

Relationship Between Droplet Size and Fluid Flow Characteristics in Miniemulsion Polymerization of Methyl Methacrylate

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ABSTRACT: Static mixer (SM) can be applied for emulsification, but the fundamental understanding of the nature of fluid flow and mixing in static mixers, is however poor. Droplet size is a very important parameter in miniemulsion systems and affects strongly the mechanism of particle formation in polymerization reactions. In this study, static mixer was used as homogenization device for emulsification of methyl methacrylate (MMA). Re number (Re) was obtained for SM inserted tube in different flow rates. It was demonstrated the nature of fluid flow was turbulent under our experimental conditions. The relationship between droplet size—the most important variable in our study—and Weber number (We) was investigated.

The results showed that the ratio of the droplet size to the pipe diameter was fit as an exponential function with an order of -0.35 . The polymerization of created droplets under certain We values by SM showed that it is possible to obtain a reasonable 1 : 1 copy of droplets to the particles. All these, indicate that using relationship between We and droplet size allow one to obtain acceptable condition of droplet nucleation in miniemulsion polymerization. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1591–1596, 2011

Key words: static mixer; emulsification; droplets size; Reynolds number; Weber number

INTRODUCTION

In miniemulsions, the monomer and aqueous solution should be mixed together and emulsified using a homogenization device to break up the monomer phase in to nanodroplets.¹ It seems that obtaining a stable miniemulsion with small enough droplet size is necessary to achieve miniemulsion polymerization in which predominant mechanism is droplet nucleation.² However, it is difficult to create a miniemulsion with preknown droplet size to ensure the capture of free radicals by nanodroplets. This is why, similar to emulsification of two immiscible fluid,^{3,4} droplet size is the most important variable in miniemulsions, and is useful to control both emulsification and polymerization processes. Thus, the estimation of this parameter can lead to a better control of the emulsification and polymer particle formation. The control of droplet size allows one also to benefit miniemulsion polymerization to incorporate hydrophobic particles into polymer particle via a 1 : 1 copy of droplet to particles.^{1,5–7}

Several homogenization devices have been used for emulsification of monomer including simple magnetic agitator, ultrasonifier, rotor-stator, etc.^{1,5,6,8} Recent studies have been shown some evidence on the beneficial features of static mixer in miniemulsification process.^{9–11} In our previous work,¹² the advantages of SM were highlighted that include high performance, continuous operation, energy saving, minimum space requirement, low maintenance costs, trouble free operation, easy measurements, and improve of product control. One can say that SM can be considered as an excellent candidate homogenization device for miniemulsion polymerization.

In emulsification process using SM, the parameters affecting droplet size can be classified into two groups: the first relates to materials properties^{13,14} which include generally the nature of materials of two phases and the concentration of surfactant. The second group of parameters affecting the droplet size in emulsification process can be called as operational parameters including: mixing time, flow rate of liquid in pump, length and diameter of the tube, dimensionless numbers (Reynolds, Weber, and capillary numbers), porosity of SM, and recycling number. Some of these parameters were investigated previously¹² and in this article, for the first time to the best of our knowledge, the relationship between nanoscale droplet

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size and fluid flow characteristics in emulsification has been investigated. Furthermore, the nanodroplets created by Polyacetal (PAC) SM were polymerized to ensure successfully conversion of each droplet to the polymer particle.

Theoretical aspects

Many research works were done to relate the drop size to dimensionless number in micro-scale emulsions obtained with different types of static mixer.^{4,15–21} The droplet size distribution of the Sauter emulsions is described using a typical average diameter. The average surface droplet diameter, d_{32} , is the more relevant in cases where the interfacial area is a control parameter for the chemical reactions, because it links the area of dispersed phase to the volume and hence to mass transfer and chemical reaction rates²²; this is why that, d_{32} has been used extensively in the characterization of liquid/liquid dispersions.^{23,24} The definition of the Sauter mean diameter is given in eq. (1).

$$d_{32} = (\sum_i n_i d_i^3) / (\sum_i n_i d_i^2) \quad (1)$$

where n_i and d_i are number and diameter of droplets, respectively. To relate this variable to dimensionless numbers, it is important to know the nature of fluid flow and droplet break-up mechanism.

Traditionally, in microscale emulsions the majority of the investigators have evaluated the mean drop diameter in an effort either to define the maximum drop diameter that can resist break-up or the collision and coalescence frequency of drops in a flow field. Some investigators have tried to combine both phenomena in models that are based on drop population balances.^{15,25,26} However, Berkman and Calabrese¹⁶ made exhaustive studies on the effect of dispersed phase viscosity on the drop size distributions in Kenics mixer and developed a correlation predicting the mean drop sizes against the physical and operating variables. The results of some studies²⁷ reported concerning to droplet size particularly d_{32}/D ratio (d_{32} and D are Suater mean diameter of emulsion droplets and diameter of tube, respectively) for SM is summarized in Table I.

It can be seen from Table I that the exponent of We number is usually between -0.75 and -0.33 , and that of Re number varies from -0.2 to 0.15 . In the other words, dependency of droplet size to We is much higher than its dependency to Re.

Despite to enormous work both on traditional emulsification of two immiscible fluid to obtain relatively large drops from one side and miniemulsion polymerization using traditional homogenization devices from other side, any effort has been done to relate droplet size in miniemulsions to dimension-

TABLE I
Relationship Between Droplet Size and Dimensionless Numbers in Emulsification with SM

Investigator	Correlation
Middleman ¹⁹	$d/D = C(We)^{-0.6} (Re)^{-0.1}$
Hass ²⁰	$d/D = 1.2(We)^{-0.65} (Re)^{-0.2} (\mu_d/\mu_c)^{0.5}$
Hinze ¹⁷	$d/D = 0.55(We)^{-0.6} f^{-0.4}$
Streiff et al. ²¹	$d/D = f_c(We)^{-0.6} (Re)^{-0.2}$
Berkman and Calabrese ¹⁶	$d/D = 0.49(We)^{-0.6}$
Chen and Libby ²⁸	$d/D = 1.14(We)^{-0.75} (\mu_d/\mu_c)^{0.18}$
Das et al. ²⁷	$d/D = C(We)^{-0.33}$
Tidhar et al. ^{18,29}	$d/D_h = C(We)^{-0.5} (Re)^{0.15}$

less number. In this study, the main aim is the study of the relationship between dimensionless numbers and droplet size, to verify whether or not the nanoscale emulsions (miniemulsions) systems follow the same behavior as microscale emulsions. This will allow us to estimate the size of droplets in nanoscale by a usual manner used for microscale emulsions.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, 99%), was supplied from ACROS. MMA was used as monomer because of it was shown previously¹² that it is possible to obtain easily stable miniemulsion of this monomer using SM as homogenizer. *n*-Hexadecane (HD, 99%), sodium dodecyl sulfate (SDS, 99%), and ammonium persulphate (APS) were all obtained from ACROS and used as received. Deionized water was used as the continuous phase.

Homogenization procedure

The commonly used method to prepare miniemulsion is dissolving the surfactant in deionized water and the hydrophobic agent in monomer. These mixtures are separately stirred, and then organic phase is added to aqueous phase while stirring and homogenized with a homogenization device.⁶

The SM was used as homogenization device purchased from Bioblock (France). It was made from polyacetal (PAC) and design is very simple, therefore, it has the advantage of being very economic. A bundle of four pieces of PAC elements with a length of 15 cm and diameter of 0.635 cm was placed in a tube with an interior diameter (ID) of 1 cm and a length of 100 cm. A pump is used to circulate the mixture through the pipe at various velocities to create miniemulsion. The pump flow rate can vary from 4 mL/s up to 60 mL/s which correspond to velocities comprised between 5.5 and 78 cm/s. A general configuration of static mixer set-up is shown

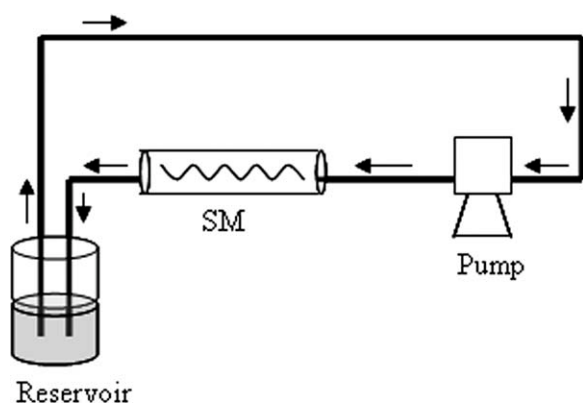


Figure 1 Schema of static mixer set up, containing SM elements, pump, and reservoir.

in Figure 1. The liquid is pumped from a reservoir by the empty head of the tube and pushed into the SM inserted section of the tube.

In a typical experiment, 4.2 g *n*-hexadecane (HD) was dissolved in 84.4 g MMA and emulsified in an aqueous solution of SDS (2 g/L) using SM.

The stability of miniemulsions was verified by measuring droplet size periodically, if the increase of droplet size was less than 10 nm after 4 h, the sample was considered as a stable miniemulsion.

In polymerization step, stable miniemulsions were polymerized in a cylindrical glass batch reactor (150 mL) with a nitrogen inlet for all the samples. After introduction of the miniemulsion into the reactor, nitrogen was bubbled through the solution for 30 min to eliminate the oxygen before beginning the polymerization process. Once this step completed, the mixture is brought to the desired reaction temperature and the initiator, APS (0.15 g for mentioned recipe) is added to the batch.

The reactor contents were mixed during polymerization with a glass anchor stirrer at a constant speed of 250 rpm, and the temperature was kept constant at 70°C, using water circulation from a thermostatic bath.

Characterization of products

Droplet and particle sizes of emulsions or latices obtained using a Malvern Autosizer (dynamic light scattering). The evolution of the polydispersity index (PI) furnished by the software of the ZetaSizer. It should be pointed out that this index is a number provided by the software and is taken as an indication of the narrowness of the distribution in question. The manufacturer announces that a PI value of 0.1 and less suggest a monomodal distribution.

Complete droplet and particle size distributions reported were measured using the Beckman-Coulter LS-230 (static light scattering). Full droplet and particle size distributions included number average (D_N),

surface average (D_s or d_{32}) and volume average (D_V) values. Note that conversion of polymerization reaction for all experiments was determined gravimetrically, and interfacial tension values used to calculate We was obtained by the method described by Lando and Oakley.³⁰

RESULTS AND DISCUSSION

The nature of fluid flow

Miniemulsions were produced by making circulate the mixture of the two immiscible liquids (oil and aqueous phases) through the pipe in which the static mixer is inserted. To characterize the fluid flow in this system, the flow rate was measured at different levels by regulating the pump control. The results of these measurements showed that the flow rate can be adjusted between 4 and 60 mL/s to have a stable fluid circulation.

The average velocity in a simple tube is defined by eq. (2):

$$U = Q/A \quad (2)$$

where Q is the volumetric flow rate, and a is the cross-sectional area of the pipe.

Similar to other types of SM,^{10,11,31,32} the PAC SM can be used both under laminar flow and turbulent operation condition. It is known that the nature of fluid flow can be characterized by Reynolds number. The definition of Reynolds number basically is the ratio of the viscosity force to inertial force. Equation (3) gives Re number for a simple pipe. However, characteristics of Re number for SM inserted pipe differ in literature based on the SM type. For example, Re can be calculated from eq. (4) for SM inserted pipe by considering pore³³ concept and eq. (5) give the definition of Re for SM inserted pipe by considering hydraulic diameter¹⁸ concept.

$$Re = \rho UD/\mu \quad (3)$$

where ρ , μ , and U are the density, viscosity, and velocity of fluid, and D is the diameter of tube.

In addition to above-mentioned definition for Re , Shah and Kale³⁴ proposed also another similar Reynolds number for a Kenics SM by incorporating porosity:

$$Re = \rho UD/\varepsilon\mu \quad (4)$$

This equation should be adapted to reflect the characteristics of the system when a static mixer is used, and various methods have been proposed for this purpose in the literature.³³ Morancis et al.³³ defined a dimensionless number analog to Reynolds

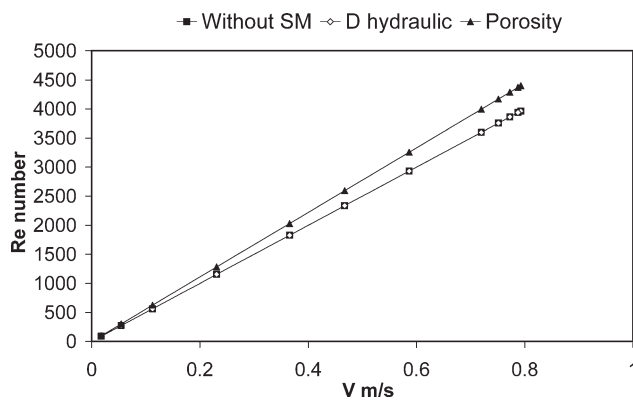


Figure 2 Re number determined by different methods for different values of velocity.

number to simulate friction factor and determination of geometric parameters in SM mixer that correspond to a typical pore in this SM.

$$Re_p = \rho U_0 \tau d_p / \varepsilon \mu \quad (5)$$

where τ is tortuosity (dimensionless), d_p is the diameter of pore, ε is the porosity of SM, and μ is viscosity.

As mentioned, Re number can be obtained also by using the concept of hydraulic diameter [eq. (6)], D_h which is a common term and it can be determined by eq. (7).

$$Re = \rho U D_h / \mu \quad (6)$$

$$D_h = 4A / P_w \quad (7)$$

where A is the cross-sectional area and P_w is the wetted perimeter of the cross section. The calculation of D_h is given here for instance at a flow rate of 60 mL/s in which most samples were prepared.

For our case, Re has been calculated for an empty pipe and also by considering the notion of hydraulic diameter for SM inserted tube in different flow rates, and the results were compared in Figure 2 with those obtained using the method proposed by Moraçais et al.³³

To use eq. (5) to calculate Re number, it is needed to know the tortuosity and the porosity. The tortuosity was obtained from the ratio of the length of the curve to the distance between the ends of the SM.

The porosity of SM was determined by the following method: the volume of a pipe with the internal diameter of equivalent to the diameter of SM and same length were measured by filling with water with and without the SM elements and the ratio of these two quantities of water gave us the porosity, which was almost 0.8.

The relationship between superficial velocity and Re number can be seen in Figure 3. In Figure 3, Re is calculated for a tube without SM and compared

with those containing SM calculating from eqs. (5) and (6) to taking in account porosity and hydraulic diameter, respectively.

As was shown in Figure 2, Re number is in the range of 2500–4000 regardless of the form of equation used to calculate it, which indicates that the fluid flow is turbulent. Since usually We number has been used particularly to characterize turbulent flow regime by the scientist (and capillary number is used for laminar flow regime)¹⁵; here we will determine this dimensionless number for the system in question.

Determination of Weber number

The Weber Number is a dimensionless value useful for analyzing fluid flows where there is an interface between two different fluids (this is the case in this study). This dimensionless number is the ratio between the inertial force and the surface tension force that can be expressed as eq. (8).

$$We = \rho U d_{\max} / \gamma \quad (8)$$

where d_{\max} is the characteristic length (m) and γ is interfacial energy (N/cm).

Note that interfacial tension values used to calculate We was obtained by the method described by Lando and Oakely.³⁰

It is worth noting that droplet breakage can occur when We is higher than a critical value $We > We_{\text{crit}}$.¹⁷ To give an idea about parameters affecting We_{crit} it is worth mentioning that under the general reasonable assumptions break up of a drop occurs when the Weber number reaches a critical value of We_{crit} .¹⁷ Critical We number can be expressed as a function of the viscosity as it has shown in eq. (9).

$$We_{\text{crit}} = C(1 + \phi(\mu_d / (\rho_d \gamma_d)^{0.5})) \quad (9)$$

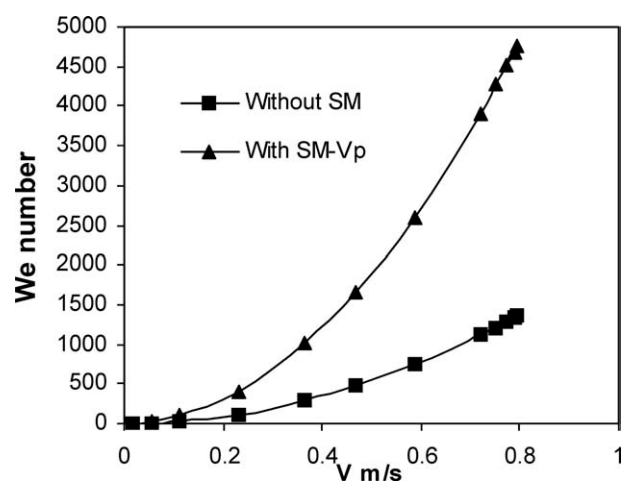


Figure 3 Weber number in empty and SM inserted pipe (V_p).

where C is a constant and ϕ is dispersed phase volume fraction, μ_d and ρ_d are viscosity and density of dispersed phase, respectively.¹⁷ The experimental results showed that the mechanism of break up is quite simple when We is equal to or slightly higher than We_{crit} . The more We exceeds its critical value, the more complicated this mechanism becomes.^{17,35}

The We number has been determined for emulsification system according to eq. (8) and was traced as a function of the average velocity under two different conditions with and without SM in Figure 3. It can be seen from this figure that the value of We number is obtained for the pores of a SM is higher than that of tube without SM. This figure shows also a considerable increase in We number especially when the velocity is higher than 0.48 m/s (the area that this study covers).

Relationships between droplet size and We number

It was discussed that much research has been done to predict the drop size obtained with different types of static mixers. Some correlations in this respect have been proposed by a number of scientists.^{15–19,36,37} These simulations are based essentially on We when the fluid flow is turbulent. It seems that in such a turbulent system, the interfacial energy plays an important role, which explains why We is so popular in this respect. However, other models to predict the droplet diameter, are based on a combination of We number with either Re number or the ratio of the viscosity of the dispersed phase to that of the continuous phase.^{15–19} In such correlations, the dependence of the droplet size on Re or the ratio of the viscosity of the two phases has a very low order of magnitude (the power is of the order of 0.2). This is why we decided to see whether or not we could develop a correlation of droplet diameter with We alone. In this correlation, the parameters of Morançais' method were used to calculate We .

To compare our correlation with those proposed in the literature, we used the same dimensionless diameters, which is the ratio of the surface average droplet size to the diameter of the pipe. The surface average droplet size was obtained using light diffraction measurement (Coulter LS 230). It is worth noting that the definition of surface average diameter (d_s) is exactly the same as that of Sauter's diameter (d_{32}). The ratio of the surface average droplet diameter to the diameter of the empty tube versus the We number is shown in Figure 4. The governing equation shows an exponent for We of the order of -0.35 [eq. (10)].

$$\frac{d_{32}}{D} = K \cdot We^{-0.35} \quad (10)$$

where K is constant value for PAC SM system and is 0.0004. The power of We number in this correla-

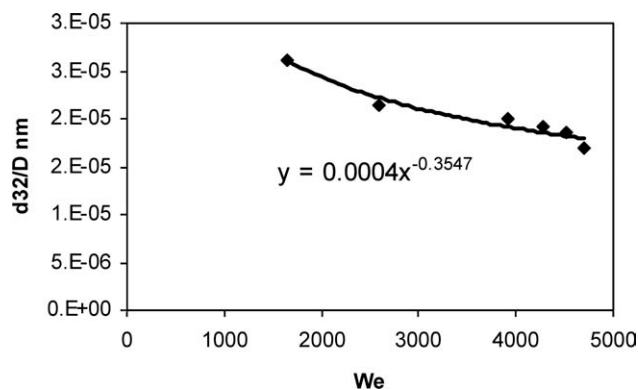


Figure 4 Experimental correlation between droplet diameter and We number.

tion is found to be in agreement with the values that have also been reported in the literature (-0.60 and -0.33).^{15–19,36}

It can be seen from eq. (10) that this correlation for emulsification of MMA using PAC SM in this work follows the same behavior as previously studied systems. Since the system of interest in this work obeys similar equation as usual microscale emulsions, it can be concluded that nanosize droplets in emulsification by SM can be estimated by classical fluid mechanics.

Polymerization of nanodroplets created by SM

Nanodroplets created by SM PAC were polymerized according to the recipe mentioned in experimental section via a batch process in a cylindrical glass reactor (150 mL) with a nitrogen inlet.

Droplet diameter (D_d) of miniemulsions after 30 min of homogenization with SM, conversion of polymerization reaction after 120 min, particle size (D_p), and polydispersity index (PI) of latices and also the ratio of the number of polymer particles to the number of droplets (N_p/N_d) are given in Table II for different flow rates.

The highest flow rate gave the narrowest droplet size distribution, which in turn could be polymerized to yield a narrow particle size distribution (PSD) with N_p/N_d closest to unity, indicating efficient nucleation of the nanodroplets.³⁸ The best condition that we obtained corresponds to the flow rate of about 60 mL/s.

On the basis of developed correlation, droplet size can be predicted to be small enough to capture oligoradicals and the majority of droplet can be nucleated. This helps us to guess the condition under which droplet nucleation is predominant mechanism of particle formation.

CONCLUSIONS

Emulsification of acrylic monomer using PAC SM was investigated to better understanding droplet

TABLE II
Effect of Flow Rate on Characteristics of Samples

Flow rate (mL/s)	D_d (nm)	Conversion (%)	D_p (nm)	PI	N_p/N_d
36	270	0.94	191	0.08	2.35
48	190	0.96	168	0.072	1.21
60	150	0.97	142	0.061	0.98

break up in SM. Re number was determined for a wide range of flow rate and showed that in the region that we obtain reasonable small droplets, the fluid flow regime is turbulent.

Relationship between droplet size and We obtained under turbulent fluid flow and showed that the surface average droplet size to the pipe diameter was fit as an exponential function of We. The governing equation for PAC static mixer shows dependency of an order of -0.35 . These results enable us to predict droplet size in final miniemulsions and help us to obtain reasonable conditions under which droplet nucleation is predominant mechanism of polymer particle formation.

Since the system of interest in this work follow the same behavior as usual microscale emulsions, it can be concluded that obtaining nanosize droplets in emulsification can be justified by classical fluid mechanics.

It was shown that at highest flow rate, miniemulsions with relatively narrow droplet size distribution was obtained and polymerization of these miniemulsions yield in a 1 : 1 copy of droplets to particles. This is in agreement with the developed correlation between droplet size and We number for microscale systems. This method will be used for incorporation of silica particles in polymer particles and results will be published in future.

References

- Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butte, A.; Fontenot, K. *Adv Polym Sci* 2005, 175, 129.
- Chern, C.; Chang, H. *Polym Int* 2002, 51, 1428.
- Sembira, A. N.; Merchuk, J. C.; Wolf, D. *Chem Eng Sci* 1988, 43, 373.
- Collins, S. B.; Knudsen, J. G. *AIChE J* 1970, 16, 1072.
- Antonietti, M.; Landfester, K. *Progr Polym Sci* 2002, 27, 689.
- Asua, J. M. *Progr Polym Sci* 2002, 27, 1283.
- Lelu, S.; Novat, C.; Graillat, C.; Guyot, A.; Bourgeat-Lami, E. *Polym Int* 2003, 52, 542.
- Qiu, G.; Qi, W.; Chao, W.; Lau, W.; Guo, Y. *Polym Int* 2006, 55, 265.
- Ouzineb, K.; Lord, C.; Lesauze, N.; Graillat, C.; Tanguy, P. A.; McKenna, T. *Chem Eng Sci* 2006, 61, 2994.
- Bakker, A.; Laroche, R. D.; Marshall, E. M. *Laminar Flow in Static Mixer with Helical Elements*. In *The online CFM Book*, 1998. Available at: <http://engbehnam.tripod.com/fluent3.pdf>.
- Gyenis, J. *KONA* 2002, 20, 9.
- Farzi, G. A.; Bourgeat-Lami, E.; McKenna, T. F. L. *J Appl Polym Sci* 2009, 114, 3875.
- Yildiz, U.; Capek, I.; Sarov, Y.; Corobea, M.; Polovkova, J. *Polym Int* 2009, 58, 1411.
- Feigl, K.; Kaufmann, S.; Fischer, P. E.; Windhab, E. *Chem Eng Sci* 2003, 58, 2351.
- Lemenand, T.; Della Valle, D.; Zellouf, Y.; Peerhossaini, H. *Int J Multiphase Flow* 2003, 29, 813.
- Berkman, P. D.; Calabrese, R. V. *AIChE* 1988, 34, 602.
- Hinze, J. O. *AIChE* 1955, 1, 289.
- Tidhar, M.; Merchuk, J. C.; Sembira, A. N.; Wolf, D. *Chem Eng Sci* 1986, 41, 457.
- Middleman, S. *Ind Eng Chem Process Des Dev* 1974, 13, 78.
- Haas, P. A. *AIChE J* 1987, 33, 987.
- Streiff, F. A.; Mathys, P.; Fischer, T. U. *Récents Progrès en Génie des Procédés* 1997, 11, 307.
- Vega-Alvarado, L.; Cordova, M. S.; Taboada, B.; Galindo, E.; Corkidi, G. *Image Analysis and Recognition*; Springer: Berlin, 2004; p 834.
- Abismail, B.; Canselier, J. P.; Wilhelm, A. M.; Delmas, H.; Gourdon, C. *Ultrasonics Sonochem* 1999, 6, 75.
- Abismail, B.; Canselier, J. P.; Wilhelm, A. M.; Delmas, H.; Gourdon, C. *Ultrasonics Sonochem* 2000, 7, 187.
- Angeli, P. *Chem Eng Technol* 2001, 24, 431.
- Angeli, P.; Hewitt, G. F. *Chem Eng Sci* 2000, 55, 3133.
- Das, P. K.; Legrand, J.; Morancais, P.; Carnelle, G. *Chem Eng Sci* 2005, 60, 231.
- Chen, S. J.; Libby, D. R. *Gas-liquid and liquid-liquid dispersions in a Kenics mixer*. In *71st Annual AIChE Meeting, USA*, 1978.
- Sembira, A. N.; Merchuk, J. C.; Wolf, D. *Chem Eng Sci* 1986, 41, 445.
- Lando, J. L.; Oakley, H. T. *J Colloid Interface Sci* 1967, 25, 526.
- Bakker, A.; Laroche, R. D. *Modeling of the turbulent flow in HEV static mixers*. In *The online CFM book*: 1998.
- Daniele, L. M.; Miroslav, S.; Jan, S.; Massimo, M. *AIChE J* 2006, 52, 158.
- Morancais, P.; Hirech, K.; Carnelle, G.; Legrand, J. *Chem Eng Commun* 1999, 171, 77.
- Shah, N. F.; Kale, D. D. *Chem Eng Sci* 1991, 46, 2159.
- Sprow, F. B. *Chem Eng Sci* 1967, 22, 435.
- Walstra, P. *Chem Eng Sci* 1993, 48, 333.
- Simmons, M. J. H.; Azzopardi, B. J. *Int J Multiphase Flow* 2001, 27, 843.
- Landfester, K.; Bechthold, N.; Förster, S.; Antonietti, M. *Macromol Rapid Commun* 1999, 20, 81.