

Mass Transfer, Micromixing and Chemical Reactions Carried out in the Rotor-Stator Mixer

Jerzy Bałdyga*, Magdalena Jasińska, Michał Kotowicz

Warsaw University of Technology, Faculty of Chemical and Process Engineering, ul. Waryńskiego 1, 00 645 Warsaw, Poland
j.baldyga@ichip.pw.edu.pl

Two pairs of fast competitive complex test reactions: neutralization competing with ethyl chloroacetate hydrolysis in the first case, and neutralization competing with 2,2-dimethoxypropane (DMP) hydrolysis in the second case, have been applied to study drop breakup, mass transfer and micromixing in two types of the rotor-stator mixers: Silverson 088/150 MS and T 50 Ultra-Turrax® - IKA. In experiments effects of process conditions on the product distribution of chemical test reactions and the drop size distribution were determined. The product distribution of complex test reactions was evaluated based on results of high-performance liquid and gas chromatography measurements. The drop size distribution was measured with the Malvern MasterSizer just after the process.

The multifractal model of intermittent turbulence as well as mass transfer and micromixing models were applied to interpret and predict the course of the processes of drop breakage, mass transfer, mixing and complex chemical reactions. The population balance modeling was applied to integrate effects of different mixing and chemical reaction effects. Based on experimental data and model predictions the energetic efficiencies of drop breakage and mass transfer in the rotor-stator mixers were identified and discussed.

The models of mass transfer in liquid-liquid systems are discussed in detail. The first models based on physics of mass transfer phenomena were proposed by Levich and Batchelor in sixties and seventies years of the 20th century, and were further developed by other researchers. Here we apply two models, the first one was proposed by Polyanin and the second one by Favelukis and Lavrenteva. Both models are based on the original concept of Levich, the second one includes effects on mass transfer of drop deformation to the shape of prolate ellipsoid. Limitations of both models are presented and possibilities of improvement of their performance are discussed.

1. Introduction

Chemical reactions are carried out in industry to produce desirable intermediate and end-products such as pharmaceutical intermediates and other fine chemicals. However, they are often accompanied by side reactions producing undesired byproducts. Creation of byproducts not only decreases the yield of desired reactions but also may require costly product separation. Using a catalyst one can make chemical kinetics of the desired reaction very fast comparing to undesired ones. However, its rate can be then controlled by mass transfer and/or micromixing, and the final product distribution would result then from competition between mixing that controls the first reaction, and the second, slower reaction that can be kinetically controlled. Hence, having information on chemical reaction kinetics and thermodynamics is not enough to predict the product distribution of complex reactions; one needs to know as well details of the flow structure, mass transfer and micromixing. Because chemical reactions are sensitive to flow and mixing, they can serve as the test reactions or the chemical probes to determine experimentally such mixing characteristics as intensity of segregation, time constant for mixing and energetic efficiency of mixing.

Two systems of chemical test reactions are applied in this work. The first one is represented by a set of two parallel reactions as given by Eq(1)



the first of them being instantaneous and the second one fast relative to mixing and mass transfer. Two of reactants, benzoic acid (*B*) and ethyl chloroacetate (*C*), initially dissolved in toluene, are transferred from a dispersed, organic phase to the continuous aqueous phase, where they react with the same for both of them third reactant, sodium hydroxide (*A*). The product distribution of this set of parallel chemical reactions is a good measure of a competition between reactions, mixing and mass transfer.

$$X_S = \Delta N_C / N_{C0} \quad (2)$$

where ΔN_C represents the number of ester moles reacting with *NaOH* and N_{C0} is the complete number of ester moles introduced into the system.

In the second system of reactions the dispersed organic phase consisted of a solvent (mixture of diisopropyl ether and ethanol) and *p*-Toluenesulfonic acid (*pTsOH*) being an acidic reactant in the system of test reactions. The continuous phase was represented by the aqueous solution of sodium hydroxide (alkaline reactant), 2,2-dimethoxypropane (*DMP*) and ethanol.



The first reaction can be treated as instantaneous, the second reaction is catalyzed by hydrogen ions H^+ and can be treated as fast. Equations (3) and (4) represent modification of the set of test reactions proposed earlier (Bałdyga et al., 1998) for homogeneous systems. The product distribution can be defined in this case by using the number of *DMP* (*D*) moles reacting in reaction (4)

$$X_S = (N_{D0} - N_D) / N_{D0} \quad (5)$$

In this paper drop breakage and mass transfer accompanied by micromixing and complex chemical reactions are carried out in two types of the rotor-stator devices: Silverson 088/150 MS and T 50 Ultra-Turrax® - IKA. The rotor-stator mixers are used in many technologies in the chemical, pharmaceutical, biochemical, agricultural, cosmetic, health care and food processing industries. They belong to the group of high-shear devices and are characterized by the rotor situated in a close proximity the stator. Such arrangement and a high rotor speed lead to a focused delivery of energy to the high-shear regions that occupy small fraction of internal mixer space. Such delivery of energy results in fast breakage of droplets and intensive mass transfer and mixing in these small regions of the mixer, but the same time there is slow mass transfer, slow mixing and no breakage in the larger regions, where the rate of energy dissipation is small. The agitation power is high and thus an energetic efficiency of processes carried out in the rotor-stator devices becomes an important issue that will be considered in this paper as well. The energy dissipation rate in the in-line rotor-stator Silverson mixers depends on the agitation rate *N* and the flow rate *Q*, and can be estimated using the swept rotor volume V_H and the power number N_P , $\varepsilon_{NQ} = N_P N^3 D_{out}^5 / V_H$. The form of N_P was proposed by Bałdyga et al., (2007), see also Hall et al., (2013) for details of experimental validation

$$N_P = N_{P1} + N_{P2} \cdot N_Q \quad (6)$$

where

$$N_Q = Q / (ND^3) \quad (7)$$

represents dimensionless flow rate or the dimensionless pumping capacity of the rotor-stator device.

As we are going to study the energetic efficiency of mass transfer in liquid-liquid systems, a reliable model of mass transfer that is based on the fundamentals of Fluid Mechanics should be chosen. Starting from publication of fundamental approaches by Levich (1962) and Batchelor (1980) there are two basic methods available in the chemical engineering and fluid mechanics literature that can be applied for modeling of an external mass transfer at small values of the particle or drop Reynolds number. The first method considers surface mobility but neglects fluid deformation (so neglects velocity variation in the vicinity of droplet), whereas the second method neglects surface mobility but takes into account deformation of fluid. The first method is

applied to describe external mass transfer of bubbles and not very viscous liquids (Levich, 1962) and predicts $Sh \propto Pe^{1/2}$, the second one predicts $Sh \propto Pe^{1/3}$ and can be applied to model mass transfer between ambient fluid and either spherical solid particles or spherical drops that behave like hard spheres. This includes very viscous drops and drops with immobilized surface. However, both kinds of the mass transfer models do not converge at infinitely high viscosity of the dispersed phase; in correlation derived for drops the dependence $Sh \propto Pe^{1/2}$ is conserved even for infinitely large viscosity of the dispersed phase, η_d . Several more advanced models were proposed after Levich (1962) and Batchelor (1980), for example Favelukis and Levrenteva (2013) included effects of drop shape deformation to the shape of prolate ellipsoid; they did not modify, however, the assumption about surface mobility.

$$Sh \cdot A^* = \frac{k_L a_{drop}}{4\pi R_{eq} D_i} = \sqrt{\frac{3}{2\pi(1+K)}} \left[1 - \frac{4(4+31K)Y}{315(1+K)} N_{Ca} \right] Pe^{1/2} \quad (8)$$

In Eq(8) $Y = (19K+16)/(16K+16)$, K is the viscosity ratio $K = \eta_d/\eta_c$, $Pe = \dot{\gamma} R_{eq}^2/D_i$, and the capillary number is defined by $N_{Ca} = \eta_c \dot{\gamma} R_{eq}/\sigma$. R_{eq} represents the equivalent radius, i.e. the radius of a sphere of equal volume to that of the deformed drop and A^* is the ratio of the surface area of deformed drop surface area a_{drop} to the area of equivalent sphere, $4\pi R_{eq}^2$. The shear rate $\dot{\gamma}$ can be expressed using the rate of energy dissipation, $\dot{\gamma} = (\varepsilon/\nu)^{1/2}$. Equation (8) describes mass transfer to or from drops. Notice that the exponent on Pe is equal to 0.5 and is independent of the viscosity ratio. Moreover for $K = \eta_d/\eta_c \rightarrow \infty$ the mass transfer coefficient becomes equal to zero! Similar predictions gives model by Polyanin (1984):

$$k_L = \frac{D_{s,c}}{d_p} 0.620 \left(\frac{\eta_d}{\eta_c} + 1 \right)^{-0.5} Pe_M^{0.5} \quad (9)$$

where $Pe_M = \frac{d_p^2}{D_{s,c}} \left(\frac{\varepsilon}{\nu} \right)^{0.5}$. It is clear that both models, Eq(8) and (9), have limitations and can be only used for $K = \eta_d/\eta_c$ only slightly larger than unity; further work is necessary to work out a model that converges from $Sh \propto Pe^{1/2}$ to $Sh \propto Pe^{1/3}$ as the viscosity ratio increases.

2. Experimental

Experiments employing the first set of test reactions, Eq(1), were carried out in-line in the experimental rig consisted of a system for supply of aqueous solution of NaOH from a constant head tank, the Silverson 088/150 MS mixer (Silverson Machines Ltd., Chesham, UK) and a valve on the outflow that was used to regulate the flow rate (Jasińska et al., 2016). The rotor-stator mixer was fitted with double concentric rotors enclosed between concentric double stators as shown in Figure 1. The natural pumping action of the Silverson was used to provide the main flow of aqueous solution, and the flow rate was measured by a Micro Motion Coriolis R-Series mass flow meter. The organic solution was introduced using the syringe pump through the separate inlet.

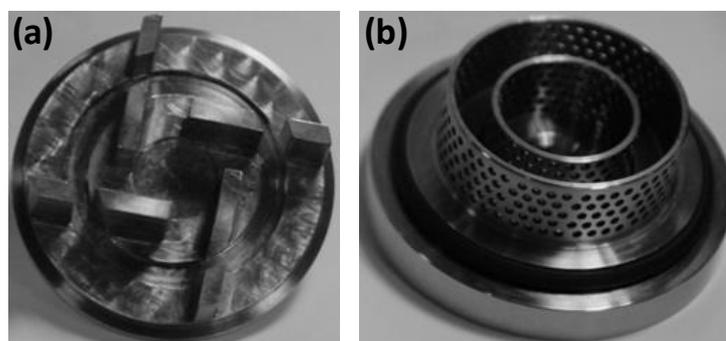


Figure 1: Double rotors (a) and double emulsor stators (b) of the Silverson 088/150 MS mixer with outer rotor diameter $D_{out} = 38.1\text{mm}$ and inner rotor diameter, $D_{in} = 22.4\text{mm}$.

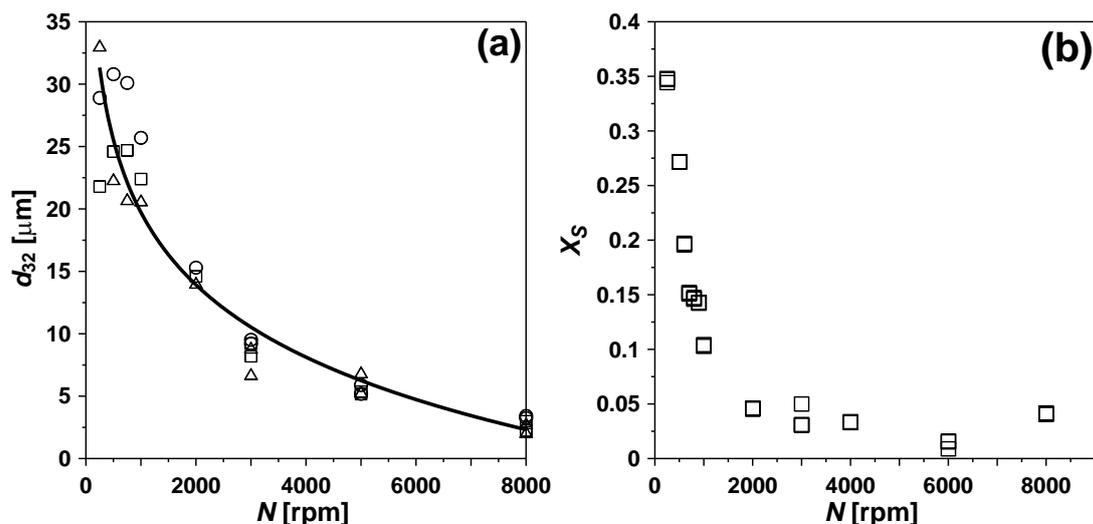


Figure 2: Examples of experimental results for in-line mixer: (a) Effect of the rotor speed on the drop size for Case 1, (b) Effect of rotor speed on product distribution X_s for Case 3.

Experimental investigations were performed for the rotation speed N from a range between 250 and 10,000 rpm for 3 values of the flow rate: $Q_{\text{aq}} = 3.32 \times 10^{-6} \text{ m}^3/\text{s}$, $Q_{\text{org}} = 3.33 \times 10^{-8} \text{ m}^3/\text{s}$ (Case 1), $Q_{\text{aq}} = 8.26 \times 10^{-6} \text{ m}^3/\text{s}$, $Q_{\text{org}} = 8.33 \times 10^{-8} \text{ m}^3/\text{s}$ (Case 2), and $Q_{\text{aq}} = 1.65 \times 10^{-5} \text{ kg/s}$, $Q_{\text{org}} = 1.67 \times 10^{-7} \text{ m}^3/\text{s}$ (Case 3). The reactant concentration were as follows: $C_{A0} = 5 \text{ mol/m}^3$, $C_{B0} = 500 \text{ mol/m}^3$, $C_{C0} = 500 \text{ mol/m}^3$. The product distribution of test reactions was determined based on the high-performance liquid chromatography (HPLC) measurements. The drop size distribution was measured with the Malvern MasterSizer 3000. A surfactant Sodium Laureth Sulfate was added to the samples after carrying out the process of mixing with chemical reaction to stabilize dispersion and avoid possible effects of droplets coalescence. Typical results are presented in Figure 2.

The second series of experiments was carried out using the system of test reactions expressed by Eq(3) and Eq(4). As mentioned earlier ethanol was used to increase solubility of pTsOH in the ether and its volume fraction in organic phase was equal to 0.25. The continuous, aqueous phase contained 2,2-dimethoxypropane (DMP), NaOH and ethanol. Ethanol was used as an internal standard for chromatographic analysis (GC). The volume fraction of organic phase was 0.014 and the molar ratio of base, acid and DMP was equal respectively 1.05:1.0:1.05. The excess of base in relation to acid was required to maintain stability of DMP before determining the concentrations after performing reactions. The concentrations of NaOH and DMP were equal to 4 mol/m^3 (Case 1) and 3.5 mol/m^3 (Case 2) respectively; concentration of pTsOH was equal to 263 mol/m^3 (Case 1) and 234 mol/m^3 (Case 2).

Experiments were carried out in the semibatch manner in the T 50 Ultra-Turrax® - IKA rotor-stator mixer shown in Figure 3. The diameters of the stator and the rotor were equal to 45 mm and 36 mm respectively; the gap size was equal to 0.5 mm. Results of experimental investigations are shown in Figure 3.

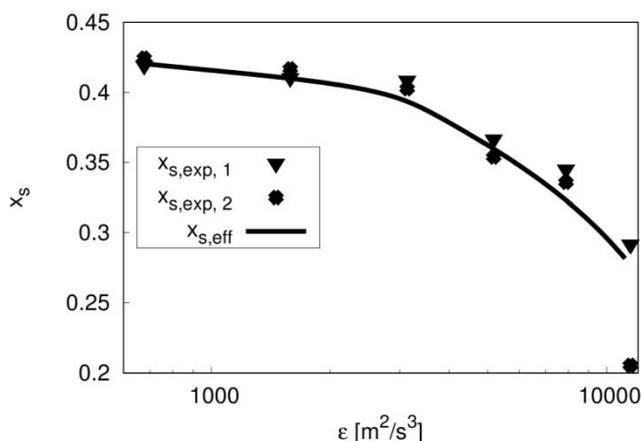


Figure 3: Left: the rotor and the stator of the T 50 Ultra-Turrax® - IKA mixer. Right: experimental values of the product distribution X_s versus energy dissipation rate. $X_{s,\text{eff}}$ is based on the process efficiency, Figure 5b.

3. Interpretation of experimental data and discussion

Efficiency of mixing and mass transfer can be interpreted as a ratio of time constants for an ideal and real process (Jasińska et al., 2013ab), $eff = \tau_{D,min}/\tau_D$. Similarly as the E-model was chosen as a reference model for mixing in homogeneous systems (Jasińska et al., 2013a), one can choose a reliable reference model for mass transfer. In present work the value of $k_L a$ will be calculated using the model of Favelukis and Levrenteva (2013), Eq(8). Efficiency of drop breakage can be thus expressed by effect of drop size on the time constants for mass transfer, τ_D . The time constant $\tau_{D,min}$ can be interpreted as the shortest mass transfer time calculated from the model of Favelukis and Levrenteva (2003) using the maximum stable drop size d_d , $R_{eq} = d_d/2$, as given by Bałdyga and Podgórska (1998), $d_d = C_x^{1.54} L \left[\sigma / (\rho_c \varepsilon^{2/3} L^{5/3}) \right]^{0.93}$, where L represents the integral scale of turbulence. This results in

$$\tau_{D,min} = \frac{\pi d_d^3}{6\varphi (k_L a_{drop})_{R_{eq}=d_d/2}} \quad (10)$$

where φ represents the mean value of the volume fraction of the organic, dispersed phase. Similar calculations but performed for $R_{eq} = d_{32}/2$ with d_{32} resulting from experiments give the time constant τ_D

$$\tau_D = \frac{\pi d_{32}^3}{6\varphi (k_L a_{drop})_{R_{eq}=d_{32}/2}} \quad (11)$$

Efficiency $eff = \tau_{D,min}/\tau_D$ of development of the interfacial area based on experimental data, Figure 2a, is presented in Figure 4a. To interpret effects observed in Figure 2b the model of mass transfer with chemical reaction was applied using film theory as described by Doraiswamy and Sharma (1984). Following Jasińska et al. (2013b) it was assumed that the neutralization reaction between benzoic acid (B) and NaOH (A) is instantaneous, and thus the enhancement factor can be expressed by $E = 1 + (D_{CA} C_{A0}) / (D_{CB} C_B^*)$, where D_{CA} and D_{CB} represent diffusion coefficients for sodium hydroxide and benzoic acid respectively, C_{A0} is the bulk concentration of sodium hydroxide, and C_B^* is equilibrium concentration of benzoic acid at the drop surface. The second reaction was identified as being in the regime between slow and very slow. Typical results of simulations are presented in Figure 4b. This curve can be used as a calibration curve, which based on experimentally determined X_S values gives the smallest, "theoretical" values of the rate of energy dissipation necessary to obtain experimentally identified X_S under ideal conditions. The really applied power input and the one resulting from the calibration curve are then used to calculate τ_D and $\tau_{D,min}$, and resulting energetic efficiency, $eff = \tau_{D,min}/\tau_D$ (Figure 5a).

To interpret results obtained using reactions Eq(3), Eq(4) and presented in Figure 3, the model of Polyanin, Eq.(9), was used to describe shrinking of droplets due to fast dissolution of ether and resulting rate of entering an acid (pTsOH) to the aqueous phase, where reaction rate was controlled by micromixing that was simulated using the E-model of (Bałdyga and Bourne, 1999). Calculated energetic efficiency, represented by the root square of a ratio of ideal, ε , and real, ε_{NQ} values of the rate of energy dissipation, is presented in Figure 5b.

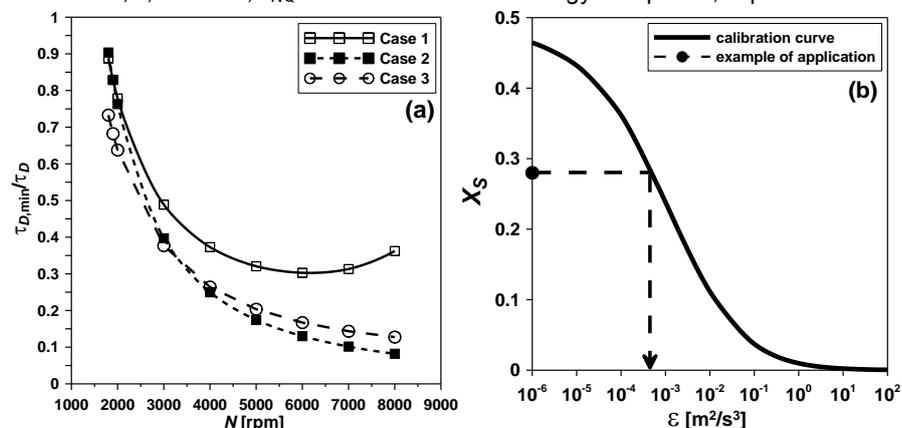


Figure 4: (a) Effect of rotor speed on energetic efficiency of drop breakage, (b) Calibration curve for parallel reactions, Eq(1).

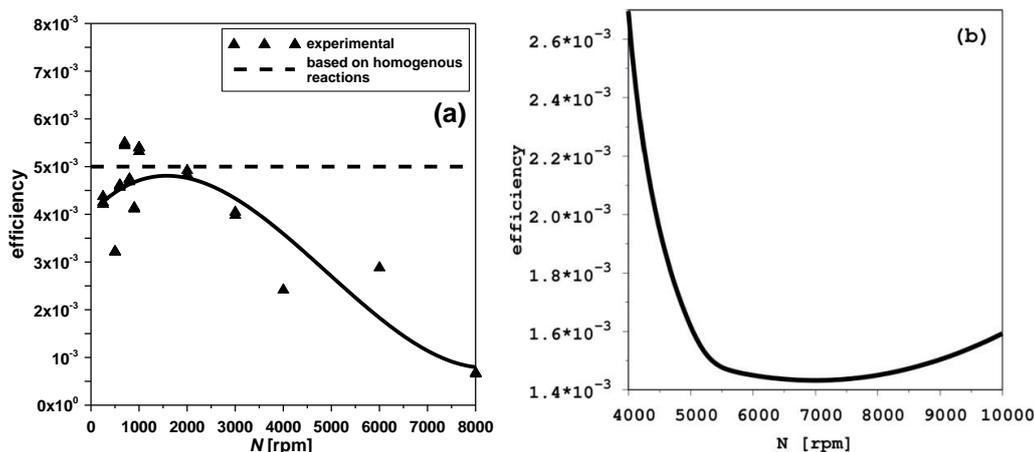


Figure 5: Effect of rotor speed on energetic efficiency of the process for (a) test reaction system given by Eq(1) , (b) test reaction system given by Eq(3) and Eq(4).

4. Conclusions

An energetic efficiency of a complex process consisting of drop breakage, mass transfer and micromixing is small and takes the values between 10^{-3} to $5 \cdot 10^{-3}$ for different mixers and different modes of operation.

Figure 5 shows that the energetic efficiency of mixing increases with increasing the rotor speed N at low rotor speed when turbulence develops and decreases with increasing N for the well-developed turbulence. Increase of efficiency at N higher than 6400 rpm observed in Figure 5b results from shrinking of the reaction zone towards the high shear region.

Presented method can be used to optimize both geometry of high-shear mixers and process conditions to carry out dispersion processes at high process rate with as high as possible energetic efficiency.

Acknowledgments

The authors acknowledge the financial support from Polish National Science Centre (Grant agreement number: DEC-2013/11/B/ST8/00258).

Reference

- Bałdyga J., Bourne J.R., 1999, Turbulent Mixing and Chemical Reactions. Wiley, Chichester, UK.
- Bałdyga J. and Podgórska W., 1988, Drop break-up in intermittent turbulence. Maximum stable and transient sizes of drops. Can. J. Chem. Eng., 76, 456-470.
- Bałdyga J., Bourne J. B., Walker B., 1998, Non-isothermal micromixing in turbulent liquids: Theory and experiment. The Canadian J. of Chem. Eng., 76(3), 641-649
- Bałdyga J., Kowalski A., Cooke M., Jasińska M., 2007, Investigations of micromixing in a rotor-stator mixer. Chem. and Process Eng., 28, 867-877.
- Batchelor G.K., 1980, Mass transfer from a particle suspended in turbulent fluid. J. Fluid Mech., 98, 609-623.
- Doraiswamy L.K., Sharma M.M., 1984, Heterogeneous reactions: Analysis, Examples, and Reactor Design. Vol. 2: Fluid-Fluid-Solid Reactions. Wiley, New York, USA.
- Favelukis M. and Lavrenteva O. M., 2013, Mass transfer around prolate spheroidal drops in an extensional flow. Can. J. Chem. Eng., 91, 1190-1199.
- Hall S., Pacek A., Kowalski A.J., Cooke M., Rothman D., 2013. The effect of scale and interfacial tension on liquid-liquid dispersion in in-line Silverson rotor-stator mixers. Chem. Eng. Res. Des., 91, 2156-2168.
- Jasińska M., Bałdyga J., Cooke M., Kowalski A., 2016. Mass transfer and chemical test reactions in the continuous-flow rotor-stator mixer. Theoretical Foundations of Chemical Engineering, 50, pp. 901-906
- Jasińska M., Bałdyga J., Cooke M., Kowalski A.J., 2013a, Application of test reactions to study micromixing in the rotor-stator mixer (test reactions for rotor-stator mixer). Appl. Therm. Eng., 57 (1-2), 172-179
- Jasińska M., Bałdyga J., Cooke M., Kowalski A.J., 2013b, Investigations of mass transfer with chemical reactions in two-phase liquid-liquid systems. Chem. Eng. Res. Des., 91, 2169-2178.
- Levich V.G., 1962. Physical hydrodynamics. Prentice-Hall, Englewood Cliffs, N.J., USA.
- Polyanin A. D., 1984. Three-dimensional diffusive boundary-layer problems. Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, 4, 71-81.