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Ultrasound precipitation of manganese carbonate: The effect of power and frequency on particle properties

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ABSTRACT

The influence of ultrasonic frequency and intensity on particle shape, tap density and particle size distribution was investigated during the precipitation of manganese carbonate. For the first time, a broad frequency range of 94 till 1135 kHz was studied in one single reactor setup. Smaller and more spherical particles were observed during sonication compared to silent conditions. Lower frequencies and increased intensities result in smaller and more spherical particles. The most spherical particles with superior tap densities are obtained at the lowest frequency and most elevated intensity. Moreover, the results indicate that a particle size threshold exists, below which the particle size cannot be reduced by a further increase of the ultrasonic intensity or reduction of the frequency. Sonication of already formed spherical powders resulted in particles with smaller sizes but unaffected shapes. Finally, one test with pulsed ultrasonic irradiation resulted in equally sized particles with similar sphericity as the ones produced under continuous sonication.

1. Introduction

Precipitation reactions are widely used in industry to manufacture paints, pigments, fine chemicals, pharmaceuticals, polymers, etc. [1–5]. The application of ultrasound during these processes is well studied in literature and has shown effects on both the particle size distribution (PSD) and the particle shape [4,6–8].

A reduction in PSD of the formed particles by application of ultrasound is observed by several authors [6,8–11]. This reduction originates from the consecutive formation, growth and collapse of cavitation bubbles and subsequent shock waves, micro jets, increased micro turbulence and elevated local pressures. These effects are well known to both enhance the nucleation rate which results in a larger amount of fine particles, and breakage of the already formed particles into smaller particles by the large shockwaves and micro jets [9,12–15]. The term grinding will be used in this paper to describe this effect of size reduction.

Besides a size reduction, ultrasound can also induce a shaping effect, namely the formation of spherical particles under sonication [16–19]. Pohl et al., for example, studied the precipitation of $BaSO_4$ in a continuous sonochemical flow reactor [18]. The creation of spherical particles, compared to flat (flaky) particles under silent conditions, was observed by sonication at 20 kHz and 20–160 W. The reactor was a conical reaction chamber with a volume of 10 mL and a residence time between 4.5 and 15 s. The ultrasound precipitation of manganese carbonate from aqueous solutions of NH_4HCO_3 and $MnSO_4$ was investigated by Byrne et al. [19]. Also in this case, spherical particles were produced by ultrasonic irradiation at 20 kHz. The power of 400 W, supplied to the ultrasonic horn, was, however, significantly higher than the 20–160 W in the paper of Pohl et al.

Although the exact mechanism behind ultrasound shaping is still unknown, there are two commonly used theories reported in literature. The first one assigns the increased sphericity of the particles to the improvement in mass transfer rate between solution and surface [20]. Ultrasonic irradiation creates cavitation bubbles which collapse, resulting in microscopic turbulence and thinning of the hydrodynamic boundary layer around the particles. It is believed that these effects are responsible for an enhanced mass transfer in the mixture, therefore increasing the possibility of the solute molecules to combine with each other and approach each side of the growing particle more uniformly and easily [21]. The second theory explains the formation of spherical particles by the melting of particles upon implosion of the cavitation bubbles [10,22–24]. Collapsing cavitation bubbles create intense shock waves which cause high velocity collisions of solid particles. These

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collisions result in extreme heating at the point of impact and as a result the particles are melted together [24]. The creation of agglomerates with smooth surfaces was observed during the sonication of Sn, Zn, Cu, Ni, Fe, and Cr slurries [7,24].

While several studies are performed on ultrasound assisted precipitation, the impact of the frequency and intensity is rarely investigated and no conclusions can be drawn. Zhang et al. tested the effect of ultrasound at 20 and 33 kHz during the precipitation of $Al(OH)_3$ [6]. At both frequencies, an acceleration of secondary nucleation was observed with the largest effect at 33 kHz. The mean size of the particles was also smaller at the frequency of 33 kHz compared to the ones at 22 kHz. The weight percentage of fine particles with sizes less than 20 μm increased from 8.3% to 25.9% and 30.3% after 12 h of sonication at 20 and 33 kHz, respectively. In the same period, ultrasound had decreased the amount of 40–60 μm crystals with 10% and enlarged the amount of crystals larger than 100 μm by 8–10%. This effect was attributed to the collision and agglomeration of coarse particles by ultrasound. These results indicate that the frequency of 33 kHz is preferable compared to 20 kHz. It should, however, be noted that the power transferred from the ultrasound source to the liquid was not measured during these experiments. Therefore the possibility exists that the power transferred from the ultrasonic source to the liquid was not the same for both frequencies. In the same paper, the effect of the ultrasonic power on the precipitation ratio, the percentage of decomposition of the supersaturated sodium aluminate solution, was investigated. An increase of this precipitation ratio was observed with augmentation of the ultrasonic power up to 286 W, but with a further increase of the power to 308 W a decrease was found. This was explained by the decoupling of the sonotrode caused by the coalescence of cavitation bubbles which will form a gas layer between the liquid and the ultrasonic source. As a result, a phase lag between the motion of the liquid and that of the ultrasound source is induced and the ultrasonic source is not able to remain in contact with the liquid during the whole acoustic cycle. Consequently, there is a loss of power transferred from the source to the liquid [6,25,26].

Kaully et al. patented a method for the creation of spherical particles with smooth and rounded surfaces by ultrasonic treatment of a slurry [9]. The precipitation of cyclotrimehylenetrinitramine (RDX) was studied at frequencies of 25 and 40 kHz and intensities of 10 to 50 W/L. Both shaping (the creation of more spherical particles) and grinding (a reduction in particle size) were observed in varying ratios during these experiments. It was reported that shaping preferred frequencies above 40 kHz, while grinding was dominant at frequencies below 25 kHz. An explanation of these observations was, however, not provided and similar observations are, to the best of our knowledge, not reported elsewhere. In contrast, Li et al. observed no impact of sonication at 15, 20, 25 or 30 kHz on the shape, mean size and the size distribution during the salting out of spectinomycin hydrochloride particles [21]. The studied frequency range of 15 till 30 kHz was however considerably smaller and the applied ultrasonic intensities of 26,666 W/L significantly higher compared to the patent of Kaully et al. It was thought that the wavelengths are much larger at these frequencies than the size of the nuclei and consequently the effects of the sonication are similar at all frequencies. This is, however, also the case in the patent of Kaully et al. as in both cases water was used as the solvent, similar frequencies are used and the largest particles were about 150 μm. More recently, Lee et al. investigated the effect of ultrasonic frequencies of 20, 44, 139, 500 and 647 kHz on the antisolvent crystallization of sodium chloride [27]. Similar size distributions were observed among the different frequencies. Slightly larger and more cubic crystals were, however, visible during sonication at 500 and 647 kHz compared to the lower frequencies. The enlarged abrasion and attrition by intense shear effects at low ultrasonic frequencies were thought to cause this change in crystal shape.

The above mentioned papers made different observations about the effect of the frequency and intensity on particle properties such as the size or shape. Furthermore, different reactor geometries, products, ultrasonic powers and frequencies are used. Therefore, it's not possible to draw a general conclusion. The purpose of this paper is to investigate the impact of the ultrasonic frequency and intensity on the shaping and grinding during the precipitation of manganese carbonate. In contrast to previous articles, the frequency will be investigated over a broad range of 94 till 1135 kHz in one single reactor geometry and one single product. The power transferred from the ultrasonic source to the liquid will also be calibrated. Furthermore, the effect of the ultrasonic intensity on the particle size, shape and tap density will be investigated at the minimum and maximum frequency of 94 and 1135 kHz. Some additional tests will be performed to investigate the effect of the insonation time and test the possibility of shaping already formed particles.

2. Materials and methods

2.1. Experimental setup

All experiments were carried out in a glass unbaffled continuous stirred tank reactor (CSTR). Fig. 1 shows the reactor setup, which consists of a glass jacketed cylinder flanged between an ultrasound transducer at the bottom and a glass cover at the top. This cover contains 4 holes for the mixer, temperature probe and two reactor inlets. The reactor had an inner diameter of 55 mm and the outlet of the reactor was positioned at 80 mm above the bottom. The temperature was controlled by a Julabo MP thermostatic bath and a VWR EU 620-0917 digital thermometer, with an accuracy of ±1 °C, was inserted to check the operating temperature. The solution was mixed during all experiments by a Cole-Parmer EW-50006-01 agitator at a constant stirring speed of 800 rpm.

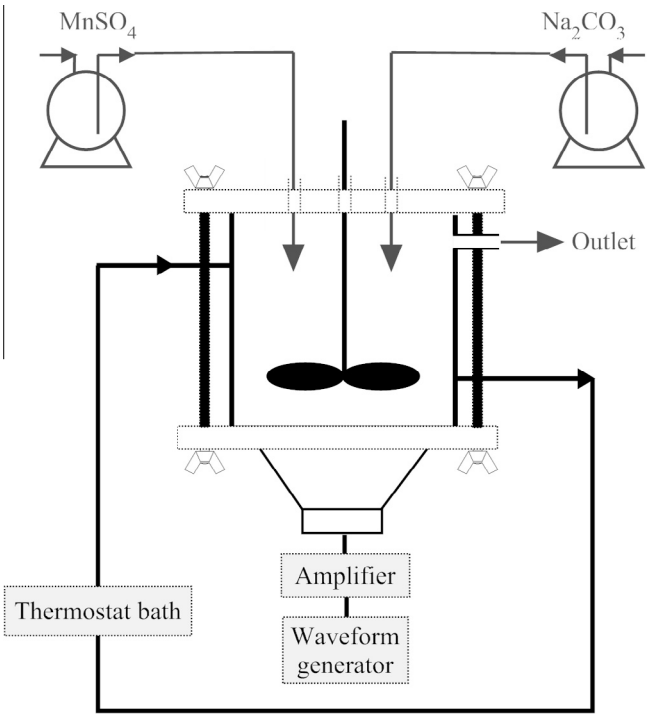

Fig. 1. Reactor setup.