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Experimental investigations of preparation of calcite particles by ultrasonic treatment

Oner Yusuf Toraman

Omer Halisdemir University, Faculty of Engineering, Mining Engineering Department, 51240, Nigde, Turkey, Corresponding author: otoraman@nigde.edu.tr (O.Y. Toraman)

Abstract: This paper investigates breakage of calcite powder (d_{50} = 25.23 μm) to fine particle sizes using an ultrasonic generator (400 W, 24 kHz). The present study focuses on comminution of calcite powder in water media by ultrasonic treatment and the effect of some operational parameters such as treatment time (5–30 min), ultrasonic power (30-100% as amplitude), solid ratio (5-30% w/w), probe positions (0.5-2 cm) and cycle on the product size. Experimental results were evaluated on the basis of average particle size (d_{50}). Sonication of calcite produced a drastic particle-size reduction (d_{50}=12.89 μm) under optimal conditions.

Keywords: *calcite, fine particle, ultrasonic treatment, product size*

Introduction

Ultrasound induced cavitation is an extremely useful and effective tool to induce mechanical shear and to perform a variety of chemical reactions (Leong et al., 2011). The use of high-intensity ultrasound for particle breakage/comminution is a potentially useful method that has many advantages. Particle breakage by ultrasound is caused by erosion of particle surfaces because of the microjets emanating from asymmetric collapse of the transient cavitation bubbles (Suslick, 1987). The primary mechanism responsible for creation of these materials is known as acoustic cavitation, which is formation and collapse of bubbles influenced by ultrasound (Leighton, 1994). Cavitation generates turbulance, which enhances mass and heat transfer, both by improving convention mechanisms and by thinning diffusion-limiting boundary layers (Santos et al., 2011). Cavitation collapse produces intense local heating (~5000 K), high pressures (~1000 atm), and enormous heating and cooling rates (>109 K/sec) and liquid jet streams (~400 km/h) (Suslick, 1988). These effects cause solid surface erosion, leading to the eventual breakage of particles (Santos et al., 2011). The ultrasound versatility is owed in part to its broad active frequency region that can be

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tuned and applied specifically to control the intensity and number of cavitation events. These can be used to control aspects of materials such as the particle size, surface roughness and structure (Leong et al., 2017). Moreover, advantages of cavitation have been reported as follows (Senthilkumar, 1997): *i*) it is one of the cheapest and energy efficient methods of generating cavitation; *ii*) the equipment used for generation cavitation is simple, and *iii*) the scale-up of the system is relatively easy. In literature, ultrasound-assisted particle size reduction for precipitated calcium carbonate powder has been reported by Isopescu et al. (2007) and the effects of ultrasound treatment on the mean particle size, crystalline structure, crystallite dimensions and specific surface area of natural muscovite and biotite samples have been investigated by Perez-Maqueda et al. (2003). Moreover, the different research studies have been used to obtain fine particles by ultrasound treatment for kaolinites and barium titanate powder and to examine the effect on the structure, shape and particle size distribution and specific surface area (Franco et al., 2007; Markovic et al., 2008). Franco et al. (2004) showed that reduction in particle size can be controlled through different variables such as the ultrasonic processor power, amount of sample and time of treatment. Raman and Abbas (2008) investigated the effect of high-intensity ultrasound (150-350 W) on the breakage characteristics of Al_2O_3 particles suspended in water (Raman and Abbas, 2008). It has been generally recognized that high-intensity ultrasound is effective for size reduction of particles. Production of sub-micron talc particles by ultrasonic was reported and resulted in the attainment of a narrow size distribution (Perez-Maqueda et al., 2005). It was emphasized that the operational conditions such as the ultrasonic power, contact time and temperature played important roles in particle breakage. The sonication power influences the level of cavitation in the fluid. At higher levels, the number of cavitation events increases because of forming larger numbers of transient cavitation bubbles. Particles exposed to longer sonication time are expected to observe increased levels of breakage. Moreover, temperature is very important since it alters the viscosity, density and vapor pressure of the medium. None of above mentioned studies has examined the effect of probe tip position and cycle (pulse control mode) on the particle size using ultrasound.

The main purpose of this study was to examine the effect of some operational parameters such as the time of treatment, power as amplitude, solid ratio, probe tip position and cycle on the particle size of calcite powder using by ultrasound.

Experimental

Materials

The material in this experiment was a highly pure (99.6%) calcite ($CaCO_3$) from Nigde (Turkey). Its chemical composition is shown in Table 1. Table 2 shows the physical and general properties of calcite. The calcite slurry was prepared with distilled water for desired solid mass fraction. Figure 1 shows the volumetric particle size distribution of feed sample.

Table 1. Chemical composition of calcite used (wt.%)

$CaCO_3$	>99.6
$MgCO_3$	<0.20
Fe_2O_3	<0.01
SiO_2	<0.01
Al_2O_3	<0.02
HCl insoluble content	<0.01

Table 2. Selected physical and general properties of sample

Physical properties	
Density (kg/m^3)	2680
Hardness (Mohs)	3
Refractive index	1.59
General properties	
Moisture ex works (%)	0.2
pH value	9
Oil absorption (g/100 g)	15
Dop absorption (g/100 g)	16
Packing density (g/cm^3)	0.79
Whiteness value	98.5

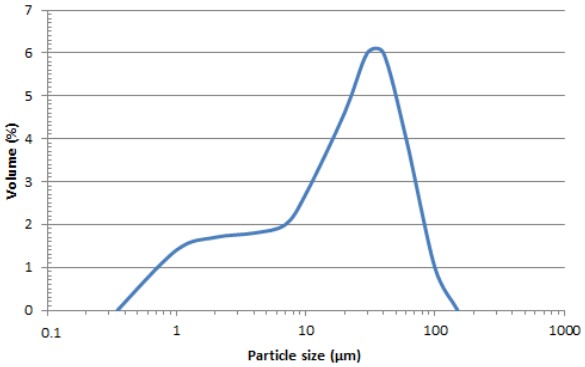

Fig. 1. Volumetric particle size distribution of feed sample

Experimental set-up and procedure

The ultrasonication experiment was performed with an ultrasonic processor (Ultrasonication Probe, UP 400S, Hielscher, Germany) of 400 W output with a 24 kHz converter and tapped titanium disruptor horn of 22 mm in diameter (Fig. 2). The horn tip was dipped into a glass beaker with a 250 cm^3, where 5–30 g of solids was mixed with 100 cm^3 of freshly deionized water. The prob tip was immersed up to 2 cm from the bottom. The suspension was mixed solely by the ultrasound horn during sonication experiments. Ultrasonic power was adjusted by means of the amplitude settings. Tables 3 and 4 show technical properties of ultrasonic processor and performance data

for sonotrode used, respectively. Experimental conditions for ultrasonic treatment are also given in Table 5.

Characterization

The well mixed feed sample was subjected to particle size distribution (PSD) measurements applying the Mastersizer Hydro 2000MU analyzer (Malvern Ltd.) which enabled evaluation of particles diameter in the range between 0.01 and 2000 μm. The standard percentile readings were calculated for volumes percentages of 10 (d_{10}), 20 (d_{20}), 50 (d_{50}) and 90% (d_{90}).

Fig. 2. Ultrasonic processor used

Table 3. Technical specifications of ultrasonic processor

Ultrasonic processor	UP400S
Efficiency	>90%
Working frequency	24 KHz
Output control	from 20 to 100%
Pulse-pulse mode factor	from 10 to 100% per second
Usable/nominal output	400 W (in aqueous media with sonotrode H22 300 W)

Table 4. Performance data for sonotrode used

	Max. submerged depth (mm)	Tip diameter (mm)	Max. amplitude (mm)	Acoustic power density (W/cm^2)
H22 - Horn 22	45	22	100	85

Table 5. Experimental conditions for ultrasonic treatment

Amplitude range (μm)	20–100
Probe position (cm)	0.5–2
Cycle	0.2–1.0
Sonication time (min)	5–20
Solid concentration (%)	5–30

Results and discussion

Figure 3 shows an example of variations in the particle size of ground product with different vibration amplitudes of 20, 40, 60, 80 and 100%. The mean particle size of the powder obtained after sonication for 80% amplitude level was approximately 18.58 μm. At lower ultrasonic power levels, the intensity of cavitation decreased due to decrease in the number of bubbles for cavitation. Based on our test results, it can be concluded that the particle size of obtained product decreased with the increase in the amplitude from 20 to 80% (Table 6). At higher amplitude, partially coarser particles were obtained as indicated by slightly larger d_{50} values than samples ultrasonicated at 80% amplitude. This clearly indicates that the optimum amplitude was 80% in terms of smaller product particle sizes.

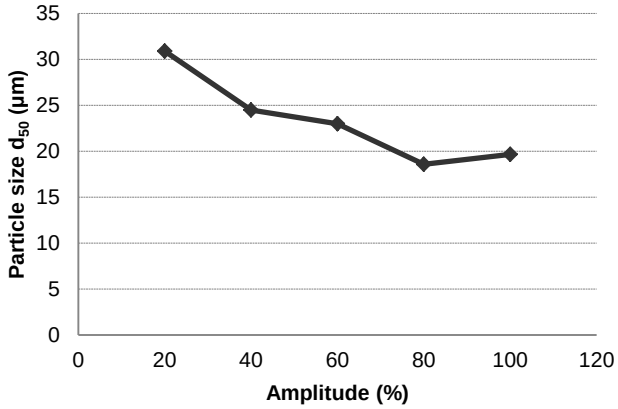

Fig. 3. Influence of different amplitude levels on the product size

As it is known, the acoustic wave, which radiated from the transducer, was perpendicular to the probe tip surface. The acoustic energy degraded in propagation because of acoustic diffraction, glass beaker wall surface reflection and absorption by fluid. If the probe tip was too close to the entrance, some of the acoustic wave would be reflected out of the glass beaker. The effect of the ultrasonic probe positions on the particle size is shown in Fig. 4a. When the distance of the tip of ultrasonic probe from the bottom was 1.5 cm, the value of breakage performance as average particle size (d_{50}=17.49 μm) were the highest, indicating that the largest effective irradiation area was obtained at this probe position.

Table 6. The treatment results in different operational parameters

Parameter		Particle size (μm)			Surface area (m^2/g)
		d_{10}	d_{50}	d_{90}	
Feed		1.87	25.23	87.61	1.10
Amplitude (%)	20	2.31	30.92	93.66	0.95
	40	1.57	24.52	90.34	1.22
	60	1.58	23.21	83.01	1.22
	80	1.33	18.58	79.34	1.41
	100	1.39	19.66	83.11	1.36
Probe position (cm)	0.5	1.31	18.44	79.47	1.43
	1.0	1.34	18.34	78.79	1.41
	1.5	1.34	17.49	75.73	1.43
	2	1.33	19.06	79.59	1.38
Cycle	0.2	1.46	22.93	86.27	1.28
	0.4	1.32	19.10	77.36	1.41
	0.6	1.18	15.52	70.43	1.59
	0.8	1.37	19.09	79.17	1.39
	1.0	1.79	27.90	90.91	1.10
Sonication time (min)	5	1.26	15.77	73.2	1.52
	10	1.14	13.08	51.15	1.69
	15	1.43	20.61	82.00	1.33
	20	1.62	25.18	87.5	1.19
Solid ratio (%)	5	1.24	16.84	79.03	1.51
	10	1.24	17.66	77.99	1.49
	15	1.08	12.89	59.59	1.75
	20	1.11	13.88	66.98	1.68
	30	1.23	18.09	79.01	1.49

Figure 4b shows the example of variations in the particle size of ground product with various cycle modes (0.2, 0.4, 0.6, 0.8 and 1). Table 7 shows the pulse control mode of the ultrasonic processor. The mean particle size of the powder obtained after sonication for 0.6 cycle setting was approximately 15.52 μm. It indicates that optimum cycle was 0.6 in terms of smaller product particle sizes. With the choice of a mode such as pulse mode, which alternated power pulses with periods of rest, the ratio was 60:40. This was called a 60% duty cycle, as each complete cycle was composed of power on for 60% of the time, then power off for 40% of the time. This ratio can be changed to alter the ratio of ultrasound energy to the rest interval. A higher duty cycle results in better breaking power but increased heat generation and more energy-related damage to the particles. Using the lower duty cycle allowed more fluidic aspiration of particles while minimizing heat and power.

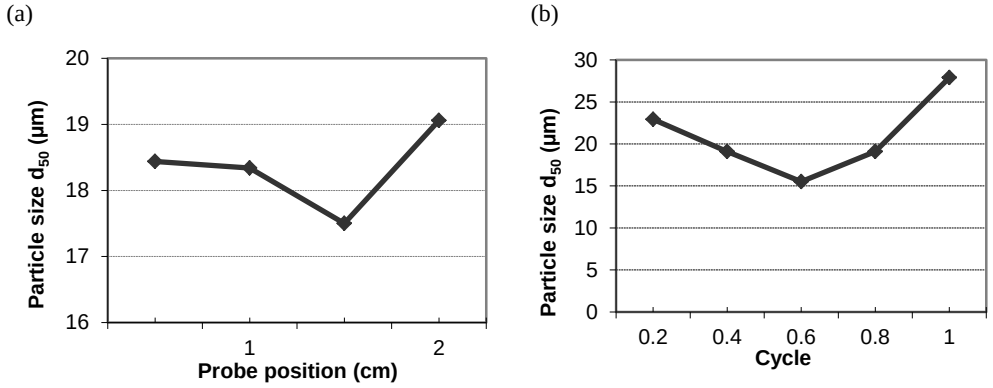

Fig. 4. Influence of (a**)** ultrasonic probe positions and (b) cycles on the product size

Table 7. Pulse control mode of the ultrasonic processor

Setting	Meaning
1	Continuously switched on
0.8	Power discharge 0.8 seconds, pause 0.2 seconds
0.6	Power discharge 0.6 seconds, pause 0.4 seconds
0.4	Power discharge 0.4 seconds, pause 0.6 seconds
0.2	Power discharge 0.2 seconds, pause 0.8 seconds

Figure 5a shows the example of variations in the particle size of ground product with various treatment times (5, 10, 15 and 20 min). The mean particle size of the powder obtained after sonication for 10 min was approximately 13.08 µm. Sonication times longer than 10 min did not produce any further decrease in the particle size of calcite. It was that because the increasing treatment time caused the increase in the slurry temperature. Therefore, in order to apply the longer time the temperature increase in the cooling system must be controlled. Figure 5b shows the example of variations in the particle size of ground product with various solid concentrations (5, 10, 15, 20 and 30%). The mean particle size of the powder obtained after sonication for 15% solid ratio was approximately 12.89 µm. It can be seen clearly from Fig. 5b that, as predicted, decreasing the amount of solid concentration led to higher size reduction. The average particle size (d_{50}) decreased from 18.09 to 12.89 µm with decreasing the solid ratio from 30 to 10%. This can be attributed to the fact that increasing number of calcite particles per unit volume prevented high speed jets of fluid to attack on the large number of calcite particles. The particle size distribution of the final powder obtained after sonication for 10 min at 15% solid ratio was broad (SF = 6.44), with the average particle size of 12.89 µm, while more than 90% of particles were less than 42.13 µm (Table 8). Figure 6 also shows the particle size distributions of feed sample and the best obtain product. Here, the best product means the test conditions where the finest product (d_{50}) is obtained.

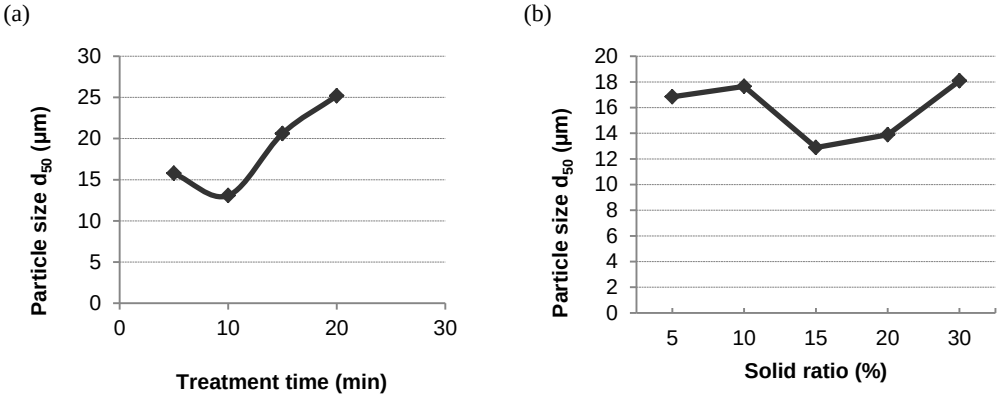

Fig. 5. Influence of (a) ultrasonic treatment time and (b) different solid ratios on the product size

Table 8. Comparison of feed sample and best product

		Feed sample	Best product *
d_{90}	µm	68.54	42.13
Mean particle size, d_{50}	µm	25.23	12.89
d_{20}	µm	6.00	2.50
d_{10}	µm	1.87	1.08
SF, d_{50}/d_{20}	-	2.53	6.44
Span, $(d_{90} - d_{10})/d_{50}$	-	2.62	3.17
Surface area	m^2/g	1.10	1.75

* Experimental conditions: ultrasonic time 10 min, cycle 0.6, amplitude 80% and slurry concentration 15% , SF > 2 "broad PSD" – SF <2 "narrower PSD". Decrease in the span means a narrower PSD

Additionally, increasing treatment time caused in the slurry temperature (Fig. 7). The maximum temperature was observed to be 64.3 °C for 20 min. Temperature alters the viscosity, density and vapor pressure of the medium, which means that it also has the significant effect on the particle size (Mason and Fogler, 2002). Increasing temperature resulted in reduction in acoustic cavitation threshold, meaning the liquids cavitated at lower intensities and reduced the viscosity of the liquid medium. The decrease in the viscosity decreased the magnitude of the natural cohesive forces, and thus decreased the magnitude of the cavitation threshold. Lower cavitation threshold translate into ease of cavity formation, thereby making higher temperatures more favorable for particle breakage. As temperature was higher than 50 °C in first 10 minutes, the increase in product particle sizes was observed. It is primarily caused by the cushioning effect of increased cavity internal vapor pressure at higher temperature (Mason and Lorimer, 2002). Because of this effect, the intensity of collapse and subsequently breakage decreased after 50 °C. The former increased with increase in temperature and had a positive effect, whereas the latter had a negative effect on the particle breakage. Thus, breakage was maximum at 50 °C.

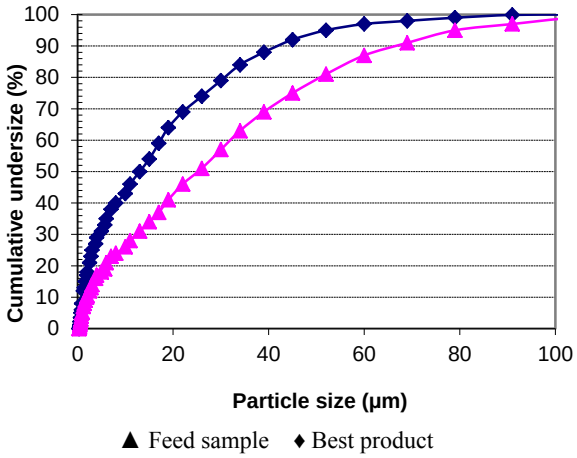

Fig. 6. Particle size distributions of feed sample and best product

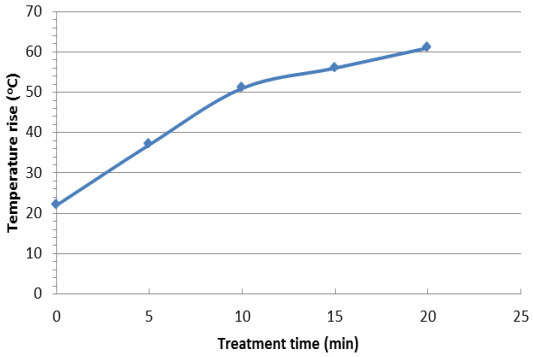

Fig. 7. Effect of treatment time on temperature (NaOH concentration 0.5 M; slurry concentration 40 g/dm^3; ultrasonic power level 85 W/cm^2)

Conclusions

The results obtained in this work showed that ultrasonic treatment was an effective method for reduction of particle size of calcite. The following conclusions can be drawn:

– The mean particle size and surface area of the powder obtained after sonication within 10 min at 15% solid concentration were 12.89 μm and 1.75 m^2/g, respectively.
– The cycle and probe tip position effected the breakage properties of calcite powder. In terms of smaller product particle sizes, the optimum cycle and probe position were 0.6 and 1.5 cm, respectively.

– The steepness ratio (SF) and span value of the final powder were 6.44 and 3.17, respectively.

The results obtained by ultrasonic treatment are promising, but they also show that further research on the longer treatment time with control of media temperature for sonication is required in order to find better solution.

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