# DROPLET SIZE DISTRIBUTION OF TECHNICAL MACROEMULSIONS: VARIATION OF PROCESS PARAMETERS

**M. Fricke**[1)], **A. Voigt**[2)] **and K. Sundmacher**[1, 2)]

[1)] Max Planck Institute for Dynamics of Complex Technical Systems,
Sandtorstr. 1, 39106 Magdeburg, Germany
[2)] Otto-von-Guericke University Magdeburg, Chair for Process Systems Engineering,
Universitätsplatz 2, 39106 Magdeburg, Germany

## ABSTRACT

The large scale production of particles with well-defined properties and a narrow property distribution is of great importance for a multitude of technical applications. The particle precipitation in water-in-oil microemulsions constitutes a suitable process for the synthesis of particles in the nanometer range. In such a process the nanosized water droplets of the microemulsion act as reaction vessel although with a quite limited reaction volume. In order to increase the effectiveness and the conversion rate of this process for industrial applications the amount of reaction volume, i.e. the water content, needs to be increased. That leads to a replacement of the microemulsion by a mini- or macroemulsion. As the size of the precipitated particles may significantly depend on the droplet size and droplet size distribution, this important control parameter of the process needs to be investigated in great detail. In contrast to microemulsions being thermodynamically stable, macroemulsions are only kinetically stable. The droplet size and size distribution in macroemulsion is mainly controlled by stirring, although more parameters such as the water/surfactant ratio, the hydrophilic-lipophilic balance (HLB) of the used surfactant as well as the salt content of the water phase will affect the droplet size and distribution. Experimental data for droplet size distributions of a water-n-decane macroemulsion containing different technical surfactants like Marlophen NP3 or Marlopen NP4 in a glass flask or a 2 liter tank stirred with a Rushton turbine will be presented for a number of process variations. An Optical Reflectance Measurement (ORM) technique, based on light back scattering, is used to obtain droplet size distributions. This technique provides fast inline measurements even at high concentrations of the dispersed phase. In addition, well stabilized macroemulsions are analyzed with dynamic light scattering (DLS) or by optical microscopy depending on the size of the droplets.

## 1 INTRODUCTION

The production of particulate products in emulsion-based precipitation processes is becoming a new and interesting topic in current research activities and industrial applications [1]. Especially in the area of new nanostructured materials and nanoparticles and its corresponding production technologies this approach has shown its effectiveness due to a number of important process features [2]. The main aspect of this new technology is the use of emulsion droplets as small reactor vessels. The precipitation of particles in such droplets is a step-wise process where exchange, chemical reaction, nucleation and growth are the main phenomena driving the production of solid particles in the system. The emulsion droplets may either constantly exchange the contained reactants via coalescence and redispersion or reactants may diffuse through the droplet surface and react later inside the droplets. These emulsion-based technologies are able to avoid certain limitations of standard wet-chemistry bulk–phase technologies like strong mixing effects and agglomeration of particles after precipitation. The usefulness of the approach has been shown already in a number of investigations, a microemulsion-based approach has been presented where nanoparticles with a tailor-made size are produced using a technical emulsion system of water, cyclohexane, and Marlipal O13/40 [3]. The microemulsion approach is still limited in its applications. For example, the recycling of the emulsion media is still not resolved and therefore under investigation. Also the amount of produced material is small due to the fact that the droplet phase in microemulsion is limited to just e few percent of the whole reactor volume. In order to produce nanoparticles at the technical scale in larger quantities the percentage of the droplet phase in the emulsion should be increased leading to a mini- or macroemulsion system. In contrast to the thermodynamically stable microemulsion, mini- and macroemulsion are kinetically stabilized by exposing the system to a constant energy input i.e. by stirring. This constant energy input together with other stabilizing factors like surfactants lead to a droplet size variation where quite a number of process conditions are playing an important role in the overall area and shape of the droplet size distribution. The properties of the produced nanomaterial inside the emulsion droplets will significantly depend not only the mean size of the droplets but on the size distribution as well. It is therefore an important and useful step to investigate for a given technical emulsion its droplet size variation with some important process parameters. This is the main aim of the presented paper.

## 2 EXPERIMENTAL SETUP

Technical emulsions consisting of distilled water, n-decane ($C_{10}H_{22}$ obtained from Merck with purity >94%) and different surfactants (Marlophen NP3 and Marlophen NP4 in technical grade from Sasol Gmbh, Marl) have been emulsified in a small laboratory flask using a magnetic stirrer or in a stirred tank reactor (DIN200 with heat jacket from Rettberg, equipped with 4 baffles) setup shown in Figure 1.

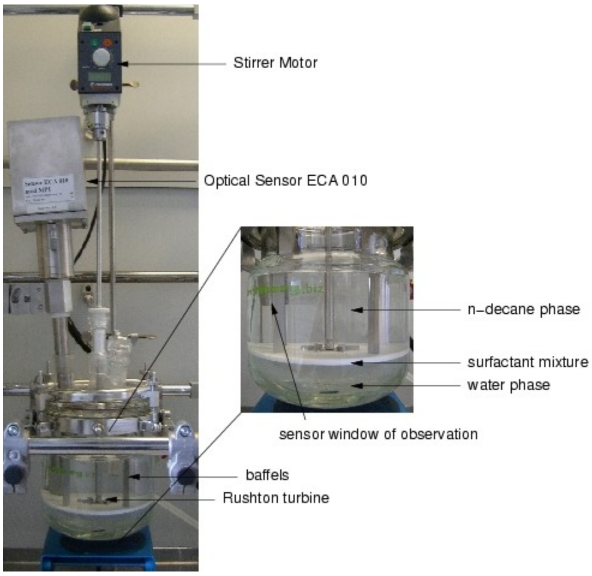

*Figure 1: Reactor set-up of a DIN200 Rettberg reactor with 4 baffles, a 6-blade Rushton turbine and the optical 2D-ORM sensor ECA 010.*

The experimental set-up includes an optical 2D-ORM sensor ECA 010 from MTS GmbH, Düsseldorf. This sensor uses an optical reflectance measurement technique (ORM) of an intensive laser light beam to obtain the arc chord lengths of emulsion droplets in close vicinity of an optical window at the end of the sensor tube (see Figure 1). Using a focused laser beam rotating with high-speed on a circular pattern over the emulsion, one is able to extract chord length distributions over thousands of droplets per second. This data can be transformed to a droplet size distribution and especially the dynamical change of a droplet size distribution can be measured with appropriate precision. This technique has been employed and evaluated by comparing to in-situ video recording by Lovick et al [4]. In this paper the author showed its validity by investigating unstable dispersion under different process conditions. The ORM technique is especially useful in high density emulsions as the droplet sizes are estimated by back reflection in close vicinity to the sensor window. Those systems are of particular interest in our investigations as an increase of the disperse phase will help to achieve the aforementioned goal of increasing the produced amount of particulate products.

## 3 EXPERIMENTAL RESULTS

Emulsions are commonly characterized by two mass fraction parameters, called $\alpha$ and $\gamma$. The oil mass fraction $\alpha = m_{oil}/(m_{oil} + m_{water})$ is important as it defines the working volume for possible reaction processes. The surfactant mass fraction $\gamma = m_{surfactant}/(m_{surfactant} + m_{oil} + m_{water})$ is important for the stability of the emulsions, but it also has a significant influence on the mean droplet size.

Our initial investigations were carried out in a laboratory flask with small volumes of about 130ml. Different emulsions were prepared stirring with a magnetic stirrer at high speeds (around 700 PRM) and small samples of emulsion liquid were put on glass plates and observed under a microscope (AxioCam from Zeiss). Especially the largest droplet sizes were measured (using the AxioVision software package) as these large droplets will have the maximum impact in a volume-based distribution function and therefore significantly influence a possible particle production process based on this droplet population. These estimates of $d_{max}$ can also be used to compare to the ORM data later on.

A first set of experiments was carried out with a fixed $\alpha$=0.82 and a variable surfactant amount with $\gamma$=0.005 up to $\gamma$=0.03 using Marlophen NP4 at room temperature (T=21°C). The maximum droplet size $d_{max}$ versus $\gamma$ are shown in Figure 2.

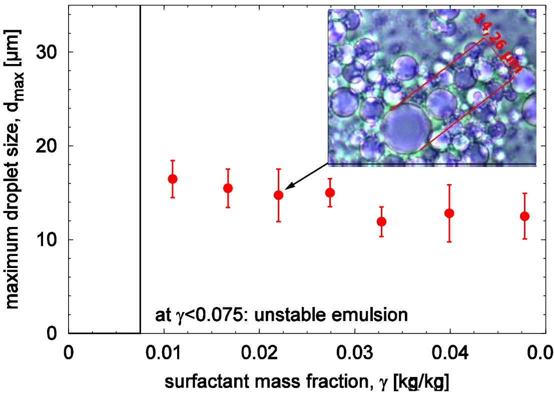

*Figure 2: Maximum droplet size* $d_{max}$ *from microscopic pictures (see inlet) as a function of the surfactant amount* $\gamma$ *(*$\alpha$*=0.82 and* T=21°C*).*

For the smallest surfactant amount $\gamma$=0.005 no stable emulsion could be obtained and no droplet sizes could be measured under the microscope. For larger $\gamma$ it could be seen that the increase in surfactant amount led to a slight decrease in the maximum droplet size. It is also observed that for this particular set of $\alpha$ and $\gamma$ the maximum droplet size is established at around 10 to 20 µm.

As it has been pointed out in the introduction the type of surfactant and especially its ability to stabilize the water-oil-interface will significantly influence the emulsion behavior and the droplet size distribution. In order to investigate this we also used Marlophen NP3 and compared the maximum droplet size data with corresponding results for Marlophen NP4. The HLB value (hydrophilic-lipophilic balance) is 9.75 for NP4 and slightly lower with 8.47 for Marlophen NP3. Lower HLB values will lead to an increase in the amount of surfactant solved in the oil part of the system. That means that the ability to stabilize the water-oil-interface will also decrease leading in turn to larger droplets in such a system. The data of our comparison is shown in Figure 3.

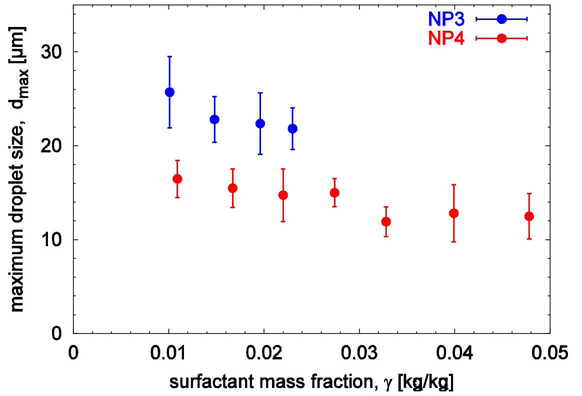

*Figure 3: Maximum droplet size* $d_{max}$ *from microscopic pictures as a function of the surfactant amount* γ *for two types of surfactant Marlophen NP3 and Marlophen NP4 (*α*=0.82 and* T=21°C*).*

The decrease of the HLB value for the system with Marlophen NP3 leads indeed to an increase in the maximum droplet sizes. We also observed that the emulsion system with Marlophen NP3 was less stable over time as a system with Marlophen NP4. This decrease in stability will significantly influence the coalescence between droplets which is now enhanced.

After these preliminary studies we investigated in more detail the droplet size distribution in the same systems now using the reactor setup and ORM technique shown in Figure 1. Especially the dynamical observation of the droplet size distribution is of great interest. Droplet breakup and coalescence, all driven just by stirring with different velocities, will impact the mean droplet size as well as the droplet size distribution in technical emulsions. The change of such process conditions in systems where particulate products are produced might be of great value when tailor-made properties of the particles should be obtained.

We started the investigations with a similar system as before. We set the initial conditions to α=0.7 and γ =0.005 using Marlophen NP3 for the first experiments. The reactor was filled with 1.050 g n-decane and 450 g of distilled water. The temperature was set at T=25°C using the heat jacket of the glass reactor. The volume-based droplet size distribution $\mathbf{q_3}$ as a function of droplet size **d** varying the stirring speed ω is shown in Figure 4.

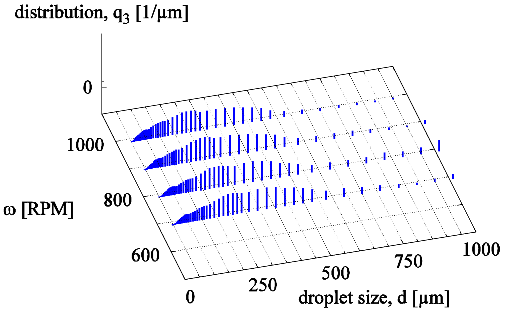

*Figure 4: Volume-based droplet size distributions* $\mathbf{q_3}$ *versus droplet size* **d** *for different stirring speeds* ω *for water, n-decane, Marlophen NP3 system (*α*=0.7,* γ =0.005 *and* T=25°C*).*

It can be seen from Figure 4 that at this particular set of α and γ no significant change in the droplet size distribution can be observed. We therefore increased the surfactant amount and investigated in more detail the dynamical change in the distribution at γ=0.015 of the same system. The data of this experiment is shown in Figure 5.

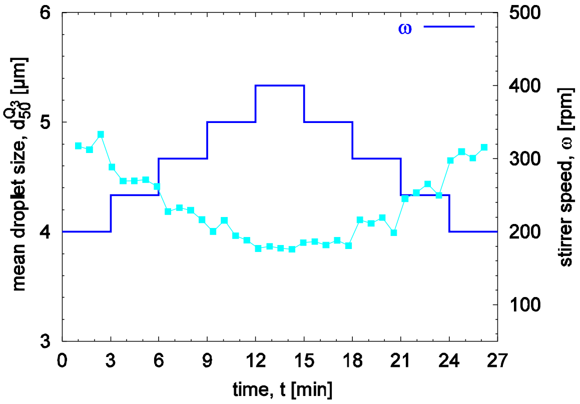

*Figure 5: Volume-based mean droplet size* $\mathbf{d_{50}}$ *versus stirring speed* ω *variation over time* **t** *for a water, n-decane, Marlophen NP3 system (*α*=0.7,* γ=0.015 *and* T=25°C*).*

During this experiment the stirrer speed has been changed every 3 minutes from 200 RPM up to 400 RPM in 50 RPM steps. The mean droplet size shows a corresponding dynamics where with increasing speed the mean droplet size decreases. The experimental data shows quite nicely that this change is reversible as by decreasing the speed the mean droplet size reaches the initial value from the beginning of the experiment. This shows some possibilities to use a change in kinetic energy input (through stirring) to dynamically change the droplet size distribution. This property of the system might therefore be used as an interesting control parameter for the particle precipitation processes which are based on such emulsions.

It is well known that emulsion properties will also change with temperature. Using the heat jacket of the reactor, we investigated the dynamical change in the droplet size and the droplet size distribution by varying the temperature. The data is shown in Figure 6.

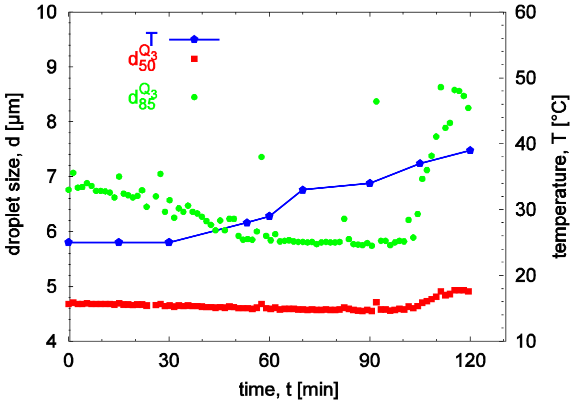

*Figure 6: Volume-based mean droplet size* $\mathbf{d}_{50}$ *and* $\mathbf{d}_{85}$ *versus changing temperature T over time* **t** *for a water, n-decane, Marlophen NP3 system (*$\alpha$*=0.7,* $\gamma$ =0.015 *and* $\omega$=400 RPM).

We started the system at a temperature T=25°C and gradually increased T up to 40°C. At the beginning the droplet size remained almost constant, only a slight decrease of the $\mathbf{d}_{85}$ could be observed. But when a temperature of 38°C was reached, the emulsion showed a significant change in mean droplet size $\mathbf{d}_{50}$ as well as in the $\mathbf{d}_{85}$ droplet size (obtained from the volume-based cumulative distribution). This behavior points to certain phase transition behavior of the emulsion [5]. For stability considerations and the process applications this might be something which should be avoided. A more detailed investigation of this effect will be carried out later.

## 4 CONCLUSIONS

The droplet size distribution of stirred water-in-oil emulsions can be influenced by a variety of process parameters like emulsion composition, surfactant type, stirring speed or temperature. By using different methods of observation, especially optical microscopy and an optical reflectance measurement technique (ORM) droplet sizes and droplet size distributions of a technical emulsion consisting of distilled water, n-decane and different surfactants like Marlophen NP3 and Marlophen NP4 have been measured and compared. Our study shows that the droplet size shows a significant variation with stirring speed. The surfactant type has also some influence on the droplet size, its influence on the size distribution is rather weak. Temperature change can significantly impact the droplet sizes when certain parameters are reached. It is know that some emulsions will show a phase transition behavior when certain temperature regions are crossed. This could be observed in our study also. The stability of the emulsion for precipitation of nanoparticles will certainly also depend on the reactants which are used in the precipitation process. This influence will be thoroughly investigated in subsequent investigations by our group to make the emulsion-based precipitation a useful tool to extend this research and to apply it to the large-scale production of particulate products.

## 5 Acknowledgements

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## REFERENCES:

[1] K.J. Klabunde: Nanoscale materials in chemistry. 2001, New York: John Wiley & Sons, Inc. 292.

[2] B. Niemann, F. Rauscher, D. Adityawarman, A. Voigt and K. Sundmacher: Microemulsion-assisted precipitation of particles: Experimental and model-based process analysis, Chem. Eng. Process. 45 (10), 2006, p. 917-935.

[3] D. Adityawarman, A. Voigt, P. Veit and K. Sundmacher: Precipitation of BaSO4 nanoparticles in a non-ionic microemulsion: Identification of suitable control parameters, Chem. Eng. Sci. 60 (12), 2005, p. 3373-3381.

[4] J. Lovick, A.A. Mouza, S.V. Paras, G.J. Lye and P. Angeli, Drop size distribution in highly concentrated liquid-liquid dispersions using light back scattering method, J.Chem.Technol. Biotechnol. 80, 545-552 (2005)

[5] M. Boutonnet, J. Kizling and P. Stenius: The preparation of monodisperse colloidal metal particles from microemulsions, Colloids Surf. 5 (3), 1982, p. 209-225.