Synthesis of Metasilicate Gel from Rice Husk and Its Application as Medium of Growth Single Crystal Calcium Tartrate Tetrahydrate (CaC4H4O6.4H2O)

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Abstract. Has been done a research about synthesis metasilicate gel from rice husk and its application as medium of growth single crystal. This research was carried out in several stage namely sample preparation, metasilicate gel synthesis, crystal CaTT synthesis, and metasilicate gel characterization. Rice husk ash that used content SiO₂ of 98.45 %, it was potential to be a sodium silicate filtrate. Filtrate of sodium silicate was reacted with tartrat acid (C₄H₆O₆) and produce metasilicate gel with pH 5.00; 5.25; 5.50; 5.75 and 6.00. The supernatant of calcium chloride (CaCl₂) diffuse into the gel and formed the clear white crystal CaTT as much as 0.2659 g at the optimum pH 5.25. Analysis of functional groups of metasilicate gel by FTIR provides the specific absorption of –OH group at 3400.05 cm⁻¹ and 920.05 cm⁻¹, C=O group at 1622.13 cm⁻¹ and C-O group at 1346.31 cm⁻¹, and the Si-O-Si group at 1064.71 cm⁻¹. Characterization of gel metasilicate by XRD indicated that metasilicate gel produced formed on Na₂C₄H₄O₆.2H₂O, compound of SiO₂ and C-Grafit. Based on the analysis of functional groups by FTIR and characterization by XRD, it was concluded that the rice husk was potentially to be a sources of metasilicate gel as medium to grow single crystal of CaTT.

1. Introduction
Rice husk as a waste from the rice milling process has the potential to be exploited by the abundance of rice production in Indonesia, especially in South Sulawesi. The rice milling process produces rice husks of about 20-30% of the grain weight [1]. Rice husk as waste, allows it to be utilized since the chemical composition contained in it can still be processed further. Rice husk ash has a high silica content of around 94.4% [2]. High silica content in rice husk ash can be used as raw material for making the material of silica based, such as for making sodium silicate [3]. Sodium silicate has been synthesized from natural ingredients by various methods. One method that can be done to synthesize sodium silicate using alkaline dissolution, which is reacted with NaOH.

Several research [3] [4], have synthesized sodium silicate from rice husk ash which is the main ingredient in making metasilicate gel and can be used as a crystal growth medium. It shows that the silica content of rice husk ash can be used as an alternative material for making metasilicate gel.

Several methods of crystal synthesis, such as hydrothermal methods, steam diffusion, coprecipitation, microwave, sol gel, and metasilicate gel. Metasilicate gel is a relatively simple method in manufacturing and production, it has a relatively stable structure [5].
Synthesized single crystal calcium tartrate tetrahydrate (CaTT) using metasilicate gel as a crystal growth medium. The synthesis of single crystals in gels is influenced by gel acidity, supernatant concentration, temperature, growth time and growth techniques [6] [7]. The effect of pH is a factor that greatly affects crystal growth.

2. Experimental

2.1. Material
The material used for sample preparation are distilled water and hydrochloric acid 0.1 M. For synthesis of metasilicate gel from rice husk, sodium hydroxide solid, tartaric acid various concentration, and distilled water.

2.2. Sample Preparation
Rice husk was heated at 700 °C for 2 hours. Rice husk ash is crushed and sieved at 200 Mesh. A total of 25 g of rice husk ash was washed with 150 mL HCl 0.1 M and stirred for 1 hour, left to stand overnight. Then filtered and washed until neutral pH. The ash is dried at 110 °C for 2 hours, and weighed. The composition of rice husk ash was analyzed using XRF.

2.3. Synthesis of Metasilicate Gel From Rice Husk
A total of 6 g of rice husk ash added 200 mL NaOH 1 M while stirring, heated for 1 hour, then left for 18 hours, filtered and sodium silicate filtrate is obtained. 5 mL of sodium silicate filtrate are added, then 0.5 M tartaric acid solution was added and stirred until pH 5.00 was obtained. The test tube is covered with aluminum foil and stored for 4 x 24 hours until a gel was formed. Then metasilicate gel was made with a pH of 5.25; 5.50; 5.75; and 6.00.

2.4. Synthesis of Single Crystal Calcium Tartrate Tetrahydrate (CaTT)
Dripped 2.5 mL of supernatant solution CaCl2 0.45 M into the gel through the tube wall and closed again with aluminum foil, then let stand for 7 x 24 hours. The crystals formed, separated from the gel, then dried and weighed. The metasilicate gel was characterized using XRD.

3. Results and Discussions

3.1. Synthesis of Metasilicate Gel From Rice Husk
The results of analysis the composition of rice husk ash ash were dominated by SiO2 compounds of 98.45%, shown in table 1.

| Compound | Percentage (%) |
|----------|----------------|
| SiO2     | 98.45          |
| K2O      | 0.913          |
| CaO      | 0.218          |
| P2O5     | 0.186          |
| FeO3     | 0.099          |
| MnO      | 0.0921         |
| SrO      | 0.0103         |
| ZnO      | 0.0088         |
| Nb2O5    | 0.0067         |

Rice husk ash is reacted with NaOH to dissolve SiO2 and produce sodium silicate filtrate based on the reaction:

\[
\text{SiO}_2(s) + 2 \text{NaOH (aq)} \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}
\] (1)
Metasilicate gel consists of rice husk sodium silicate and tartrate acid as difference pH. The appearance of metasilicate gel shown in figure 1.

![Figure 1. Rice Husk Metasilicate Gel.](image)

Sodium silicate in water forms several monosilicate acids (H₄SiO₄) which form three-dimensional system polymers Si-O-Si and water chains based on reactions as shown in Figure 2.

![Figure 2. Hydrogen Bonding Between ≈Si-OH](image)

The structure of the gel is strongly influenced by the pH of the gel. At pH > 5.25, the gel becomes harder then at pH <5.25. At pH>5.25 less water is produced during the formation of silanol group, as shown in Equation (2).

\[ \text{Si}^3\text{O}^+ + \text{H}_3\text{O}^+ \rightarrow \text{Si-OH} + \text{H}_2\text{O} \quad (2) \]

Conversely, at pH < 5.25, the addition of tartrate acid excessively all protonated silanol (≈Si-OH) groups form siliconium ions and two water molecules formed as by-products such as the reaction in Equation (3).

\[ \text{Si-OH} + \text{H}_3\text{O}^+ \rightarrow \text{Si}^+ + 2\text{H}_2\text{O} \quad (3) \]

The number of water molecules formed will increase by the number of \([\text{H}^+]\) ions. The amount of water molecules in the gel can cause the gel cavity to be more tenuous by the presence of hydrogen bonds between water molecules and two molecules ≈Si-OH as shown in Figure 3.
3.2. Synthesis of Single Crystal CaTT by Metasilicate Gel Method

In the metasilicate gel, tartrate acid will react to form sodium tartrate based on the Equation (4):

$$2\text{NaOH} + \text{H}_2\text{C}_4\text{H}_4\text{O}_6 \rightarrow \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + 2\text{H}_2\text{O}$$ \hspace{1cm} (4)

CaTT crystals are synthesized by dripping the supernatant CaCl$_2$ solution and reacting with the tartrate in the gel based on the reaction in Equation (5).

$$\text{CaCl}_2 + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O} \rightarrow \text{CaC}_4\text{H}_4\text{O}_6.4\text{H}_2\text{O} + 2\text{NaCl}$$ \hspace{1cm} (5)

The optimum pH of CaTT crystal synthesis using metasilicate rice husk gel was obtained at pH 5.25 with a mass of 0.2649 g. The relationship between pH gel metasilicate rice husk and the mass of crystals produced is shown in Figure 4.

Crystal with the highest mass is 0.2649 g. At the pH of the gel <5.25 which is soft, the supernatant solution does not diffuse properly, while the pH of the gel >5.25 is relatively hard so that the supernatant solution is difficult to diffuse. Crystal synthesis of CaTT with supernatant CaCl$_2$ using metasilicate rice husk gel produced white crystals that were insoluble with distilled water with a size 1.5 mm x 7 mm as shown in Figure 5.

3.3. The XRD Analysis

The results of X-Ray Diffraction (XRD) analysis as a qualitative analysis to identify the content of the metasilicate gel compound of rice husk and pure metasilicate gel are shown in Figure 6, it was a similar
diffractogram. It has a peak with a small intensity indicating that both have a crystalline phase. The crystalline phase contained in the metasilicate gel is a crystalline sodium tartrate dihydrate (Na₂C₄H₄O₆·2H₂O) at 2θ = 31.92° and 32.059°, which is formed tartrate acid (C₄H₆O₆) with the remaining NaOH synthesized sodium silicate (Na₂SiO₃).

Three-dimensional cavity structures by crosslinking silanol and siloxane groups were identified by diffractogram in the presence of SiO₂ compounds at 2θ = 25.517° and 25.61°. The metasilicate rice husk gel showed a peak at 2θ = 26.27° which is a C-graphite compound, while pure metasilicate gel showed a peak at 2θ = 43.98° C-diamond compound. This is due to the presence of other oxide compounds contained in rice husks which are used as samples, so that the carbon compounds identified in the metasilicate rice husk gel and pure metasilicate gel are not similar.

4. Conclusions
Based on the results obtained from the research conducted, it can be concluded that the optimum pH of metasilicate rice husk gel formation as a single crystal CaTT growth medium is pH 5.25, produce clear white CaTT crystals with a mass of 0.2649 g which is insoluble with distilled water. Based on XRD analysis the rice husk gel metasilicate is formed from Na₂C₄H₄O₆·2H₂O salt, SiO₂ and C-graphite compounds.

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