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Application of the reactive tracer method to study chaotic mixing in a twisted bend mixer

Introduction

Mixing operations carried out in the industry should meet various requirements, e.g.: low energy input per unit mass, high production rate, effective use of mixer volume, narrow residence time, high product homogeneity or good product morphology in the case of multi-phase systems. It is very difficult to meet these practical demands when mixing highly viscous liquids; especially when these liquids suffer from thermal and mechanical degradation, as it often happens in the polymer, cosmetic or food industry. Continuous mixing of very viscous liquids is usually conducted in static mixers or extruders. However, a material processed in these devices may be exposed locally to very high shear rates resulting in its degradation. The material can also stick to mixing elements and screws (except for twin-screw extruders), causing fouling and reduction of mixing efficiency. If this happens, mixing has to be stopped in order to clean the mixer from unwanted deposits.

A good alternative to static mixers and extruders is a twisted bend mixer, often called a *chaotic* mixer. This is a tubular mixer constructed from multiple 90° pipe bends rotated alternately by 90°. During flow of a fluid through the pipe bend, a pair of symmetric Dean roll-cells is formed in the tube cross-section due to imbalance between centrifugal and viscous forces [*Mokrani et al., 1997*]. These roll-cells exist even at very low Reynolds numbers and induce material transport between the pipe centre and pipe walls. At higher Reynolds numbers but still in the laminar regime, flow destabilises and an additional pair of Dean vortices is formed. When the plane of the curvature of each pipe bend is alternately rotated with respect to the preceding one, then Dean vortices periodically change their orientation in space. As a result, fluid trajectories become chaotic in stationary three-dimensional laminar flow and mixing in the transverse direction is considerably improved [*Jones et al., 1989; Yamagishi et al., 2007*]. Furthermore, because there are no mixing elements or other obstacles inside the pipe bends, the head loss along the "chaotic" mixer is comparable to that in the straight pipe [*Changy et al., 2000*]. The operation of the twisted bend mixer has been studied mainly in the area of macromixing (residence time distribution, axial dispersion), flow resistance and heat transfer, e.g. [*Castelain et al., 2000; Changy et al., 2000*]. In contrast, studies of the effect of micromixing (mixing on the molecular scale) on the course of chemical reactions are still rare and limited to the use of just a single chemical reaction: [*Seader and Southwick, 1981; Sawyers et al., 1996; Boesinger et al., 2005*].

In the present work, a system of two competitive-parallel reactions: instantaneous acid-base neutralisation and fast ester hydrolysis has been used to investigate the effect of chaotic advection of micromixing in the twisted bend mixer operating in the laminar regime. Selectivity of test reactions, directly correlated with the course of micromixing, was determined with a fast analytical technique based on measurement of the pH of a post-reaction mixture.

Experimental setup

The experimental system used in the study is presented in Fig. 1. A diluted aqueous solution of hydrochloric acid and ethyl chloroacetate (main stream) was pumped into the twisted bend reactor by a gear pump. A concentrated solution of sodium hydroxide (side stream) was added centrally to the main stream by a syringe pump via a small pipe of 4 mm diameter. The reactor was assembled from

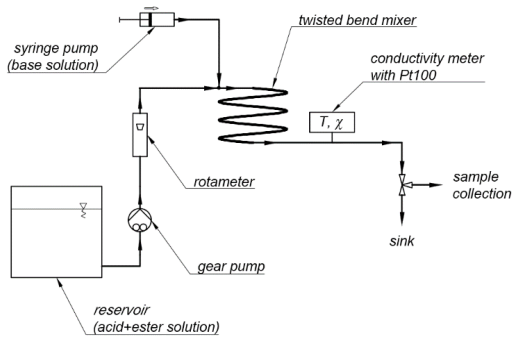

Fig. 1. Scheme of the experimental system

18/36 pipe bends connected by short straight sections (Fig. 2). The pipes had multilayer walls (polyethylene-aluminium-polyethylene) and their inner diameter was equal to 12 mm. The curvature radius of each 90° pipe bend was equal to 75 mm.

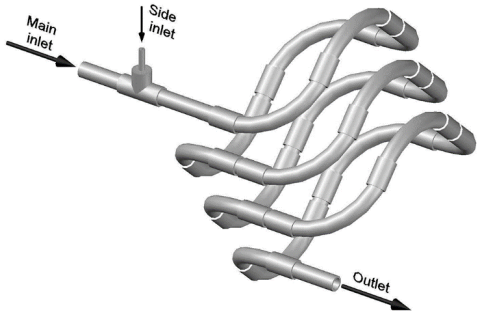

Fig. 2. The twisted bend mixer under study

The substrates introduced into the mixer react as follows:

$$NaOH + HCl \xrightarrow{k_1} NaCl + H_2O \quad (1)$$

$$NaOH + CH_2ClCOOC_2H_5 \xrightarrow{k_2} CH_2ClCOONa + C_2H_5OH \quad (2)$$

The first reaction is instantaneous $k_1 \approx 10^8$ m^{3}mol^{-1}s^{-1} (and completely controlled by mixing, while the second reaction is fast enough $k_1 \approx 0{,}033$ m^{3}mol^{-1}s^{-1} to be affected by mixing in the laminar flow regime [*Rożeń, 2009*]. Inlet molar streams of all substrates were equal to one another:

$$\dot{N}_{NaOH} = \dot{N}_{HCl} = \dot{N}_{ester} \quad (3)$$

$$\dot{N}_{NaOH} = Q_i\, c_{i0} \ \ [\text{mol}\cdot\text{s}^{-1}] \quad (4)$$

where Q_i [m^{3}s^{-1}] is the volumetric flow rate and c_{i0} [mol·m^{-3}] is the initial reactant concentration. *NaOH* supplied with the side stream was the limiting reactant. The final selectivity of the test reactions:

$$X = \frac{\dot{N}_{ester}}{\dot{N}_{NaOH}} \quad (5)$$

tends to zero (no ester hydrolysis $\Delta\dot{N}_{ester} \to 0$) when mixing becomes instantaneous.

The reactant solutions were pumped into the mixer with constant flow rates. As soon as conductivity and temperature of the outlet stream stabilized, a mixture sample was collected and analysed. Experiments were conducted at room temperature (~25°C).

Ester concentration in the post-reaction samples was determined by measuring the solution *pH* and solving a system of equations consisting of:
- ion charge balance

$$[Na^+] + [H_3O^+] = [Cl^-] + [RCOO^-] + [OH^-] \quad (6)$$

- water ionization constant equation

$$K_w = a_{H_3O^+} \cdot a_{OH^-} \quad (7)$$

- chloroacetic acid dissociation constant equation

$$K_A = \frac{a_{H_3O^+} \cdot a_{RCOO^-}}{a_{RCOOH}} \quad (8)$$

where a_i [mol·m^{-3}] denotes molar activity. The activity coefficients of all ions were obtained from the *Debye-Hückel* equation. It was also assumed that the activity coefficient of chloroacetic acid equals unity.

Results and discussion

Four series of experiments were conducted in the twisted bend reactor. The ratio of the volumetric flow rate of the main stream (Q_1) and the side stream (Q_2) was kept constant in each series, while the total volumetric flow rate (Q) through the mixer was changed from 2.6 up to 38 dm^3/h . The *Reynolds* and *Dean* numbers characterising the flow inside the chaotic mixer were defined as follows:

$$Re = \frac{4Q\rho}{\pi d\mu} \quad (9)$$

$$Dn = \sqrt{\frac{d}{R}} Re = 0.4Re \quad (10)$$

where d [m] – pipe diameter, R [m] – radius of pipe curvature, ρ [kg·m^{-3}] – density, μ [Pa·s] – dynamic viscosity. The initial concentration of acid and ester in the main stream was set to 1 mol·m^{-3}. The initial base concentration in the side stream was changed according to Eqs (3) and (4).

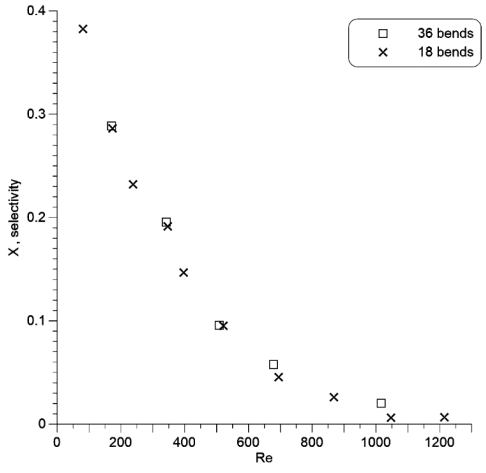

Fig. 3. Selectivity of the competitive-parallel reactions; $Q_1/Q_2 = 50$

In order to check if the mixer constructed from 18 pipe bends is long enough to achieve 100% conversion of the limiting reactant (NaOH), one series of experiments was conducted for a twice longer mixer made from 36 bends. A comparison of selectivity values obtained for the 18 and 36 bend mixer, presented in Fig. 3, indicates that doubling the mixer length had practically no effect on the product composition. In both cases the final selectivity monotonically decreases with the increasing *Reynolds* number. The final selectivity falls from 38% for Re = 80 (Dn = 32) to 5% for Re ≈ 700 (Dn = 280) and further to 0.6% for Re = 1215 (Dn = 486). These results prove that the chaotic mixer can be very effective for intermediate laminar flows, as it was earlier suggested in [*Boesinger et al., 2000*].

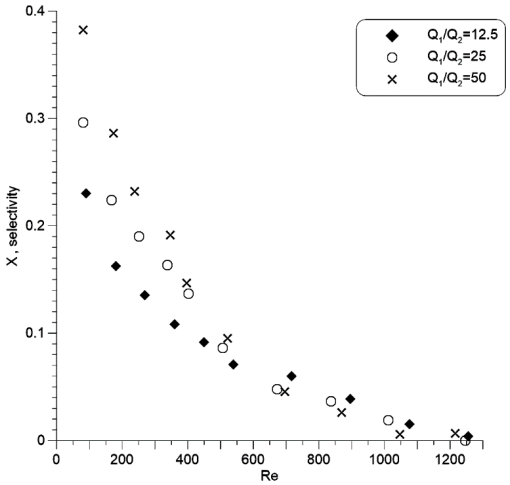

Fig. 4. Selectivity of the competitive-parallel reactions; 18 pipe bends

The final selectivity of the test reactions and consequently the rate of mixing on the molecular scale is also influenced by the ratio of volumetric flow rates (Fig. 4). This is so because it is more difficult to mix a small amount of a highly concentrated solution of one reactant with a large volume of a diluted solution of other reactants than in the case when differences between solution volumes and reactant concentrations are smaller. The lower the *Reynolds* number (the slower mixing rate) is, the bigger the magnitude of this effect is observed.

Conclusions

Experiments with competitive-parallel reactions have proven that the reactive tracer method is well suited to study micromixing in the twisted bend reactor in the laminar flow regime.

The final selectivity of the test reactions was found to be dependent on two key process parameters: the *Reynolds* number and the ratio of volumetric flow rates of the reactant solutions.

Further study should focus on two research fields: a detailed comparison of the characteristic of the chaotic mixer and other on-line mixers used in the industry, and on application of the chaotic mixer to non-*Newtonian* or multi-phase systems.

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