of fertilizer can optimize plant growth and development, but the timing of fertilizer application is also no less important. If the application time is not right, it can cause potassium nutrients to be washed out or lost so that plants cannot meet their needs for potassium nutrients. Based on these conditions, the dosage and timing of KCl fertilizer application on plant growth and yield (Alfy, 2022).

Based on this explanation, a crystallization process of potassium chloride using an ethanol solution is proposed. Since the solubility of potassium chloride in ethanol is low (0.288 grams per liter at 25°C), crystal formation is possible. Crystallization using ethanol will produce more crystals compared to the cooling and evaporation methods. This is because ethanol acts as an antisolvent, which correlates with crystal mass, melting point, and moisture content.This study aims to investigate the effect of ethanol concentration and crystallization time on pore diameter, K and Cl content in the product, and the amount of KCl produced. The objective of this research is to study how ethanol concentration and crystallization time influence the pore diameter, K and Cl content, and the total amount of product produced.

RESEARCH METHODS

In this study, the main materials used are potassium chloride (KCl) waste solution obtained from the calcium oxide (CaO) industry, with a potassium chloride concentration ranging from 7-10%, and an ethanol solution. The equipment used in this study includes beakers, burettes, magnetic stirrers, stands, and clamps. The research procedure is divided into two main stages: evaporation and crystallization.In the evaporation stage, the KCl waste solution with a concentration of 7-10% is filtered using filter paper to separate suspended solids. The filtered KCl solution is then heated at 90°C for 30 minutes until it reaches a saturated KCl solution with a concentration of 33%. The next stage is crystallization, where the saturated KCl solution is crystallized using ethanol solution with varying ethanol concentrations according to the experimental variables. The saturated solution is then mixed with ethanol and stirred at a specific speed for a designated crystallization time, as determined by the variables. The variables used include ethanol concentrations of 70%, 75%, 80%, 85%, and 90%, as well as crystallization times of 20 minutes, 40 minutes, 60 minutes, 80 minutes, and 100 minutes. After crystallization, the resulting crystals are separated from the filtrate by filtration, using filter paper. The KCl crystals are then dried in an oven at 100°C for 15-20 minutes to remove the moisture content from the product. Finally, the product is analyzed using BET analysis, KCl concentration analysis, and SEM-EDX analysis.

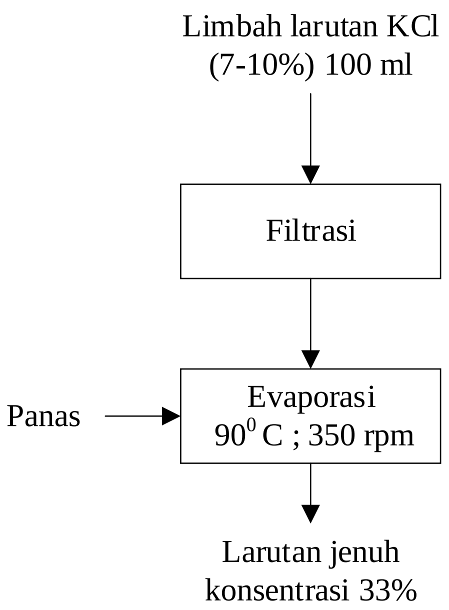

Figure 1. Flowchart of KCl Solution Evaporation Process

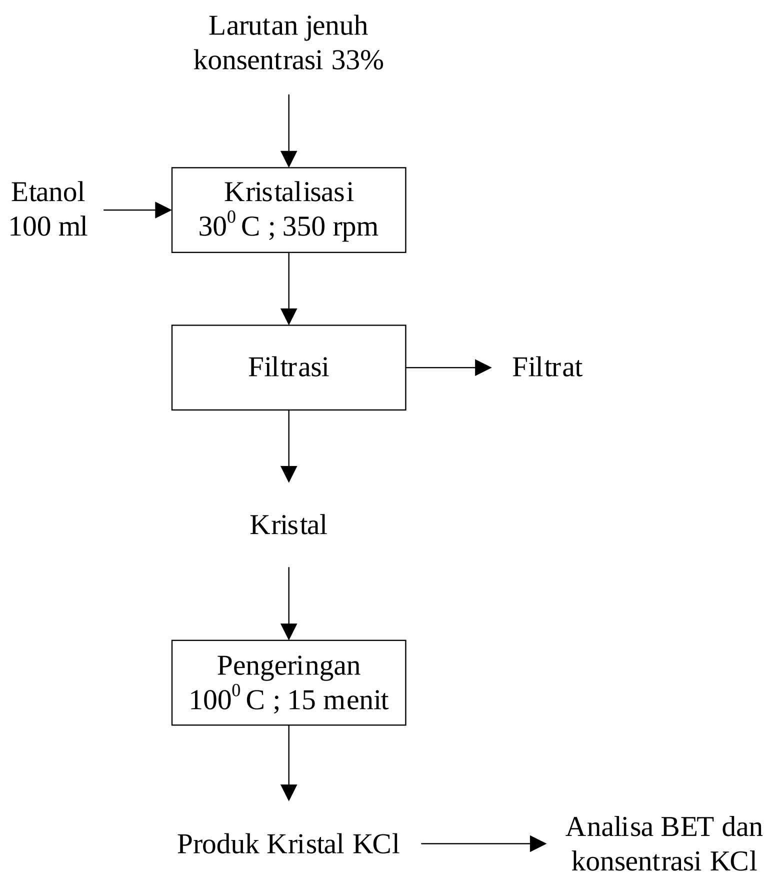

Figure 2. Flowchart of KCl Solution Crystallization Process

RESULTS AND DISCUSSION

1. Effect of Ethanol Concentration and Crystallization Time on the Weight of KCl Product Produced

Table 1. Wastewater Quality

Content	Results
K	0,24%
Cl	3,61%

In this study, observations were made on raw materials in the form of KCl waste obtained from the calcium oxide (CaO) industry. Analysis of KCl waste with a volume of 100 ml showed that the potassium (K) content was 0.24% and the chloride (Cl) content was 3.61%. In Table 1. These levels still do not meet the standards set in SNI 02-2805-2005 for KCl fertilizer. To improve the quality of waste and achieve the KCl fertilizer standard, a crystallization process was carried out using the anti-solvent method. This process is used to increase the concentration of potassium and chloride in waste, so that the final product can meet the requirements set in the national standard and ensure its effectiveness as a fertilizer.

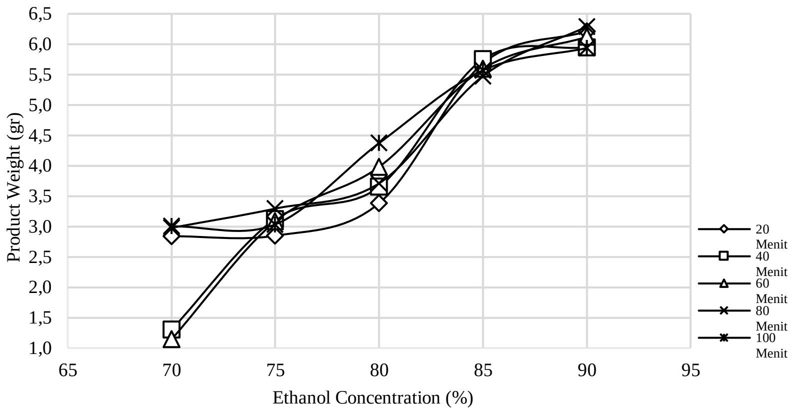

Figure 3. Relationship between Ethanol Concentration (%) and KCl Product Weight (gr) with Various Crystallization Time Variations (minutes)

The figure above shows that the greater the concentration of ethanol used in the crystallization process, the greater the weight of the KCl product produced. A sufficiently large ethanol concentration will increase the solute precipitation ratio well. So that it will accelerate the rate of nucleation and crystal formation with a lower solute concentration. With the increase in the long chain of alkyl alcohol, it will form more crystals at a certain time. Research conducted by Hervelly in 2016 explained that the higher the ethanol concentration, the more crystals are produced. The crystallization process is influenced by the supersaturation state of the parent solution. Where the more water in a solution, the more difficult it is to achieve supersaturation, because some of the solution will bind to the water component in ethanol. Therefore, the use of higher ethanol will produce more crystals compared to the use of lower ethanol.

2. Effect of Ethanol Concentration and Crystallization Time on Product K Content

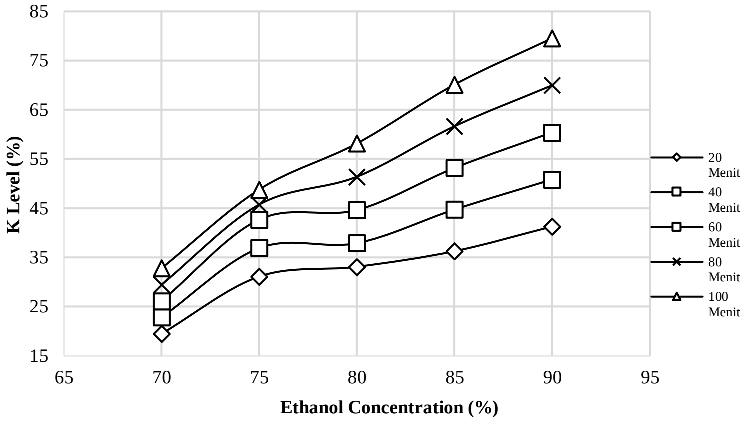

Figure 4. Relationship between Ethanol Concentration (%) and K Level (%) with Various Variations of Crystallization Time (minutes)

Figure 4 shows that the higher the ethanol concentration used in the crystallization process, the higher the K level of the resulting product. Ethanol solution added to KCl solution will bind the water in KCl, causing the resulting crystal product to have a fairly high concentration. This is because the solubility of ethanol in water is high so that ethanol is able to bind the water in KCl. The addition of ethanol with a high concentration will increase the K level of the product, because the water content in the ethanol solution which is getting smaller is able to bind the water in the KCl solution maximally. So that the concentration of potassium (K) contained in the product will be higher. The most optimum condition in this crystallization process is at a crystallization time of 100 minutes with an ethanol concentration of 90%. The crystallization process under these conditions produces a Potassium (K) level of 79.55%. The results of this level can be said to be good because they have met the quality requirements according to SNI 02-2805-2005. Where the standard potassium content contained in KCl fertilizer is a minimum of 60% while the maximum is not specified. According to Zang et al (2009), where the addition of antisolvent in large quantities will increase the precipitation of solutes due to the dilution effect and strengthening of solvent molecular bonds through hydrogen bonds. This will accelerate the rate of nucleation and crystal formation, while the concentration of solutes continues to decrease. The longer the alkyl chain in alcohol, the more crystals are formed in a certain period of time.

3. Effect of Ethanol Concentration and Crystallization Time on Product Cl Content

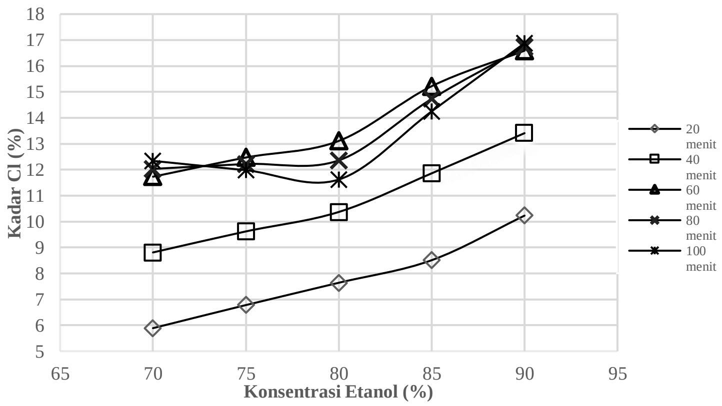

Figure 5. Relationship between Ethanol Concentration (%) and Cl Level (%) with Various Variations of Crystallization Time (minutes)

Figure 5 shows that the Cl level in the sample forms crystals with an anti-solvent crystallization process. The optimum condition in this crystallization process was obtained at 100 minutes with an ethanol concentration of 90%. The crystallization process under these conditions obtained a Cl level of 16.88%, and from the graph, a decrease in Cl level was obtained at a concentration of 80%. According to Zang et al (2009), where by adding a large amount of antisolvent, the precipitation of the extracted solute will increase due to the dilution effect and strengthening of the solvent molecular bonds through hydrogen bonds. This will accelerate the rate of nucleation and crystal formation, while the concentration of the solute continues to decrease. The longer the alkyl chain in alcohol, the more crystals are formed in a certain period of time. The main driving force in this crystallization process is the difference in chemical potential between the solution and the solid phase, which is achieved through supersaturated conditions such as cooling, evaporation, and the addition of antisolvent.

4. Effect of Ethanol Concentration on Surface Area

Table 2. Effect of Ethanol Concentration on Surface Area

Ethanol Concentration (%)	Crystallization Time (minutes)	Pore Diameter (m^2/g)
70%	40	0,024
90%	40	0,000

Based on table 2 the effect of ethanol concentration on the pore diameter above, the results of the pore diameter test were obtained, where at an ethanol concentration of 70% at the 40th minute, a pore diameter of 0.024 m2/g was obtained. While at an ethanol concentration of 90% at the 40th minute, a pore diameter of 0.00 m2/g was obtained. so that at an ethanol concentration of 90% the product produced is a crystal that does not have pores. This is because the higher the ethanol concentration, the larger the product produced so that the pore diameter is smaller.

5. SEM-EDX Analysis Results

Table 3. SEM-EDX Analysis Results

Element	Weight (%)	Atomic (%)	Error (%)
C	4,55	12,17	16,34
O	4,85	9,72	14,25
Cl	45,42	41,12	3,27
K	40,93	33,59	4,59
Ca	4,25	3,41	17,14

Based on the results of the SEM-EDX test on KCl crystals, several other compound elements were obtained that were not potassium (K) and chloride (Cl). The SEM-EDX test results contained potassium (K) compound elements with a weight of 40.93% and chloride (Cl) with a weight of 45.42%. Other elements contained in KCl crystals include carbon (C) with a weight of 4.55%, oxygen (O2) with a weight of 4.85%, and calcium (Ca) with a weight of 4.5%. From the SEM-EDX test, it can be seen that the Cl content has a higher content than the content of other elements. The presence of other elements such as C, O and Ca is due to the content of raw materials in the research process. Where the raw materials used come from calcium oxide (CaO) industrial waste.

CONCLUSION

The potassium (K) content in KCl fertilizer that meets the SNI 02-2805-2005 standard must be at least 60%. This potassium content can be achieved by using an ethanol concentration of at least 85% with a crystallization time of 80 minutes. Under these conditions, the potassium (K) content obtained is between 60-79%. The pore diameter at an ethanol concentration of 70% for 40 minutes, with a product weight of 1.3013 grams, is 0.024 m^2/g, while at an ethanol concentration of 90% for 40 minutes, with a product weight of 5.9503 grams, the pore diameter is 0.000 m^2/g. As the ethanol concentration increases, the resulting product size also increases, leading to smaller pore diameters in the crystals. At higher ethanol concentrations, the produced product lacks pores. The higher the ethanol concentration used, the greater the amount of KCl crystals produced. Therefore, to obtain a larger quantity of KCl product, a higher ethanol concentration is required. With the results obtained, the implication for further research is to combine antisolvent crystallization and cooling crystallization methods to achieve higher K and Cl concentrations in the product.

ACKNOWLEDGEMENTS

This study can be continued by using the cooling crystallization method, in order to achieve higher K and Cl content in the resulting product.

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