

JERZY BAŁDYGA, MAGDALENA JASIŃSKA, JUSTYNA TRENDOWSKA,
WIKTORIA TADEUSIAK*, MIKE COOKE**, ADAM KOWALSKI***

APPLICATION OF TEST REACTIONS TO STUDY MICROMIXING AND MASS TRANSFER IN CHEMICAL APPARATUS

WYKORZYSTANIE REAKCJI TESTOWYCH DO BADAŃ MIKROMIESZANIA I TRANSPORTU MASY W APARATURZE CHEMICZNEJ

Abstract

Chemical parallel test reactions are used to investigate micromixing efficiency in homogeneous systems and effects of mass transfer on selectivity of complex reactions in two-phase liquid-liquid systems. Mixing phenomena in stirred tanks, rotor-stator mixers and microreactors are investigated.

Keywords: mass transfer, micromixing, test reaction

Streszczenie

Równoległe, testowe reakcje chemiczne zastosowano do badań efektywności mikromieszania w układach jednofazowych oraz badań wpływu transportu masy na selektywność przebiegu reakcji złożonych w układach dwufazowych ciecz-ciecz. Badania prowadzono w reaktorach zbiornikowych, mieszalnikach typu rotor-stator i mikroreaktorach.

Słowa kluczowe: mikromieszanie, transport masy, reakcje testowe

* Prof. PhD. Eng. Jerzy Bałdyga, PhD. Eng. Magdalena Jasińska, MSc. Eng. Justyna Trendowska, MSc. Eng. Wiktoria Tadeusiak, Faculty of Chemical and Process Engineering, Warsaw University of Technology.

** PhD. Mike Cooke, The University of Manchester.

*** Prof. Adam Kowalski, Unilever Research & Development Port Sunlight.

1. Introduction

Chemical test reactions are usually applied in experiments designed either to validate models of mixing on the molecular scale (micromixing) or models of mass transfer in the case of the liquid-liquid two-phase systems. Once the models are validated they can be used together with test reactions to characterize local mixing conditions, energetic efficiency of mixing and mass transfer coefficients by experimental identification of the product distribution. This means that they can be used to characterize reactors and mixing equipment from the point of view of interactions between mass transfer and chemical reactions. In this work we are interested in both: new test reactions to be applied in homogeneous and two-phase systems, and application of test reactions to study methodology for identification of process conditions that minimize creation of by-products.

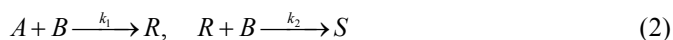
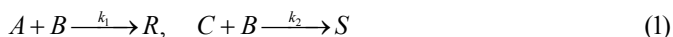
The criteria for test reactions are presented in detail by Bałdyga and Bourne [1]. Such criteria were applied in present work to choose the new systems of 2 parallel, competitive test reactions.

In what follows we use several test reactions to study mixing. We start from systems of 2 parallel reactions in homogeneous systems to study mixing in the stirred tank, to discuss the rules of choosing such reactions, and validate the new system of test reactions by comparing their performance with performance of the old, validated system. Then the test reactions are applied to study mixing in microreactors and the rotor-stator mixers, and to characterize their energetic efficiency. Finally, a possibility to apply similar idea to study mass transfer in the two-phase liquid-liquid system is presented by using experiments.

2. Test reactions in a single phase system

2.1. Method for choosing test reactions and their application to study micromixing in the semibatch stirred tank reactor

There are many complex schemes of multiple reactions that can be used to characterize mixing performance. They are usually made up of combination of two primary reaction types: competing or parallel, eq. (1), and consecutive or series eq.(2):



The first reaction from both schemes of elementary test reactions should be fast enough to be controlled by mixing, the second one should be slower, so that there would be competition between the mixing process controlling the first reaction and chemical kinetics controlling the second one. This can be checked using the time constant analysis [1]. Amount of the product of the second reaction that for ideal mixing on the molecular scale would be close to zero, stores the history of mixing and can be used to determine energetic efficiency of mixing. Such applications will be shown in what follows.

When choosing test reactions for homogeneous systems one should remember that all reactants and products should be soluble, the reactions should be irreversible and species concentrations easy to measure. Finally, the mechanisms and kinetics of test reactions must be fully known. A good example of such reacting system is competitive neutralization of hydrochloric acid and alkaline hydrolysis of monochloroacetate methyl or ethyl esters of monochloroacetic acid [1]. Hence, in what follows in this section we use as reference system the one given by eq. (1) with $A = \text{HCl}$, $B = \text{NaOH}$, $C = \text{CH}_2\text{ClCOOC}_2\text{H}_5$, $R = \text{H}_2\text{O}$ or NaCl , $S = \text{C}_2\text{H}_5\text{OH}$ or $\text{CH}_2\text{ClCOONa}$ and propose a new one, with C replaced by $\text{CHCl}_2\text{COOC}_2\text{H}_5$ and thus S represented this time by $\text{CHCl}_2\text{COONa}$. To compare both test systems and show possibilities of application of the new one, both experiments and simulations have been performed.

Experiments were carried out using the semibatch stirred tank reactor of diameter $T = 145$ mm, equipped with the Rushton type impeller of diameter $D = 50$ mm and 4 baffles of a width equal to 15 mm. The process was carried out in a semibatch manner with the base solution (B) fed to the tank containing initially the premixture of acid (A) and ester (C). The volume ratio of both solutions, $a = V_{AC}/V_B$, was equal either 10 or 50. The feeding time was long enough to eliminate effects of feeding rate (15 minutes). Diameter of feeding pipe was equal to 1mm and two feeding positions were used: the first one on the level of impeller $z = 0$, for the radial position $r = 0.45 \cdot T/2$ (position I close to the impeller), the second one was close to the liquid surface $z = 1.3 \cdot T/2$, $r = 0.5 \cdot T/2$ (position far from the impeller). The product distribution was represented by the ratio of number of reacted moles of the ester to the number of moles of the base (B), for $N_A = N_B = N_C$.

$$X_S = \frac{\Delta N_C}{N_A} \quad (3)$$

Concentrations of esters before and after reaction were measured using HPLC (Perkin Elmer Series 200).

Simulations were carried out using the model of engulfment (E-model) of Baldyga and Bourne [1] and the multi-zone model of the flow and dissipation of kinetic energy of turbulence (see pages 700-703 in [1] and [2]).

Figure 1 compares results of application of both test reaction systems: the system with ethyl chloroacetate and the system with ethyl dichloroacetate. Fig. 1 shows that application of ethyl chloroacetate is limited to smaller rates of agitation but it offers slightly higher sensitivity to agitation rate. Clearly, much wider range of agitation rates is covered when the ethyl dichloroacetate is applied, so this new system is better for studying effects of agitation on mixing and will be used in what follows. Fig. 2 shows that the product distribution X_S increases with feed concentration and volume ratio "a"; this is because in both cases the time constant for the second reaction decreases. Figure 3 shows how important are conditions of mixing close to the feeding; clearly choosing a proper feeding point in the tank allows to use 5 to 7 times slower agitation, so to reduce agitation power by factor 100 to 300 and obtain the same selectivity. This shows how important is efficient mixing; clearly it is important to use agitation power for mixing, not just for the flow that is not effective for contacting reactants but just keeps liquids flowing.

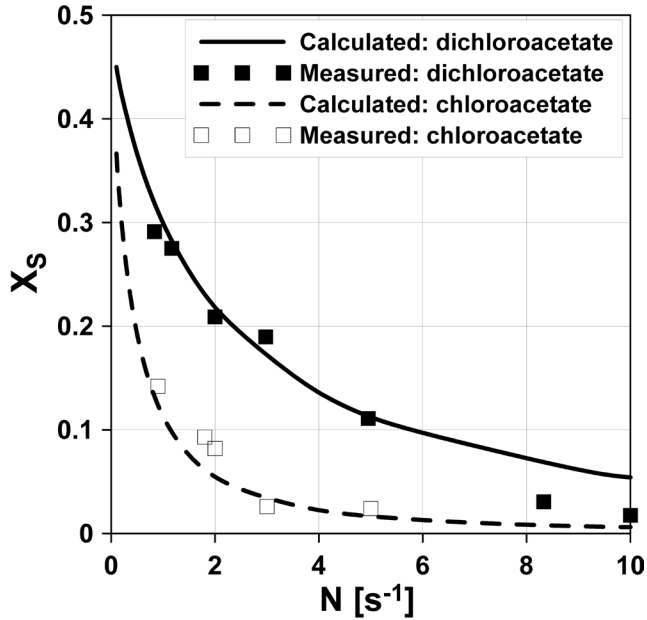


Fig. 1. Effect of agitation rate on selectivity X_s for ethyl chloroacetate and ethyl dichloroacetate; $c_B = 1 \text{ M}$, $c_A = c_C = 0.02 \text{ M}$, $a = 50$, feeding position A close to the impeller

Rys. 1. Wpływ szybkości mieszania na selektywność X_s dla chloroocetanu etylu i dichloroocetanu etylu; $c_B = 1 \text{ M}$, $c_A = c_C = 0,02 \text{ M}$, $a = 50$, zasilanie w pobliżu mieszadła (A)

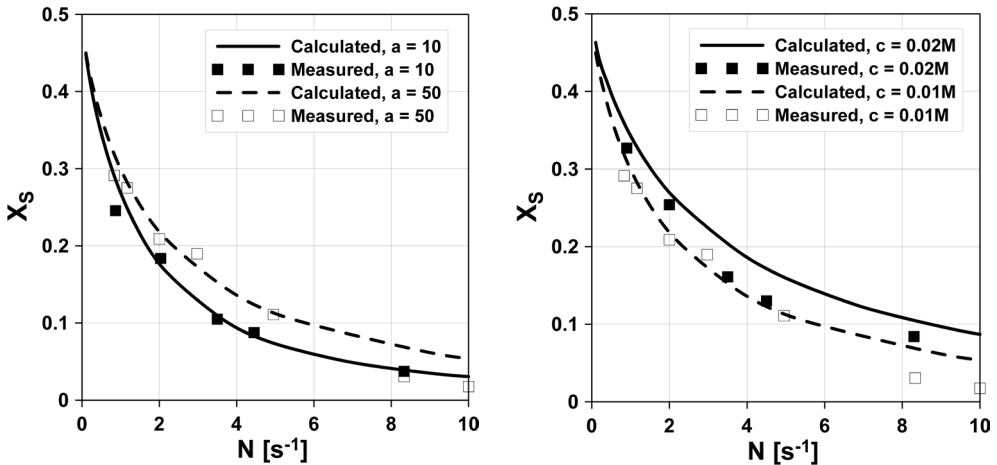


Fig. 2. X_s for ethyl dichloroacetate: effects of volume ratio and concentration (left) $c_B = 1 \text{ M}$, $c_A = c_C = 0.02 \text{ M}$ for $a = 50$; $c_B = 0.1 \text{ M}$, $c_A = c_C = 0.01 \text{ M}$ for $a = 10$ (right) $a = 50$, feeding position I

Rys. 2. X_s dla dichloroocetanu etylu; wpływ stężenia i stosunku objętości; (po lewej) $c_B = 1 \text{ M}$, $c_A = c_C = 0,02 \text{ M}$ dla $a = 50$; $c_B = 0,1 \text{ M}$, $c_A = c_C = 0,01 \text{ M}$ dla $a = 10$ (po prawej) $a = 50$, punkt zasilania I

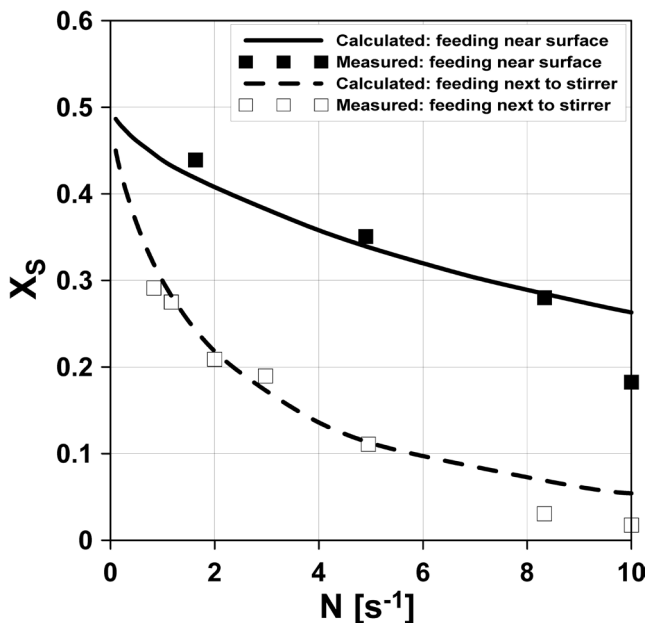


Fig. 3. X_s for ethyl ethyl dichloroacetate; $c_b = 0.5$ M, $c_A = c_C = 0.01$ M, $a = 50$, effect of feeding position

Rys. 3. X_s dla dichlorooctanu etylu; $c_b = 0,5$ M, $c_A = c_C = 0,01$ M, $a = 50$, wpływ miejsca zasilania

2.2. Efficiency of mixing in microreactors and rotor-stator mixers

The problem of effective mixing on micro-scale and related problem of construction of micro-mixers have been considered in recent publication [4]. Consider the process of mixing between elongated slabs. Extent of mixing can be represented by the rate of creation of the intermaterial area per unit volume, a_v [m²/m³], and expressed using the local value of deformation tensor \bar{D} and efficiency of mixing $eff(t)$ [3]:

$$X_s = \frac{\Delta N_C}{N_A} \quad (3)$$

Eq.(4) shows directly that orientation of the intermaterial area with respect to the principle axes of deformation determines effectiveness of mixing. Indirectly it represents the root square of the ratio of energy that is really necessary to increase intermaterial area to the total energy dissipated during the flow. Substituting for $(\bar{D} : \bar{D})^{1/2} = (\varepsilon_T / (3v))^{1/2}$ [4] we get:

$$eff(t) = \frac{1}{a_v} \frac{da_v}{dt} \left(\frac{\varepsilon_T}{3v} \right)^{-1/2} \quad (5)$$

where ε_T represents the total energy used in the process, and $a_v^{-1} \cdot da_v/dt$ can be expressed using the minimum value of energy that can be used to obtain the same effect of mixing. To this end we will use the E-model and related rate of energy dissipation. This method we have used to compare performance of serpentine and meander micromixers. More strict

application of this method to obtain efficiency of serpentine [4] and the planar micromixer with diamond obstructions [5] is given below. As the test reaction system a simultaneous diazo- coupling between 1- and 2-naphtols (A1 and A2 respectively) and diazotized sulphanic acid (B) is applied [1]. The products are two mono-substituted dyes (ortho o-R) and (para p-R), a bisazo dye, S, and a single monoazo dye, Q. As a measure of the product distribution the yield of the competitive product Q is applied.

$$X_Q = \frac{c_Q}{c_{oR} + c_{pR} + c_Q + 2c_S} \quad (6)$$

Definition of X_Q expresses yield of Q relative to the limiting reagent B . The method of determination of efficiency is as follows; we plot the product distribution X_Q versus the experimental rate of energy dissipation $\varepsilon_{\Delta P} = Q\Delta P/(\rho V_R)$ where V_R is the reactor volume, and similarly X_Q is plotted against the theoretically determined ε value from the E-model. This way, for any experimental value X_Q , we can find efficiency of mixing $eff = \sqrt{\varepsilon / \varepsilon_{\Delta P}}$.

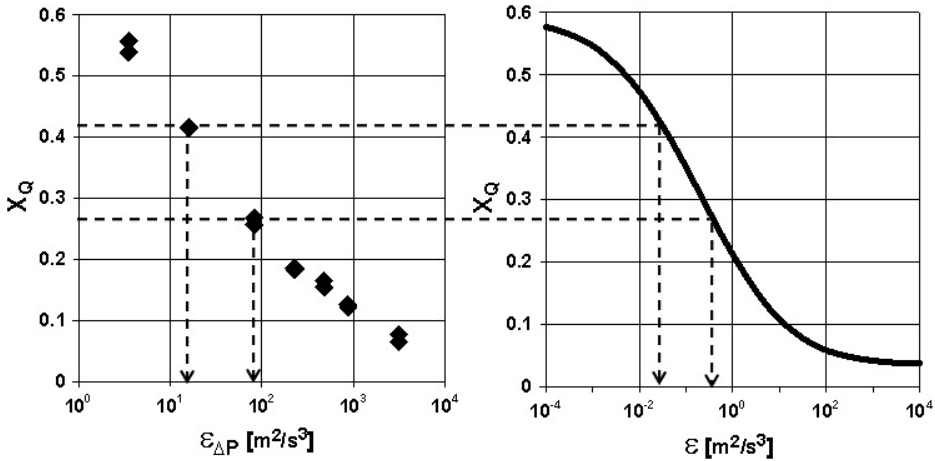


Fig. 4. X_Q characterizing the serpentine micromixer: (left) experimental data [4], (right) predictions of E-model

Rys. 4. X_Q charakteryzujące mikromieszalnik typu serpentina (po lewej) dane doświadczalne [4], (po prawej) obliczone przy użyciu modelu E

Figure 5 shows efficiency of mixing as a function of the energy applied to mix reacting solutions. As one can see mixing becomes more effective with increasing mixing power in this case; of course this results from more effective destabilization of the flow due to inertial effects, and resulting development of stretching and folding mechanisms. Consider now another mechanism of mixing at small scale in the passive planar micromixer with diamond obstructions designed for mixing at low Reynolds numbers [5]. The micromixer incorporates diamond-shape obstructions to break-up the flow and elongate material elements. Dimensions of micromixer channel are: width = 200 μm , height = 55 μm and diamond shaped obstructions are 100 μm x 90 μm in size.

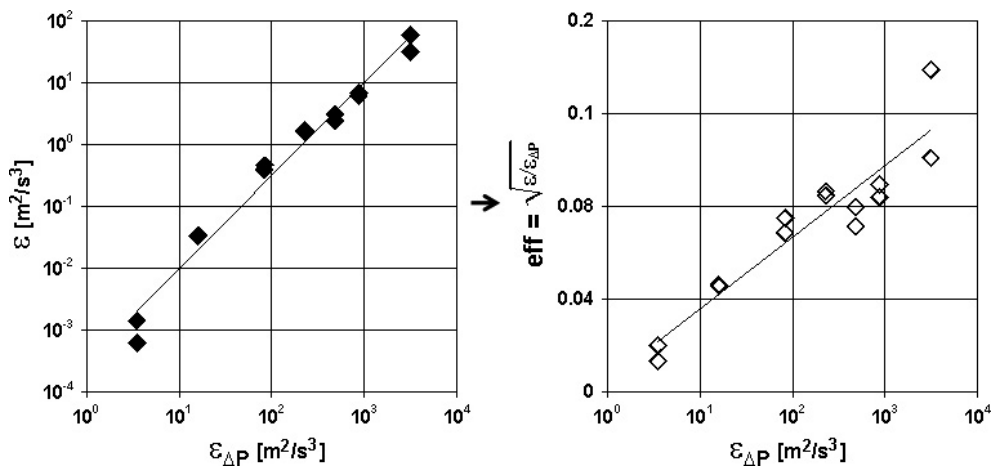


Fig. 5. Energy necessary for mixing in serpentine mixer: (left theoretical against experimental rate of energy dissipation, (right) effectiveness of mixing as a function of applied energy

Rys. 5. Energia mieszania w mieszalniku typu serpentina; (po lewej) relacja między eksperymentalną a teoretyczną wartością szybkości dysypacji energii, (po prawej) efektywność mieszania jako funkcja wydatku energii

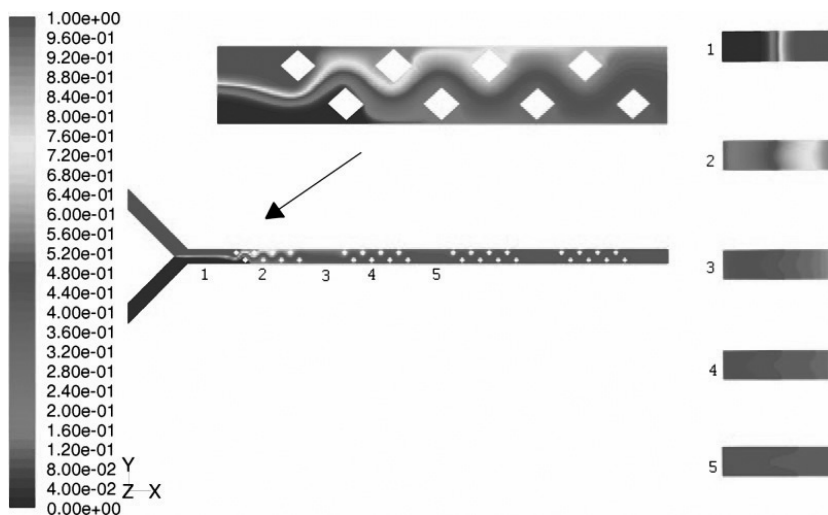


Fig. 6. Mixing of passive scalar in passive planar micromixer with diamond obstructions for $Re = 4.8$

Rys. 6. Mieszanie traseru w mikromieszalniku z przeszkodami w kształcie rombów dla $Re = 4,8$

Figure 6 presents geometry of this mixer and illustrates mechanism of mixing showing how homogenization of the passive scalar proceeds. Applying now the same procedure of application of diazo-coupling reactions as for the serpentine micromixer we get for this mixer results presented in Fig. 7. There is significant difference between Figs 5 and 7.

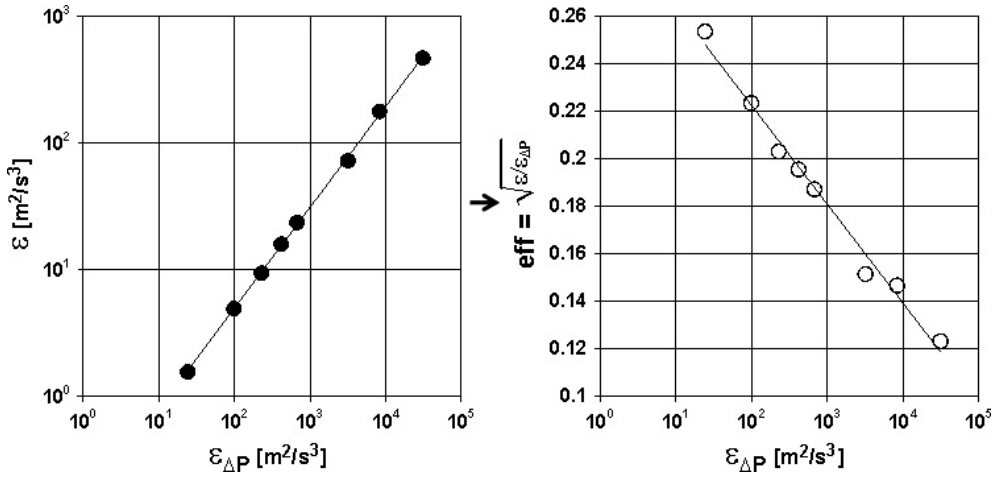


Fig. 7. Energy necessary for mixing : (left) theoretical against experimental rate of energy dissipation, (right) effectiveness of mixing as a function of applied energy. Diamond obstructions. Results for $4.8 < \text{Re} < 119.4$

Rys. 7. Energia mieszania; (po lewej) relacja między eksperymentalną, a teoretyczną wartością szybkości dyssypacji energii, (po prawej) efektywność mieszania jako funkcja wydatku energii. Przeszkody w kształcie rombów. Wyniki dla $4.8 < \text{Re} < 119.4$

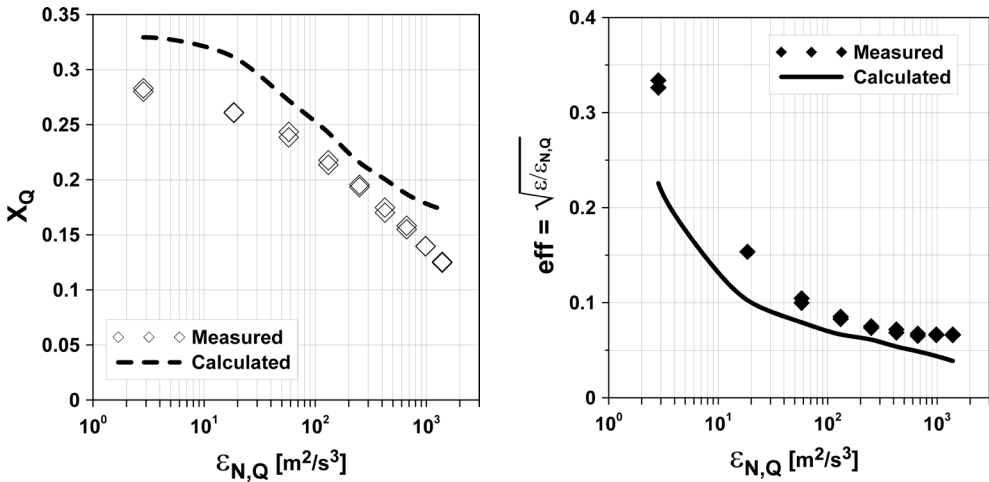


Fig. 8. Problem of effectiveness of mixing in the rotor-stator mixer: (left) effect of energy of mixing on product distribution X_Q , (right) effectiveness of mixing as a function of applied energy

Rys. 8. Problem efektywności mieszania w mieszalniku typu rptor-stator; (po lewej) wpływ energii mieszania na selektywność X_Q , (po prawej) efektywność mieszania jako funkcja wydatku energii

Presented results show that the highest efficiency (higher than 0.2) is for $Re < 10$, and it decreases in this case with increasing the flow rate and related input of energy per unit mass of the mixture, $\varepsilon_{\Delta P}$. This is because in this case increasing of the flow velocity creates inertial effects that increase more the friction factor than accelerate mixing. Similar phenomenon is observed when efficiency of the rotor-stator mixers is studied. Fig. 8 shows an effect of energy of mixing on the product distribution X_Q and related efficiency of mixing in the rotor-stator mixer. One can see as expected that with increasing energy input the product distribution X_Q decreases, so mixing becomes faster. However, it becomes less efficient as well. This results from features of the developed turbulence, namely, the ratio of the rate of viscous-convective mixing, proportional to $\varepsilon^{1/2}v^{-1/2}$, to the rate of inertial-convective mixing, proportional to $\varepsilon^{1/3}L^{-2/3}$ can be expressed by $\varepsilon^{1/6}L^{2/3}v^{-1/2} = Re_L^{-1/2}$, where L represents integral scale of turbulence and the Reynolds number Re_L is defined by $Re_L = u'L/v$, with u' being the root-mean-square velocity fluctuation. Clearly, for the same feed concentration energetic costs of decreasing the rate of creation of by-products increase more significantly in the range of small by-product concentrations and high energy than large by-product concentrations and smaller input of energy.

3. Test reactions in two-phase system

In this section we present preliminary results to prove that the parallel test reactions can be applied to study efficiency of mass transfer in two-phase liquid-liquid systems. In experiments the continuous phase was an aqueous solution of NaOH of concentration 0.005 mol/dm^3 and the dispersed phase was a solution of benzoic acid and ethyl chloroacetate in toluene, both of concentration 0.5 mol/dm^3 . Volume fraction of organic phase was 0.01. During experiments the reaction between the sodium hydroxide and either benzoic acid (instantaneous) or ethyl chloroacetate (fast) was localized in the aqueous phase. Experiments were carried out in the batch reactor of diameter 12 cm, equipped with the Silverson rotor-stator mixer. A four blade rotor of diameter 31.2 mm and height 12.45 mm, was used, and two stator geometries were investigated: standard emulsor screen (SES) and general purpose disintegrating head (GPDH) – Fig. 9ab. NaOH solution (990 cm^3) was present in the vessel and the organic solution (10 cm^3) was added to start the process. The drop size and pH were measured during experiments, and concentrations of ethanol and ethyl chloroacetate were measured after experiment using Gas Chromatography Mass Spectroscopy. The selectivity was defined as a fraction of moles of ester reacting with NaOH. Effects of rotor speed on the selectivity for both stators are presented on Figure 9c. Figure 9c shows that for the GPDH the selectivity is smaller, so mass transfer faster. The drops are also smaller for GPDH, for example for $N > 5000 \text{ rpm}$ $d_{32} = 5 \mu\text{m}$ for GPDH, and $d_{32} = 14 \mu\text{m}$ for SES. This shows that proposed system of parallel reactions can be used as a test system for studying efficiency of mass transfer in liquid-liquid systems.

One can conclude that the complex test reactions can be used to characterize energetic efficiency of mixing in homogeneous systems. First results are presented to show that the method can be extended to characterize mass transfer in two-phase liquid-liquid systems.

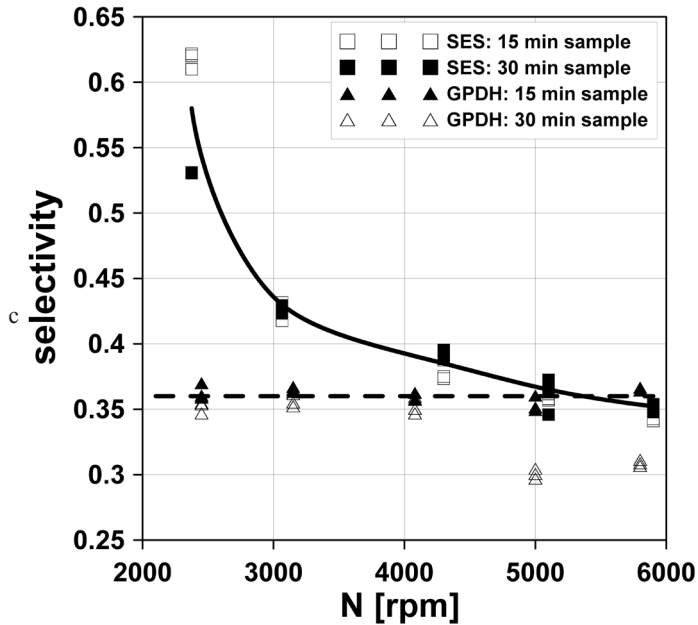
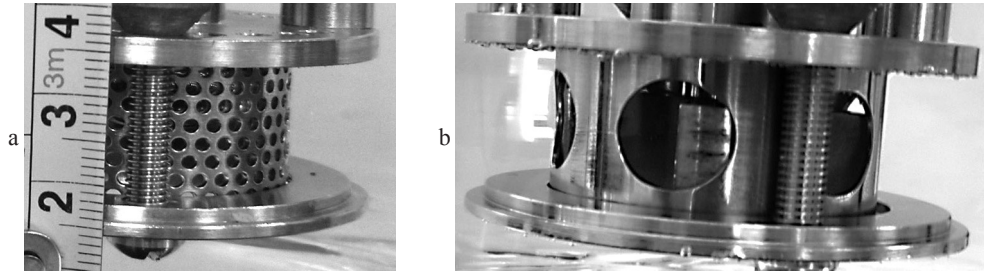


Fig. 9. Silverson geometries and results: (a) standard emulsor screen, SES (b) general purpose disintegrating head, GPDH (c) effect of rotor speed on selectivity

Rys. 9. Geometria i wyniki dla „mieszalnika Silverson: (a) standardowy stator SES (b) uniwersalny stator GPDH (c) wpływ częstotliwości obrotów rotora na selektywność

References

- [1] Bałdyga J., Bourne J.R., *Turbulent mixing and chemical reactions*, Wiley, Chichester 1999.
- [2] Bourne J.R., Yu S., *Ind. Eng. Chem. Res.*, **33**, 1994, 41-55.
- [3] Ottino J.M., *AIChE Journal*, **27**, 1981, 184-192.
- [4] Melecha K., Golonka L.J., Bałdyga J., Jasińska M., Sobieszuk P., *Sensor and Actuators B*, **143**, 2009, 400-413.
- [5] Bthagat A.A.S., Peterson E.T.K., Papautsky I., *J. Micromech. Microeng.*, **17**, 2007, 1017-1024.