Controlled droplet size distribution in ultrasonic spray pyrolysis

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This paper presents new findings concerning to the effects of the physical properties of precursor and its concentration, ultrasonic frequency, gas flow rate and surface active additives on droplet size in ultrasonic spray pyrolysis. The calculated and measured values of droplet size were compared. Measurements were conducted at same conditions for three different precursor systems which are commonly used for production of nanoparticles. Influence of physical properties and concentration of precursor solution, flow rate of carrier gas, addition of supplements to precursor solution and different operating frequencies were tested. Measured values are higher than theoretical ones, which is the consequence of coagulation under the real conditions.

Ultrasonic Spray Pyrolysis (USP) is a simple and rapid method for continuous synthesis of nanoparticles with adjustable, narrow size distribution, high crystallinity and good stoichiometry. Therefore ultrasonic spray pyrolysis can be widely used to produce fine-grained dense, porous or core-shell nanoparticles, which include metal oxides, sulfides, composites and especially metals, since it is possible to run process under reductive atmosphere [1-4]. High homogeneity of mixture for different precursors and short residence time in reactor lead to high purity and uniformity of the phase composition in new generated particles (especially multicomponent powders) [5]. Further advantages of the process are ideally spherical particle, continuous, low cost and simple handling process with high flexibility of process parameter control. A disadvantage of this process is small production rate of few grams per hour.

In general the essence of the method is to produce a fine aerosol medium from a precursor solution by atomization, using an ultrasonic generator. The mist-like aerosol, formed by numerous fine droplets, is transported by a carrier gas into an oven and undergoes thermal decomposition producing a fine dispersed powder. One of the advantages of this method is that each droplet/particle is subjected to the same reaction conditions (one-particle-per-droplet mechanisms). Since the whole method is based on these mechanisms, it is obvious that the characteristics of the droplet, especially droplet size and size distribution have the most important influence on the final particle size [5]. From this reason the most important initial point of understanding of this process is to investigate the role of the various factors related to the droplet formation from different precursors.

The principle of aerosol generation and transport and also part of ultrasonic aerosol generator is presented in Fig.1.

The average size of the final particles can be rated when knowing the size of the droplet diameter. Influence of physical properties of the atomized solution and frequency of the ultrasound on droplet size was studied by Lang et al. [6-7]. They developed a model leading to the relationship shown in equation 1.

$$D = 0{,}34\cdot\left(\frac{8\cdot\pi\cdot\gamma}{\rho\cdot f^2}\right)^{1/3} \quad (1)$$

(D: mean droplet diameter; γ: surface tension of the solution; ρ: density of the solution; f: frequency)

It becomes clear that with increasing ultrasonic frequencies the droplet size decreases. Theoretically, the final particle size can be predicted with the droplet size and the solution concentration. Assuming that the water evaporation and the reaction go to completion and the particles reach theoretical density, the final diameter D_p of a particle is directly proportional to the initial droplet diameter D:

$$D_p = D\cdot\left(\frac{c_{pr}\cdot M_p}{\rho_p\cdot M_{pr}}\right)^{1/3} \quad (2)$$

(c_{pr}: precursor concentration, M_p: powder molecular weight, ρ_p: powder density, M_{pr}: precursor molar mass)

A limited number of studies were conducted to compare calculated results with experimentally obtained results [4-6].

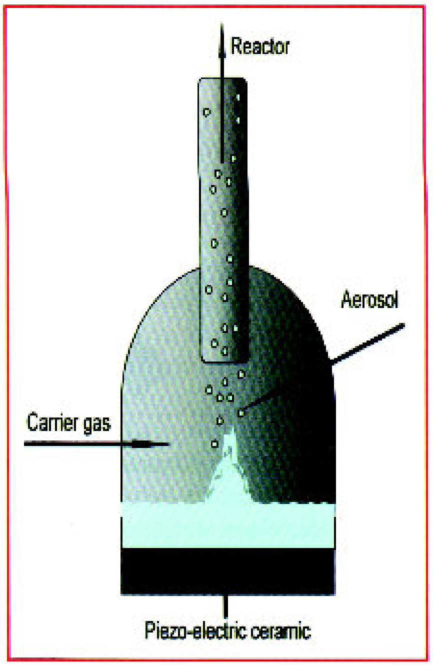

Fig. 1: Aerosol production by an ultrasonic generator

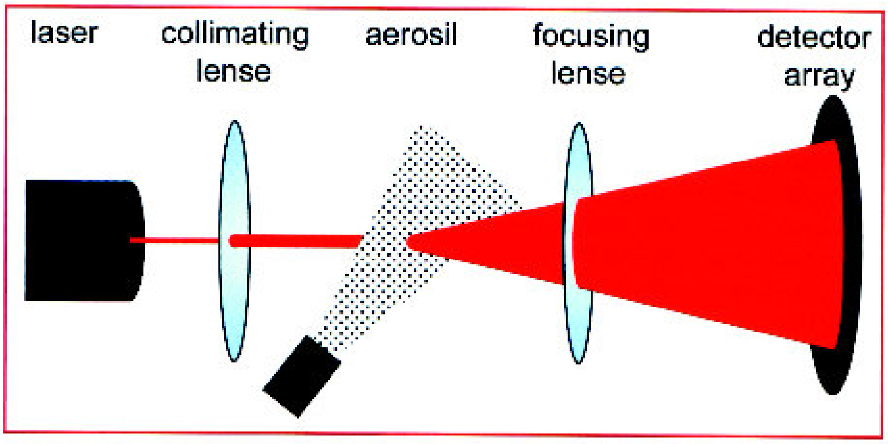

Fig. 2: Scheme of laser diffraction measurement setup used for measurement of aerosols

Although the above mentioned dependences for theoretical prediction of droplet size have shown satisfactory results, there was still deviation between experimental and calculated values of particle diameter. Reasons for this deviation can be various: formation of porous particles, coagulation, and coalescence. One of the biggest mistakes in calculation comes from using only a mean value for the droplet size. Until now there are no systematic measured results available for an aerosol droplet size distribution generated by ultrasonic devices for many solutions and for different process parameter (flow rate, different carrier gas, an initial solution concentration). Most producers were giving calculated mean values of droplet size in aerosols using a value for water solutions instead for the real solutions used in their processes. In a systematic approach it is necessary to conduct experiments without dilution of aerosol. It is important to determine which of theoretically predicted parameters has the biggest influence on final droplet size.

The main aim of the present study is to measure the droplet size distribution of aerosol produced by ultrasonic generator from real solution used for nanopowder production by USP method in order to determine the influence of properties of solution and process parameters on the formed droplets. With this knowledge, the droplet size might be controlled by designing the characteristics of the solution. Therefore the nanoparticle size might be better controlled and designed.

Experimental part

Procedure and materials

Droplet size distributions were measured without dilution of the aerosol and at same atomization and carrier gas parameters like in the synthesizing process parameters. A laser diffraction system (Malvern Spraytec) equipped with a 300 mm focusing lens was utilized for these investigations shown in figure 2. Size measurement by laser diffraction is based on the size dependent scattering angle of light at a droplet or particle and therefore the scattering signal from the aerosol is detected in order to determine the droplet size distribution.

Due to beam steering effects caused by evaporation of the precursor solutions the scattering data from the detectors 1 to 6 were not taken into account in the processing like proposed by Mescher [8]. Detectors 1 to 6 are nearest to the center of the beam and are responsible for the scattering signal of large droplets in the upper measurement range which ends in case of the 300 mm focusing lens at 900 µm. The respective refractive index of the solutions was measured with a refractometer (Carl-Zeiss) and considered during processing of the scattering data according to Mie [9]. Each aerosol was measured for at least 20 seconds with 1 Hz and the droplet size distributions were determined from the averaged scattering data.

Three series of experiments were conducted with different precursor solutions. Solutions, aimed nanoparticle type and structure are summarized in table 1.

All experiments were conducted using ultrasonic atomizers (GAPUSOL 9001, RBI, France), one with 0.8 MHz and another with 2.5 MHz operating frequency. Solutions were prepared in different concentrations; carrier gas flow rate of nitrogen was changed to test its influence. In some experiments surface active additives were added to precursor solutions to test influence of physical properties of solution (surface tension and density) on droplet size distribution.

Precursor	aimed nano-oxide	application	Nanoparticle structure
$Al(NO_3)_3 \cdot 9H_2O$	Al_2O_3	hardening	spherical, oxidic nanoparticle
$C_{16}H_{36}O_4Ti$, $RuCl_3$; HCl	RuO_2/TiO_2, Ru/TiO_2	catalyst	core-shell structure
H_3PO_4 $FeCl_2$ Li_2SO_4	LiFePO4	battery	complex nanoparticle

Table 1: Precursor solution, type of obtained nanoparticle and their structure

Physical properties of precursor solution

As already shown in Lang's equation (1) it is expected that physical properties of precursor solution have big influence on characteristics of formed aerosol, first of all droplet size and droplet size distribution. Surface tension, density and concentration are the one with the biggest influence. Summary of the most influenced physical properties of used solutions is given in table 2.

Low concentration precursor solutions were prepared since precursor concentration has big influence on particle size (lower concentration lead to smaller particles). In this case a balance between particle size and production rate has to be found (low concentrations lead also to lower production rate).

The surface tension of prepared solutions was determined based on measuring the maximum pressure which is essential to create and release a gas bubble from a capillary submerged in a solution. [11]

Since used solutions are low concentration solutions, density of solution is not much different from the water. But if we compare surface tension of solutions with surface tension of the water, we can see that even thou in small concentrations, influence of organic salt is big (for example by $C_{16}H_{36}O_4Ti$).

	Solution, concentration [mol/l]	Surface Tension [10^{-2} N/m]	Density [10^3 g/l]
$Al(NO_3)_3$*$9H_2O$,	0,025	6,51	1,0
$LiFePO_4$,	0,025	6,69	0,997
Molar ratio Ru/Ti	0,33	3,72	1,010
Water	-	7,29	1,0

Table 2: Physical properties of precursor solution

In further measurements it is going to be investigated how those physical properties influence aerosol characteristics. Influence of the temperature of precursor solution wasn't investigated, since most commercial ultrasonic generators are having limited temperature area in which one they can work under optimal conditions.

Results and discussion

Influence of ultrasonic frequency and concentration of solution

The influences of concentration and ultrasonic frequency on most frequent droplet size (mod diameter Dm) and droplet size distribution are presented in figures 3 to 5. From obtained results it is possible to conclude that ultrasonic frequency has a much bigger influence on droplet size and distribution than concentration when using the same precursor solutions. The impact of a concentration change on droplet size distribution at constant frequency is very small.

In all measurements the mean droplet diameter decreases with an increase of frequency as can be expected from Lang's theoretical model. Here is a small difference in most frequent droplet size for the individual solutions, which can be attributed to different physical properties like density, surface tension, viscosity). At same experimental conditions we can observe that the most frequent droplet size varies from 4,31 (2,33) µm for Ru/Ti based solution to 5,86 (3,70) µm for $Al(NO_3)_3$*$9H_2O$ at 0,8 (2,5) MHz frequency.

An increase of concentration does not influence the droplet sizes distributions significantly in all cases. This is the case for solutions with very low concentration (under 1 mol/l), but exactly those solutions are interesting for synthesis of nanoparticles. From this reason, solutions with higher concentration were not tested.

Influence of physical properties of solution on droplet size

The above mentioned Lang's theoretical model (equation 1), uses physical properties like surface tension and density of the solution, for prediction of droplet size. Physical properties of used solutions were measured and are presented in table. 2.

Like it was pointed out, the density values of real solutions do not differ significantly from pure water, which is explained by low salt concentration. Values of surface tension for the precursor solution are smaller than pure water, especially by using an organic salt as precursor.

The influence of droplet size distribution from all three test solutions is shown at Fig. 6. Based on Lang's equation and measured values of physical properties it is expected that surface tension has the biggest influence.

As it can be seen in Fig. 6, all droplet size distributions are similar, what can be explained by low concentration solution. Solution with organic salt und lower surface tension ($C_{16}H_{36}O_4Ti$, $RuCl_3$) shows small shifting in direction of lower droplets. This was also expected, since in Lang's equation predicts that lower surface tension leads to smaller droplets.

Influence of gas flow rate on droplet size

Besides influence of frequency and concentration of prepared solutions, the impact of an increasing carrier gas flow rate on droplet size distribution was

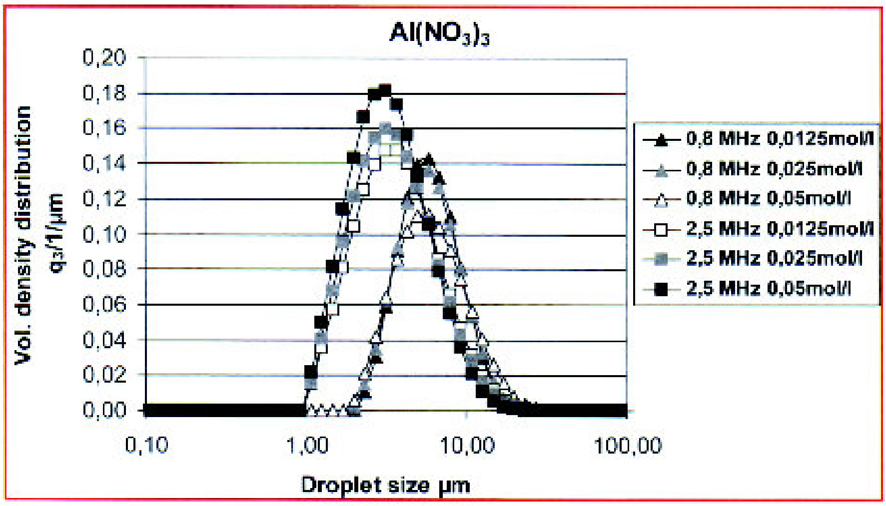

Fig. 3: Dependence of droplet size distribution from concentration of $Al(NO_3)_3$ precursor solution and ultrasonic frequency

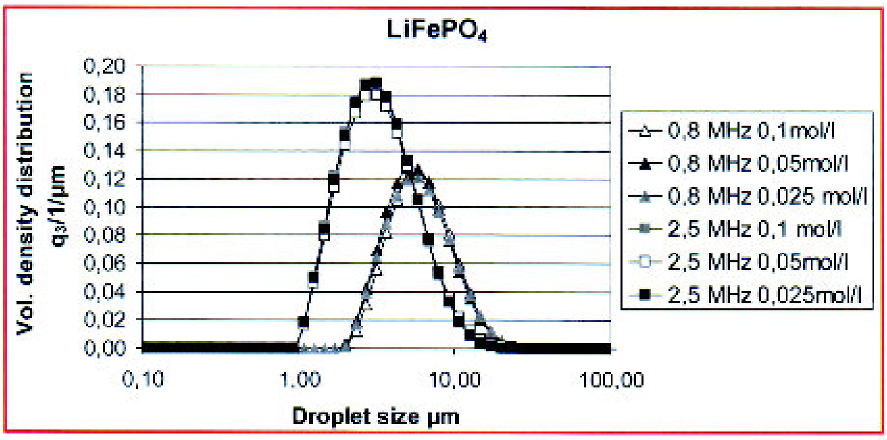

Fig. 4: Dependence of droplet size distribution from concentration of $LiFeP0_4$ precursor solution and ultrasonic frequency

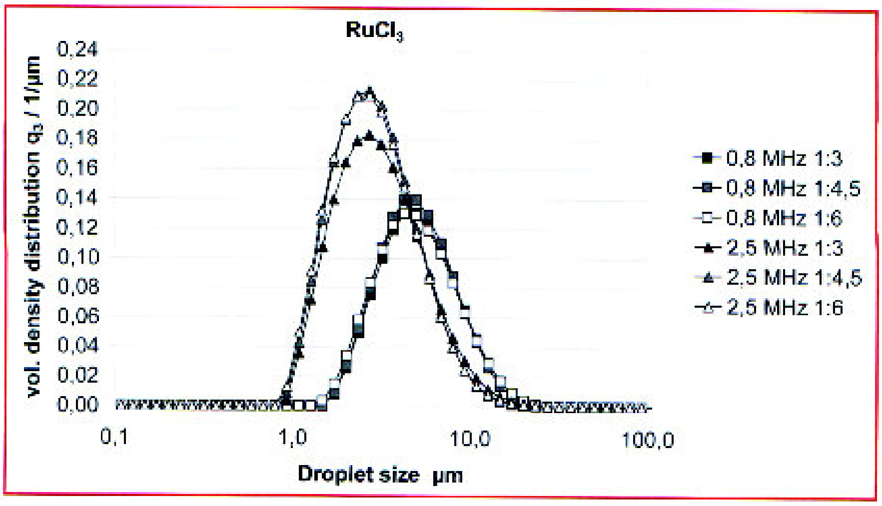

Fig. 5: Dependence of droplet size distribution from ratio of precursors in solution ($RuCl_3$:$C_{16}H_{36}O_4Ti$) and ultrasonic frequency

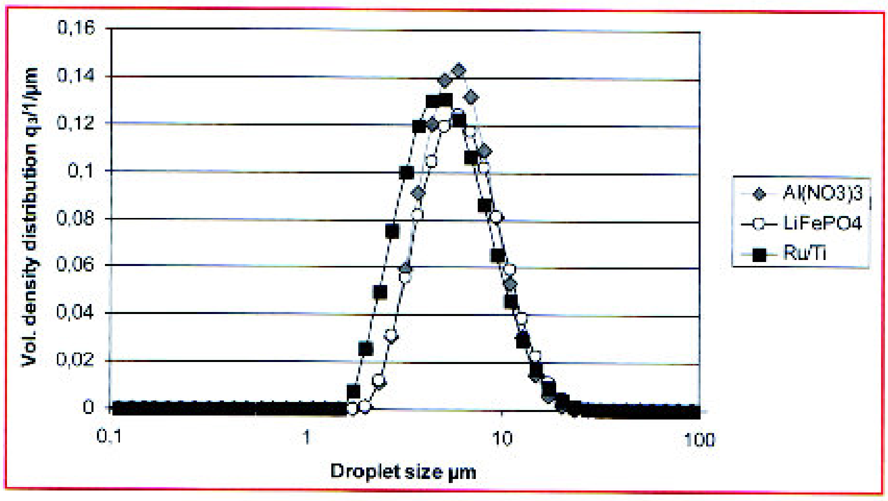

Figure 6: Droplet size distribution for precursor solutions with different physical properties

investigated. For this purpose, a series of experiments with $Al(NO_3)_3$*$9H_2O$ precursor solution was conducted, where all parameters were constant except carrier gas flow rate, which was changed in a range from 4 to 14 l/min. Obtained results are shown in figure 7.

From measured results presented in figure 7 it was concluded that carrier gas flow rate has no significant influence on droplet size distribution. It was expected that with an increase of carrier gas flow rate the level of coagulation increases resulting in larger droplets. From obtained results we can see that influence of higher carrier gas flow rate in this range is not as expected. Mean diameter for flow rate of 4 l/min is 3.17 µm and by increasing flow rate to 10 l/min, mean diameter decreases to 2.72 µm. For flow rate of 14 l/min droplet size distribution is almost identical like at 10 l/min. It seems that the number of larger droplets was increased by higher flow rate. This increase of number of larger droplets can be explained by higher coagulation rate. Increasing aerosol transport into the reactor is necessary with respect to a large intended amount of produced nanopowder. To obtain nanosized particles with defined morphological characteristics, coagulation of droplets has to be controlled. As mentioned previously by Tsai et al. [12], only 5 to 10 % of the particles obtained in spray pyrolysis of 6 - 9 µm precursor droplets were of the sizes predicted by one particle per droplet mechanism. The droplet sizes of used zirconium-hydroxyl-acetate were ranged from 6 and 50 µm for precursor concentration of 0.2, 1.0 and 5.0 wt %.

From obtained results it can be concluded that as long as transport of aerosol is in laminar flow regime. No significant influence of coagulation on droplet size can be registered.

Influence of surface active additives on droplet size

It was already discussed that surface tension and density are playing the most important roles in droplet formation in order to obtain desired droplet size distribution. Therefore this tendency was observed in investigation of an influence of precursor physical properties on droplet size. An influence of additives given to the $LiFePO_4$ precursor solution was investigated aiming droplet size distribution. The ethanol was added to reduce the surface tension. Obtained results are presented in figure 8.

Sugar was also added to the precursor, as it delivers the carbon for a coating, needed to provide sufficient electrical conductivity of $LiFePO_4$.

Again it was ascertained that no significant change in droplet size distribution occurs as a result of changes in the precursor chemistry. Only a small difference can

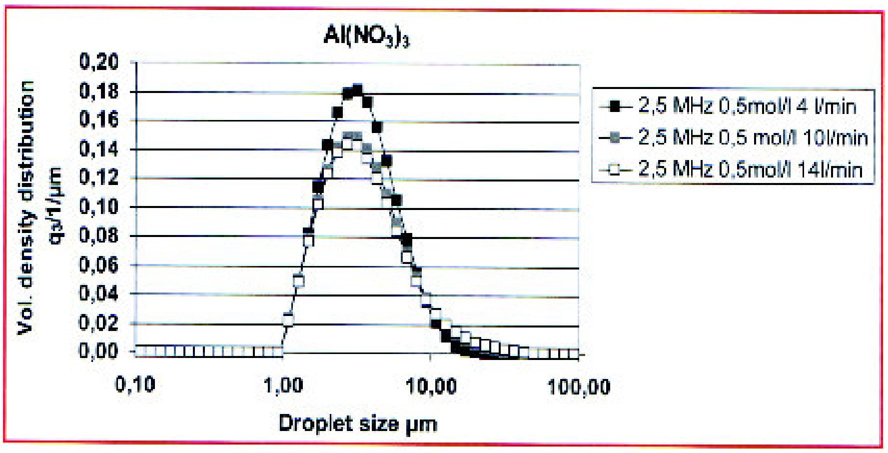

Fig. 7: Influence of carrier gas (N_2) flow rate on droplet size distribution in case of $Al(NO_3)_3$ ultrasonic spray formation

be seen between the addition of sugar and ethanol. The mean droplet diameters of solutions were 5.86 µm against 5.01 µm for ethanol and 5.92 µm for solutions without any additives. Physical properties of the used solutions are given in table 3.

By adding saccharine the surface tension of the solution was increased, which can be expected since saccharine is a molecule with several -OH functions. Saccharine leads to an increase in solution density and in sum to a minor decrease of droplet size. Addition of ethanol has a much stronger influence on surface tension but also decreases the solution density. During the experiment with precursor containing 10 % ethanol the surface tension was so low that there is no aerosol/droplet formation, as the surface tension supports the separation of droplets from the surface by ultrasonic wave.

Generally the droplet size in aerosol generated from precursor solution with additives is smaller than that generated from pure precursor solution, but less than calculated ones. But as mentioned before, all calculated values are smaller than measured, probably due to coagulation of droplets.

In further investigations it is required to test an influence of an addition for some surfactant supplement that has higher capability to decrease a surface tension of solution to significantly lower value.

Conclusions

Three series of experiments were conducted in order to measure droplet size distribution of aerosol produced by ultrasonic atomizer. These precursor solutions were prepared with different concentrations and transformed into aerosol with two ultrasonic atomizers (0.8 and 2.5 MHz). Influence of carrier gas flow rate and addition of additives that have influence on physical properties of precursor solution was investigated. Calculated and experimental results were compared leading to the following findings and conclusions:

1. Mean droplet diameter decreases with increasing an ultrasonic frequency proved by calculated and experimental means, what was expected
2. Obtained values of droplet size are in all cases higher than theoretically predicted most probably due to immediate coagulation that occurs in the aerosol production chamber.
3. The concentration of used solution has no influence on the droplet size in the investigated range from 0.1 to 0.0125 mol/l.
4. Physical properties (surface tension and density of precursor solutions) have a much smaller influence on droplet size distribution than an influence of an ultrasonic frequency.
5. An increase of the carrier gas flow rate decreases the mean droplet diameter, but at the same time the number of larger droplets increases. This factor shall be further tested.
6. Droplet size in aerosol generated from precursor solution with additives (saccharine or ethanol) is smaller than in aerosol, due to reduced surface tension.

Because of the precursor droplet size dictates product particle sizes and morphology the relationship between measured droplet sizes of different solutions and prepared nanoparticles by ultrasonic spray pyrolysis will be explained in detail in the future

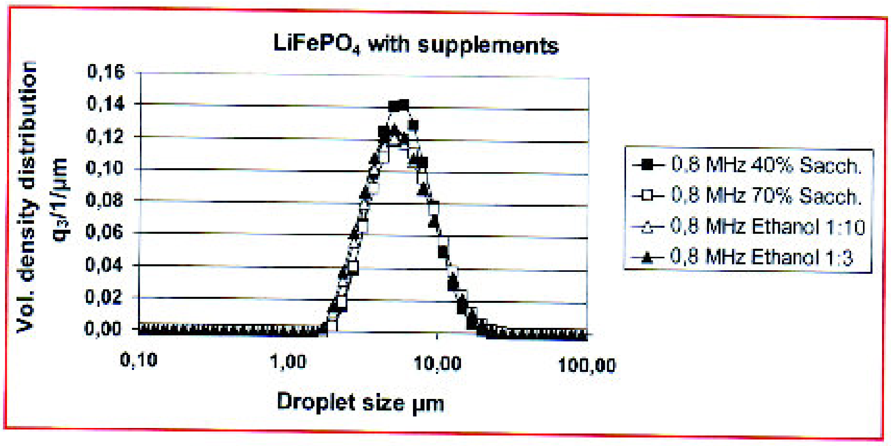

Fig. 8: Influence of surface active ethanol as well as sugar addition to the 0.05 mol/l Li-precursor solution on droplet size distribution

Precursor solution [mass percent % of additive]	Surface tension [10^{-3} N/m]	Density [g/l]
40 (Saccharine)	5,518	986
70 (Saccharine)	6,651	1009
33 (Ethanol)	1,850	918
10 (Ethanol)	1,496	884

Table 3: Physical properties of LiFePO$_4$ precursor solution with additives

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