CZASOPISMO TECHNICZNE M
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ

z. 5-M/2008
ISSN 0011-4561
ISSN 1897-6328

SEBASTIAN MAAß, STEFAN HORN, MATTHIAS KRAUME*

MEASUREMENT TECHNIQUES FOR DROP SIZE DISTRIBUTIONS IN STIRRED AND FAST COALESCING LIQUID–LIQUID SYSTEMS

TECHNIKI POMIAROWE ROZKŁADU WIELKOŚCI KROPEL W MIESZANYCH KOAGULUJĄCYCH SYSTEMACH CIECZ–CIECZ

Abstract

Complete models in stirred tanks for the drop size distribution as a function of power-input, material and process parameters are rare and relatively inaccurate. Furthermore industrial applications, like e.g. suspension polymerization processes, require a distinct average drop diameter and a small standard deviation of the distribution. An overview is given for already existing measurement technique: sound, laser and photo based techniques. The Lasentec FBRM® [22], which gives online, and in-situ information and an in house developed endoscope technique [21] will be discussed in detail. It is clearly shown, that the laser based method gives only qualitatively good but fast results for the tested system toluene/water. The quantitatively accurate experimental results of the endoscope technique gave a good base for testing and developing numerical models for even transient behavior of drop size distributions.

Keywords: drop size distribution, measurement technique, laser technique, endoscope technique

Streszczenie

Kompletne modele rozkładu wielkości kropel w mieszalnikach mechanicznych w funkcji zapotrzebowania mocy, składników i parametrów procesu występują rzadko i są stosunkowo niedokładne. Dodatkowo, zastosowania przemysłowe, np. zawiesinowe procesy polimeryzacji wymagają dokładnego określenia średniej wielkości kropli i niskiej wartości odchylenia standardowego w rozkładzie. Przedstawiono przegląd stosowanych technik pomiarowych: akustycznych, laserowych i fotograficznych. Porównano zastosowanie i możliwości pomiarowe układu FBRM Lasentec ® [22] z oryginalnym endoskopowym układem pomiarowym [21] dla układu toulen–woda. Widoczne jest, że technika laserowa daje szybkie wyniki, ale tylko jakościowe. Dokładne, ilościowe wyniki uzyskane techniką endoskopową stanowić mogą podstawę dla modeli numerycznych nawet w przejściowym zakresie rozkładu wielkości kropel.

Słowa kluczowe: rozkład wielkości kropel, technika pomiarowa, technika laserowa, technika endoskopowa

* Dipl.-Ing. Sebastian Maaß, Stefan Horn, Prof. Dr.-Ing. Matthias Kraume,
Institut für Prozess- und Verfahrenstechnik, Technische Universität Berlin.

1. Introduction

Liquid–liquid dispersions in stirred vessels or mixers are one of the most frequently used technical applications in chemical, pharmaceutical, mining, petroleum and food industry. For controlling and optimizing these systems exact knowledge about the drop size distribution and its transient behavior under changes of energy input, temperature or composition is of major importance. Current descriptions of dispersion properties like the drop size distribution (DSD) as a function of process and physical parameters in an inhomogeneous flow field typical for a stirred tank are still inaccurate. With accurate models it would be much easier and cheaper to design and set up such reactors. The DSD describes the interfacial area, the minimum factor for the mass transfer which is a key parameter for industrial systems and scale up. But scale up on the base of theoretical assumptions is not possible without trustful model validation. In conclusion sizing of particles in industrial processes is of great technical interest and therefore different physically based techniques have been developed.

2. Measurement techniques

Today many different techniques for sizing drops are available. Some work in-situ but a lot of them analyze a sample outside of the system [3, 7] and thus are not useable for technical applications with fast coalescing systems. A totally different drop size distribution will be measured for a sample taken out of the system. Even for unloading times less than one second, because of fast coalescence and drastic change in the flow condition during sampling.

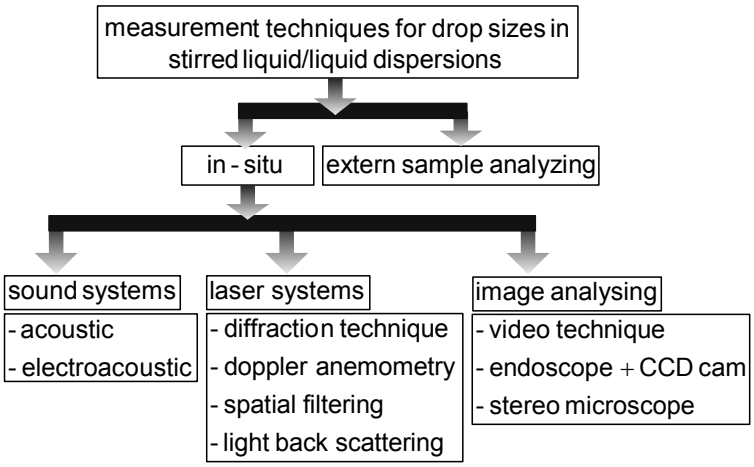

Fig. 1. Overview of measurement techniques able to analyze fast coalescing systems

Rys. 1. Przegląd technik pomiarowych do analizy układów z szybką koalescencją

In the following work we want to focus on inline measurement techniques. These can be divided into three main types (see Fig. 1):

1. Sound techniques working with ultrasonic.
2. Laser techniques.
3. Photo based methods working with digital images and image recognition.

An overview of these techniques is given in Fig. 1. It is known to the authors, that other techniques also exist [6, 8, 13], but ultrasound, laser and photo based techniques are the ones with major importance today.

2.1. Sound systems

Many attempts to determine particle sizes in industrial application by means of ultrasonic have been reported in the past. An overview and the theoretical background is given in [20]. This particle size analyzing method can be subdivided into acoustic and electro acoustic spectroscopy analysis. Dukhin & Goetz [9] describing both very detailed. Summarized you can say that acoustic spectroscopy deals only with the acoustic properties of the dispersion such as sound speed and attenuation while electro-acoustic spectroscopy is related to the coupling between the acoustic and electric properties of the system. This measurement technique is up to now limited on the concentration of the dispersed phase fraction φ around ten percent [20]. Other authors have reported even limits of only five percent [4]. While this is not a relevant concentration for most of the industrial applications this technique is still missing its spreading through out the chemical industry community. So the authors will focus in the next chapter on measurement techniques which are able to analyze high concentrated dispersions with up to 50 percent dispersed phase fraction. Nevertheless acoustic techniques should not be neglected especially for the measurement of very fine particles [12].

2.2. Laser systems

As shown in Fig. 1, the laser methods can be subdivided into four main groups, based on their specific operating principle. Generally all are very fast and so able to be used online but they give only qualitatively accurate results which need at least additional calibration to provide correct mean particle sizes.

The first introduced method is the application of Fraunhofer diffraction [24]. The beam of a low-power laser is expanded to 9 or 18 mm diameter. Drops passing through the beam scatter light, this is detected by concentric annular detectors placed at the focal point of a Fourier transform lens. So each detector picks up light scattered at a specific angle and independent of the position of the drops. Some problems occur by transforming the energy distribution into a DSD.

The measurement principle of Phase Doppler anemometry is presented detailed in [27]. Since this technique is limited to a dispersed phase fraction (φ) of less than one percent it was not further exposed.

The Inline Particle Size Probe IPP 30 [19] allows determining online the transient changes of drop size distributions. This technique is a method of determining the velocity and the size of the investigated particles simultaneously. It uses the spatial filtering velocimetry (SFV) and additionally the fibre-optical spot scanning (FSS). The basic operation of this technique is to observe the shadow of the particles moving through a small channel.

This influences the flow field and thereby the DSD. The IPP 30 is limited analyzing dispersed phase fractions smaller than 20 percent.

The last and most common method is „simply" analyzing the intensity of light back scattering. The first example is the 3D ORM technique (3 Dimensional Optical Reflectance Measurement techniques). This technique uses a rotating laser beam whose light is scattered back. A chord length is measured, each time it intercepts a particle. The cord length distribution is transformed into a drop size distribution [15]. Other examples for this method are described in [12, 18, 23, 24].

2.2.1. Fiber Optical FBR-Sensor

The physical principle of the FBR-Sensor (forward-backward-sensor) is based on the analysis of the spatial intensity pattern of light scattered into the forward and backward direction, which becomes significant for particles outside the Rayleigh regime. The ratio of light intensities scattered in both regimes can be used to invert the mean size of a particle ensemble. Dependent on the sensor configuration and the type of light source a size range from 50 nm to 200 μm can be detected [23]. The design of the fiber optical FBR-sensor is shown in Fig. 2 (left). Three optical fibers are positioned with an angular spacing of 60°. One fiber is used for illumination and the other two fibers are used to detect scattered light at angels of 60° and 120° with a receiving half angle of 10°. By this set-up a measuring volume of 1 ml is obtained. The scattering intensities can be superimposed and a mean particle size be derived from the intensity ratio from 60° and 120° by using Mie theory [5].

2.2.2. FBRM®

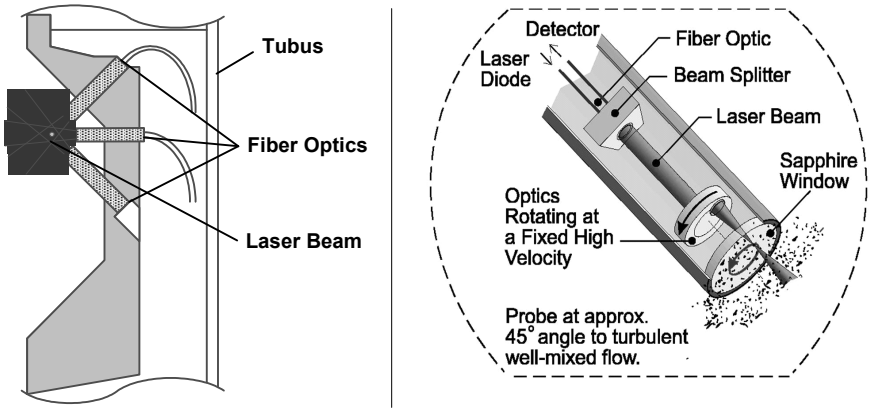

Fig. 2. Design of the fiber optical FBR-Sensor (left) and intrusive FBRM® probe [22] using light back scattering effects for drop sizing (right)

Rys. 2. Układ światłowodowego sensora FBR (z lewej) i sondy FBRM® [22] wykorzystującej odbite światło rozproszone do określenia wielkości cząstek (z prawej)

Another in-situ, laser based measurement technique which uses light back scattering effects is the Focused Beam Reflectance Method (FBRM) [14, 22]. The principle of the cylindrical FBRM probe, which can be easily installed in stirred tanks or pipes, is shown in Fig. 2 (right). The optic rotates at a high velocity and focuses the laser beam near to the

sapphire window. Passing particles backscatter the laser beam so that the chord length of the particle is computed by multiplying the scanning time with the beam speed. Usually, thousands of chord lengths are measured each second. This allows determining a robust chord length distribution, which can be used to illustrate changes in particle dimension, particle population and particle shape in time.

2.3. Photo methods

The second major type of measurement techniques sizing drops in-situ are photo based methods working with image recognition. This method gives accurate values for the drop sizes in the analyzed system. With exact knowledge about the drop size distribution, validation of simulation of stirred liquid/ liquid systems becomes possible [10]. Only this leads to predictive models for the mathematical description of drop size distributions which is necessary for optimal process design and control. As shown in Fig. 1, the photo methods can be subdivided into three groups.

Pacek et al. [17] uses a conventional 700 line high quality video camera and takes images through a stereo microscope from outside the vessel near the wall (8 mm at most) or inside the vessel through a light tube. Both methods are intrusive since lighting is provided from behind the focal plane by a strobe light guided through a thick fibre optic tube. The light was edited to be synchronous to the camera. 50 fps are taken, later on scanned and non-overlapping drops detected by recognition software. This requires human intervention for correction and to categorize drops pictured inside of larger drops. Diameters of 25μm up to a few millimeters can be recognized. The fast and continuous data acquirement and the flexible positioning of the light tube are of advantage. The intrusiveness of this tube and the fiber optic tube as well as the obsolete hardware is of disadvantage. Presumably the technique can be expanded to a digital video camera and improved image recognition.

The in-situ system used by Galindo et al. [11] takes 3D images with a color CCD camera through a stereo microscope from outside the vessel. The focal plane has to be near the wall and is illuminated from behind by a fiber optics guided strobe light which is synchronized with the frame grabber controlling the camera. 50 fps are obtained and the particles are automatically detected by image recognition software using the Hough transformation. The method is able to analyze 4 phase systems of gas and liquid semi automatically and only false positives have to be removed by hand [25]. Disadvantages are limitation to focal planes near the wall and its disturbances of the flow field by the fiber optic light guide.

2.3.1. PVM®

In cooperation with the BAYER AG it was possible for the work group to test the particle vision and measurement (PVM) probe (Lasentec®) [26]. The PVM probe (Lasentec, Model 700L) has a maximum wetted length of 300 mm and a diameter of 25 mm. Light from six independent laser sources is focused using a hexagonal array of lenses to provide a fixed region of illumination with an area of 2 mm². A micrometer adjustment of the probe optics allows the positioning of this area relative to the probe window. Particles passing through the illuminated region scatter the incident light diffusely in all directions. A lenses system within the probe collects light backscattered toward the probe window and relays it to a CCD array. A reflector plate, attached to the probe window improves image contrast, which can be further enhanced by a manual adjustment of the intensity of the individual

laser sources. The field of view of the processed digitized image is 860 μm by 645 μm [16].

The focusing effect of the six diodes is clearly identifiable (see Fig. 3). This effect creates a strong switch in the grey scale which becomes even clearer on the negative picture (see Fig. 3, right side). With this grey value structure full automatic image recognition becomes possible.

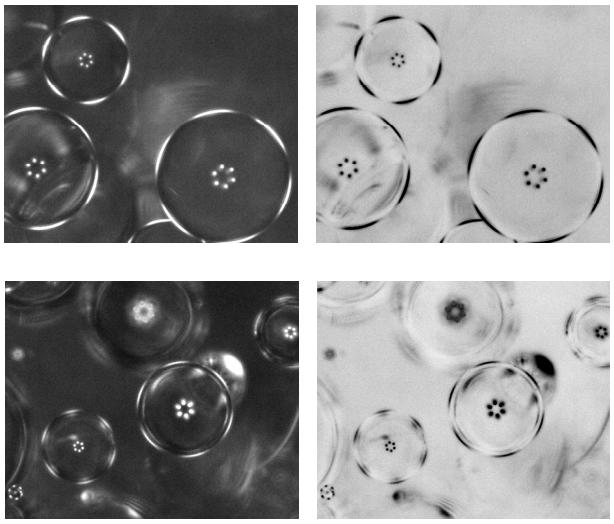

Fig. 3. Example pictures with negative picture for toluene–water φ = 10% [26]

Rys. 3. Przykładowy obraz negatywowy dla układu toulen–woda φ = 10% [26]

2.3.2 Endoscope technique

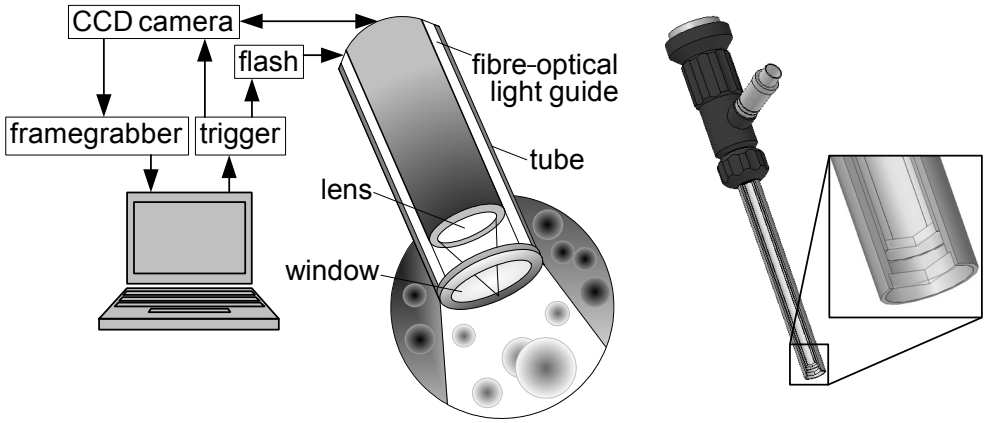

Fig. 4. Endoscope probe and set up (left) and detail 3D drawing (right)

Rys. 4. Sonda endoskopowa i stanowisko badawcze (z lewej) oraz szczegółowy rysunek sondy (z prawej)

With the endoscope technique images are taken intrusively from inside the vessel by placing a 7 mm thick endoscope in front of a CCD camera as a microscope lens [1]. To avoid disturbances by drops in front of the focal plane a covering tube with a window is placed at the tip of the endoscope lens. Nevertheless minimal influence on the flow pattern is made. A strobe flash is guided by a fibre optic cable surrounding the endoscope to ensure sharp pictures even in vicinity of the stirrer where speeds up to 1m/s are reached [21], see Fig. 4.

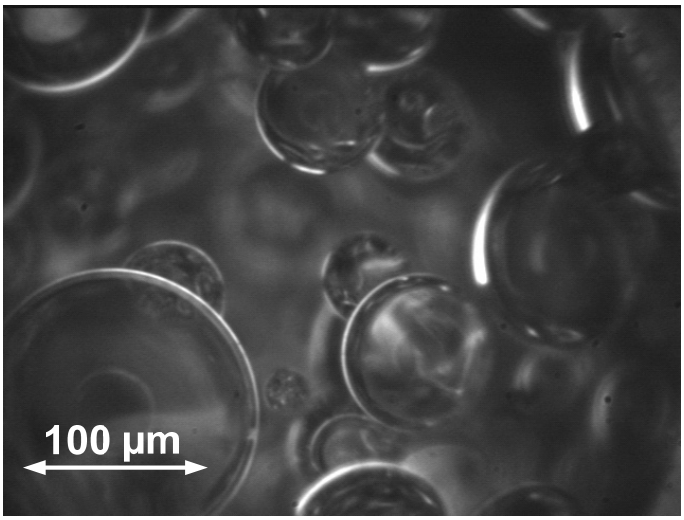

Fig. 5. Example photo of the system toluene and water, 10% dispersed phase fraction

Rys. 5. Przykładowa fotografia układu toulen–woda, 10% fazy rozproszonej

The drops are semi-automatically measured and counted. The counting has to be done manually at a pace around 400 drops an hour. The technique is capable of measuring drops of 25 µm to 1000 µm at any dispersed phase fraction. This technique offers reliable in-situ measurement of drop sizes from any part of the mixer vessel. Currently efforts are made to fully automate the drop count. Fig. 5 shows a typical photograph of the system toluene/water, toluene as dispersed and water as continuous phase with 10% dispersed phase fraction.

3. Experiments and results

While there are so many different possibilities for sizing drops in stirred liquid–liquid dispersions an evaluation for specific applications is necessary. The FBRM® and the endoscope technique seem to be the most promising techniques in their categories for analyzing drop size distributions and have therefore been chosen for a comparison. A third technique, the Fiber Optical FBR-Sensor was also available to the authors and used for the comparison experiments. They all have been tested for the system toluene/water at pH7,

varying stirrer speed and dispersed phase fraction. The same experimental set-up (T = 150 mm, Rushton turbine, D/T = 1/3, h/H = 1/3, H/T = 1) was used for all three in-situ probes. The respective one was introduced into the tank close to the stirrer at the same position to eliminate influence of the local position. Transient drop size distributions were measured for each parameter combination for about one hour for the endoscope technique and the FBRM®. The Sauter diameter ($d_{32} = \sum d_i^3 / \sum d_i^2$) is calculated out of the measured distribution. The values of the d_{32} can now compared with the results for a mean diameter from Fiber Optical FBR-Sensor.

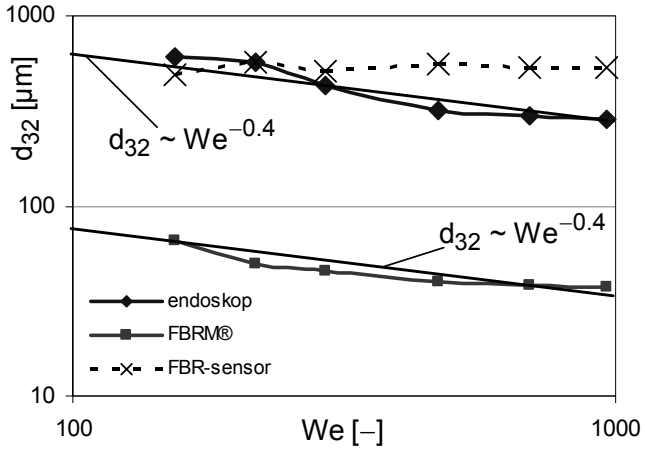

Fig. 6. Sauter diameter as function of Weber number for toluene/water, pH 7 and φ = 20%

Rys. 6. Średnica Sautera w funkcji liczby Webera dla układu toulen–woda, pH 7 i φ = 20%

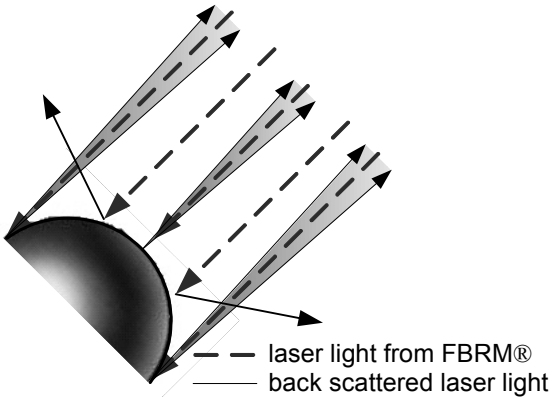

Fig. 7. Structural and functioning drawing of the back scattered laser light by exterior smooth surfaces, resulting in pure liquid–liquid systems like toluene–water

Rys. 7. Strukturalny i funkcjonalny obraz światła rozproszonego odbitego przez zewnętrzną powierzchnię, wyniki dla przezroczystych układów ciecz–ciecz, np. toulen–woda

The results of the direct comparison of the three measurement techniques in Fig. 6 show a clear deviation of the drop sizes from each other. With the endoscope it is possible to analyze single drop sizes, these data are trustful. The results of the FBR-sensor do not reflect the change of the Weber number. The values generated from the measuring signal stay nearly constant. Many different set-ups were used to adapt the FBR-sensor the used system of toluene and water but all tries were not successful. Only a suspension with a particle size smaller then 10 µm could be satisfactorily analyzed.

The drop sizes measured with the FBRM® are definitely too small. This results from the exterior smooth surface of droplets as opposed to solid particles. The reflection of the laser beam from such surfaces is not diffuse over the whole surface area but punctuated. Independent from the size of the droplets only three points of the surface reflect the laser light back to the probe (see Fig. 7). That was proven with single particle experiments.

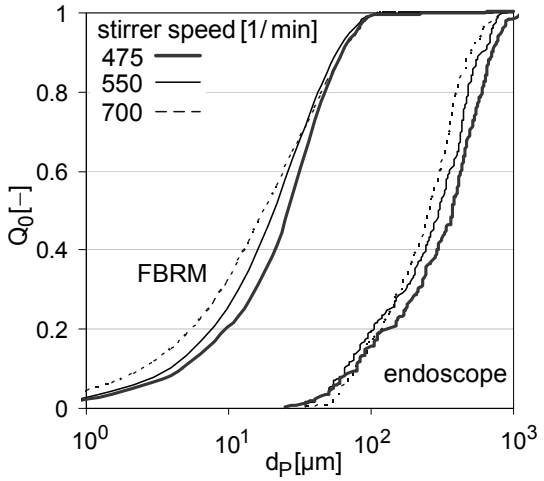

Fig. 8. Comparison of drop size distribution resulting from the two measurement techniques FBRM® (left curves) and endoscope (right curves). Toluene/water at pH 7 and φ = 20%

Rys. 8. Porównanie rozkładów wielkości kropel uzyskanych dwoma technikami pomiarowymi; FBRM® (krzywe z lewej) i endoskop (krzywe z prawej), układ toulen–woda, pH 7 i φ = 20%

One droplet scatters the laser light back to the probe as three separated beams. Therefore, the measured chord length is too small and the number of measured particles is too high. For the size of comparable ceramic spheres with a rougher surface, both measurement techniques achieve the same result for the particle size. Recapitulating, both measurement techniques give qualitatively representative values for the change of drop sizes. For the same dispersed phase fraction they even show nearly the same proportionally of the mean Sauter diameter over Weber number (represented by the black curves in Fig. 6). So it should be possible to use the FBRM® probe in liquid–liquid dispersions to analyze and control the change of DSD (see also Fig. 8). For detailed information about the accurate drop sizes of the analyzed system only the endoscope technique was useable. Further challenges are investigations with high dispersed phase fraction around 50%. Both measure-

ment techniques, endoscope and FBRM®, were able to reflect a change of DSD by varying φ from 10–60% for the presented system of toluene and water.

4. Conclusion and outlook

Summarizing the information from literature together with the experience of experimental work which was carried out, it has to be said that laser techniques, including the FBRM®, are able to show the change of the drop size distribution and the point of time, where the change starts, but they are not able to measure the exact size of the drops. They are interesting for the control of processes but not able to provide exact data for modeling and simulation validation. While photo based methods, including the endoscope technique, are currently the only measurement principles which are able to analyze high dispersed liquid–liquid systems quantitatively, it will be a long term goal to automate them. Therefore it is necessary to improve image algorithms to analyze the taken pictures automatically as the next step. This should be possible in the nearer future [2, 25].

Symbols

D	–	stirrer diameter	[m]
d_{32}	–	Sauter diameter	[m]
d_P	–	particle diameter	[m]
H	–	liquid level of the tank	[m]
h	–	distance between stirrer and tank bottom	[m]
Q_0	–	cumulative number distribution	
We	–	Weber number	
φ	–	dispersed phase fraction	

References

[1] Aakre H., Solbakken T., Schuller R.B.: *An in-line NIR/endoscope technique for observations in real hydrocarbon multiphase systems*, Flow Measurement and Instrumentation, **16**(5), 2005, 289-293.

[2] Alban F.B., Sajjadi S., Yianneskis M.: *Dynamic tracking of fast liquid-liquid dispersion processes with a real-time in-situ optical technique*, Chemical Engineering Research & Design, **82**(A8), 2004, 1054-1060.

[3] Bae J.H. Tavlarides L.L.: *Laser Capillary Spectrophotometry for Drop-Size Concentration Measurements*, Aiche Journal, **35**(7), 1989, 1073-1084.

[4] Cents A.H.G., Brilman D.W.F., Versteeg G.F., Wijnstra P.J., Regtien P.P.L.: *Measuring bubble, drop and particle sizes in multiphase systems with ultrasound* , Aiche Journal, **50**(11), 2004, 2750-2762.

[5] Chylek P., Kiehl J.T., Ko M.K.W.: *Narrow Resonance Structure in Mie Scattering Characteristics* , Applied Optics, **17**(19), 1978, 3019-3021.

[6] Denkova P.S., Tcholakova S., Denkov N.D., Danov K.D., Campbell B., Shawl C., Kim D.: *Evaluation of the precision of drop-size determination in oil/water emulsions by low-resolution NMR spectroscopy*, Langmuir, **20**(26), 2004, 11402-11413.

[7] Desnoyer C., Masbernat O., Gourdon C.: *Experimental study of drop size distributions at high phase ratio in liquid-liquid dispersions*, Chemical Engineering Science, **58**(7), 2003, 1353-1363.

[8] Dukhin A., Goetz P.: *Evolution of water-in-oil emulsion controlled by droplet-bulk ion exchange: acoustic, electroacoustic, conductivity and image analysis*, Colloids and Surfaces a-Physicochemical and Engineering Aspects, **253**(1-3), 2005, 51-64.

[9] Dukhin A.S. Goetz P.J.: *Acoustic and electroacoustic spectroscopy characterizing concentrated dispersions emulsions* , Advances in Colloid and Interface Science, **92**(1-3), 2001, 73-132.

[10] Gäbler A., Wegener M., Paschedag A.R., Kraume M.: *The effect of pH on experimental and simulation results of transient drop size distributions in stirred liquid-liquid dispersions*, Chemical Engineering Science, **61**(9), 2006, 3018-3024.

[11] Galindo E., Larralde-Corona C.P., Brito T., Cordova-Aguilar M.S., Taboada B., Vega-Alvarado L., Corkidi G.: *Development of advanced image analysis techniques for the in situ characterization of multiphase dispersions occurring in bioreactors* , Journal of Biotechnology, **116**(3), 2005, 261-270.

[12] Heffels C., Polke R., Radle M., Sachweh B., Schäfer M., Scholz N.: *Control of particulate processes by optical measurement techniques* , Particle & Particle Systems Characterization, **15**(5), 1998, 211-218.

[13] Hollingsworth K.G., Sederman A.J., Buckley C., Gladden L.F., Johns M.L.: *Fast emulsion droplet sizing using NMR self-diffusion measurements* , Journal of Colloid and Interface Science, **274**(1), 2004, 244-250.

[14] Hukkanen E.J. Braatz R.D.: *Measurement of particle size distribution in suspension polymerization using in situ laser backscattering*, Sensors and Actuators B-Chemical, **96**(1-2), 2003, 451-459.

[15] Lovick J., Mouza A.A., Paras S.V., Lye G.J., Angeli P.: *Drop size distribution in highly concentrated liquid-liquid dispersions using a light back scattering method* , Journal of Chemical Technology and Biotechnology, **80**(5), 2005, 545-552.

[16] O'Rourke A.M. MacLoughlin P.F.: *A comparison of measurement techniques used in the analysis of evolving liquid-liquid dispersions* , Chemical Engineering and Processing, **44**(8), 2005, 885-894.

[17] Pacek A.W. Nienow A.W.: *Measurement of Drop Size Distribution in Concentrated Liquid-Liquid Dispersions – Video and Capillary Techniques*, Chemical Engineering Research & Design, **73**(A5), 1995, 512-518.

[18] Pankewitz A., Behrens C.: *In-line Crystal size analysis with a highly adaptable and industrially approved sensor based ultrasonic Extinction*, 15th International Symposium on Industrial Crystallization, 15-18 September, Sorento 2002.

[19] Petrak D.: *Simultaneous measurement of particle size and particle velocity by the spatial filtering technique*, Particle & Particle Systems Characterization, **19**(6), 2002, 391-400.

[20] Riebel U., Löffler F.: *The Fundamentals of Particle-Size Analysis by Means of Ultrasonic Spectrometry*, Particle & Particle Systems Characterization, **6**(4), 1989, 135-143.

[21] Ritter J., Kraume M.: *On-line measurement technique for drop size distributions in liquid/liquid systems at high dispersed phase fractions*, Chemical Engineering & Technology, **23**(7), 2000, 579-582.

[22] Ruf A., Worlitschek J., Mazzotti M.: *Modeling and experimental analysis of PSD measurements through FBRM*, Particle & Particle Systems Characterization, **17**(4), 2000, 167-179.

[23] Sachweh B., Heffels C., Polke R., Rädle M.: *Light scattering sensor for in-line measurements of mean particle sizes in suspensions*, 7th European Symposium on Particle Characterization, PARTEC 1998, Nuremberg.

[24] Simmons M.J.H., Zaidi S.H., Azzopardi B.J.: *Comparison of laser-based drop-size measurement techniques and their application to dispersed liquid-liquid pipe flow*, Optical Engineering, **39**(2), 2000, 505-509.

[25] Taboada B., Vega-Alvarado L., Cordova-Aguilar M.S., Galindo E., Corkidi G.: *Semi-automatic image analysis methodology for the segmentation of bubbles and drops in complex dispersions occurring in bioreactors*, Experiments in Fluids, **41**(3), 2006, 383-392.

[26] Wegener M.: *Experimentelle Untersuchungen und Modellierung von transienten Tropfengrößenverteilungen in gerührten Flüssig-flüssig-Systemen*, Diplomarbeit TU-Berlin, Fachgebiet Verfahrenstechnik, 2004.

[27] Wille M., Langer G., Werner U.: *PDA measurement of drop size distribution for liquid-liquid dispersing in agitated tanks*, Chemical Engineering & Technology, **24**(5), 2001, 475-479.