The effect of alcohol media in the synthesis of calcium carbonate nanoparticles by ultrasonic waves

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Abstract. The process of destroying kidney stones using ultrasonic waves at certain frequencies has long been known in the medical field. The process of granular destruction using ultrasonic waves is very possible to produce a very fine grain size due to the large number of micro bubbles from the cavitation effect on the ultrasonic probe. The purpose of this research is to determine the effect of alcohol media in the destruction of calcium carbonate granules by ultrasonic waves to obtain carbonate calcium with nano-sized particles. The alcohol used in this study was 2-butanol, Ethylene glycol and n-propanol. The raw material of calcium carbonate was calcium carbonate precipitates originating from the Bayat region, Klaten Regency, Central Java, which was processed first by the carbonation method into calcium carbonate precipitates. The best result of experiments on the destruction of precipitated calcium carbonate by ultrasonic waves was the use of ethylene glycol media with ultrasonic time of 10 minutes and 30% amplitude. The result of the particle size analysis (PSA) at the best condition obtained with the average size of the granules of calcium carbonate precipitate was 72 nm.

1. Introduction

The concept of nanotechnology is a technology that presents phenomena or material properties on a nanometer scale that have special properties. Because it has a very small particle size in the nano meter scale, the experts agree that so-called nanoscale materials are materials that have dimensions of 1 nm up to 100 nm in size [1]. One way to produce nano-size material from a suspension of a solution is to break down particles in suspension with the help of ultrasonic waves [2]. Generally ultrasonic waves used are greater than 20,000 Hz and up to 1 MHz units, depending on the material used [3].

Several studies have been developed to explain sonic radiation of 20 KHz can break chemical bonds. The essence of sonochemical events is the formation, growth and breakdown of microbubble produced during the process of radiation in liquids. The growth level of microbubble occurs by diffusion from evaporation of the solution in the microbubble volume. The last stage is the breakdown of microbubble, which occurs when the microbubble is in the maximum size [2].

Calcite and Aragonite are the two main constituents of CaCO₃, which are known to be easily formed in large quantities in nature [4]. Natural calcite is a mineral formed through the crystallization process in shallow sea areas. Calcites are included in the carbonate group with the same chemical composition,
carbonate (CaCO$_3$), but sometimes these minerals also compose rocks that have different compositions [5].

Limestone (CaCO$_3$) is one of the many industrial minerals that are needed and used both directly and indirectly. The direct use of limestone is in the cement, sugar, ceramic, and additive materials in the process of smelter and building materials, while indirect use still needs to be processed in advance which can be in the form of light calcium carbonate or quicklime (CaO). Light calcium carbonate and calcium lime are as much needed for Industries of the paint, toothpaste, paper bleaching, cosmetics, soil neutralization, building materials and others [6].

The Research center of metallurgy and materials (P2MM) has succeeded in making light calcium carbonate precipitate derived from limestone in various regions in Indonesia [7-8]. If this light calcium carbonate material can be made in nano size, this will increase the added value because it has superior properties. In this study, calcium carbonate precipitate nanoparticles were synthesized by Ultrasonic method using alcohol-based media such as propanol, butanol and ethylene glycol.

2. Method

2.1. Materials

The raw material used in this research is light calcium carbonate which comes from the processing of limestone originating from Bayat, Klaten, Central Java. The raw material for limestone from the Bayat area, Klaten Region, Central Java has superior quality and can be made of high quality calcium carbonate precipitate with little impurity [9]. As a medium for ultrasonic processes in this activity using materials 2-Propanol, 2-Butanol and Ethylene Glycol with analytical grade (Merck) were obtained from commercially available. The use of ultrasonic media 2-Propanol, 2-Butanol and Ethylene Glycol with analytical grade (Merck) was carried out on magnesium carbonate and was able to produce nano particle hydromagnesite with a size below 100 nm [10].

2.2. Experiment

Limestone is processed in the stages of calcination, slaking, carbonation and drying processes. The detail synthesis of light calcium carbonate nanoparticles was performed using the previous method [7-8]. The process of mixing between Light Calcium Carbonate that has been produced with various types of alcohols: 2-Propanol, 2-Butanol and Ethylene Glycol. In this study, the experimental variables were the type of solvents and amplitude of the ultrasonic process. The solvents used in this experiment were 2-Propanol, 2-Butanol and Ethylene Glycol, with the amplitude were 20%, 25%, 30%, 35% and 40%. The fixed variable used in this experiment was the temperature of ultrasonic process which was maintained at a maximum of 90°C, the media volume was 200 ml, the addition of 10 g material and the ultrasonic time was about 10 minutes. The result was then measured of sediment rate using the Stokes method, measurement of the particle size with PSA Nano and characterization of the surface morphology of particles using SEM.

3. Result and Discussion

3.1. Analysis of limestone as raw materials by X-Ray Fluorescence and X-Ray Diffraction

X-Ray Fluorescence (XRF) analysis results show that limestone from the Bayat region has a large amount of impurities such as magnesium, silicon and iron. Calcium contents in the limestone oxide are only 90%, then magnesium impurities are 6.54% and iron impurities are 0.71%. After a series of processes obtained light calcium carbonate with a high purity level of 99.16%, and impurities are only very small amounts of phosphorus and sulfur.
Table 1. XRF analysis on limestone from Bayat, Klaten Regency and after processing into light calcium carbonate precipitate and compared with Merck.

| Component | Before Process (% wt) | After Process (% wt) | Comparison with CaCO$_3$ from Merck (% wt) |
|-----------|-----------------------|----------------------|------------------------------------------|
| CaO       | 90.93                 | 99.16                | 99.40                                    |
| MgO       | 6.54                  | Nd                   | Nd                                       |
| SiO$_2$   | 0.74                  | Nd                   | Nd                                       |
| Al$_2$O$_3$ | 0.47                | Nd                   | Nd                                       |
| P$_2$O$_5$ | 0.27                 | 0.14                 | Nd                                       |
| SO$_3$    | 0.05                  | 0.14                 | 0.16                                     |
| Fe$_2$O$_3$ | 0.71                 | Nd                   | Nd                                       |

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The X-Ray Diffraction analysis conducted at NanoTech Laboratory shows that limestone from the Bayat region shows peak of calcite and impurities were not detected. This can be seen in the XRD analysis image as shown in the figure 1.

![Figure 1. The X-Ray Diffraction analysis of the limestone as raw materials](image)

After a series of work processes on raw calcium carbonate are carried out, a light calcium carbonate precipitate product is obtained. The results of the XRD spectra at 2 theta shows that there are no significant shifts in the sample resulted from the experiments compared with the natural limestone, but there are differences in the intensity of CaCO$_3$. The results of the matching-lab analysis, it is seen that only the peak of CaCO$_3$ presented in the spectra while the peak of other calcium compounds such as
CaO, Ca(OH)$_2$, and Ca(HCO$_3$)$_2$ is undetectable. The reaction take place perfectly by forming CaCO$_3$ again, and the side reaction of bicarbonate formation does not occur. The below spectra showed that CaO has been formed with a percentage of 86.6% and the by-product is a portlandite which is an impurity in the form of CaO$_2$H$_2$.

![X-Ray Diffraction spectra](image)

**Figure 2.** The X-Ray Diffraction analysis of light calcium carbonate precipitate

### 3.2. Measurement of precipitation rate by Stokes Method

The stokes method is a method of measuring the precipitation speed of solids in a liquid medium. According to Stokes method, if the particle size is smaller, the deposition process is longer so that the the grain become smaller and the precipitation speed is also smaller. In liquid media, in addition to grain size, the deposition process is also influenced by solid density, media density and binding capacity between media molecules and solid molecules.

![Correlation between precipitation rate and amplitude](image)

**Figure 3.** The results of precipitation rate measurements on the amplitude of ultrasonic waves in alcoholic media
In general, the experimental results on the three-alcohols media shows a similar tendency, the higher of the amplitude, the precipitation rate become smaller so that the size of the particle become smaller. From the results of precipitation rate measurements, it is seen that the use of 30% ultrasonic waves shows the lowest deposition speed. But the tendency changes at amplitude 30%, where above 30% of amplitude the precipitation speed rises again. So it can be concluded that the use of 30% amplitudes is the best point that produces the smallest average size of particles.

3.3. Analysis of particle size by particle size analyzer (PSA)
In this study, the particle size of calcium carbonates before ultrasonic process and after ultrasonic process are measured by PSA in alcohol media, The results of the PSA measurement can be seen in the table below:

Table 2. Analysis result of particle size by PSA (Source: Laboratorium of Nanotech LIPI Serpong)

| No | Alcohol Media     | Particle size by PSA (Nanometer) | Size ratio |
|----|-------------------|---------------------------------|------------|
|    |                   | Before ultrasonic | After Ultrasonic |   |
| 1  | 2-Propanol        | 524                | 195          | 2,687       |
| 2  | 2-Butanol         | 234                | 133          | 1,759       |
| 3  | Ethylene glycol   | 207                | 72           | 2,875       |

The measurement of PSA shows that using ethylene glycol media gives the best results, where the average grain size is 72 nm, compared to 2-propanol which gives a grain size average of 195 nm. Based on the size ratio between before being subjected to ultrasonic and after being subjected to ultrasonic, it is also seen that the use of ethylene glycol as the media is the most effective. In terms of solution density, the highest density is ethylene glycol 1.11 g/cm² while butanol 0.806 g/cm³ and 2-propanol 0.786 g/cm³. Seeing the density of each solvent, it shows that ethylene glycol should have been the longest. By looking at the density of each solvent, it shows that indeed using ethylene glycol will result in the longest deposition due to the highest density, thus giving the smallest particle size.

3.4. Analysis of surface morphology and particle crystal by scanning electron microscopy (SEM)
The result of SEM analysis for calcium carbonate precipitate without ultrasonic process can be seen in figure 4.

Figure 4. Measurement of SEM analysis of calcium carbonate precipitate in alcohol media without ultrasonic process
It can be seen that the granules appeared to be large enough indicating that the granules undergo a coagulation process in drying process. This is because the granules cluster together to form a fairly large lump and not in a single grain with a compact shape. The results of SEM analysis of calcium carbonate precipitate show a grain size range of 100 nm to 300 nm.

The results of SEM analysis for samples in alcohol media subjected to ultrasonic waves within 10 minutes can be seen in figure 5. It shows that there is a tendency for reduction of particle size of calcium carbonate precipitate, although the coagulation process still occurs. the drying process carried out at 150°C, which is above the boiling point of alcohol, was still unable to break down the coagulant. If the temperature is raised above 600°C, it will be able to break the coagulant because all organic compounds undergo the pyrolysis process. But if the drying process is raised above 600°C, the calcination process will occur so that calcium carbonate changes to calcium oxide which is alkaline and hygroscopic. In SEM observations, it can be seen that the particle size of calcium carbonate precipitate in ethylene glycol media shows the best decrease after being subjected to ultrasonic waves.

4. Conclusion
The ultrasonic process has succeeded in reducing the size of calcium carbonate precipitates using alcohol media. From the results of precipitation rate measurements, it can be seen that there has been a decrease in precipitation speed with the best results on the use of 30% amplitude. Based on the analysis of the particle size analyser, it is seen that the reduction in particle size is best in the use of ethylene glycol media which produces particle size up to 72 nm and a particle reduction ratio of 2.875. The use of alcohol media has a disadvantage, among others, the emergence of the coagulation process in drying process of calcium carbonate precipitates. This coagulation process can be proven based on SEM analysis of the granules which is seen as large clumps with a crystal structure that is not in a single grain.

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