ELSEVIER

Chemical Engineering Journal 121 (2006) 147–152

Chemical Engineering Journal

www.elsevier.com/locate/cej

Short communication

Characterization of micromixing efficiency in rotating packed beds by chemical methods

Hai Jian Yang, Guang Wen Chu, Yang Xiang, Jian Feng Chen [*]

Research Center of the Ministry of Education for High Gravity Engineering and Technology, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

Received 12 January 2006; received in revised form 21 April 2006; accepted 26 April 2006

Abstract

Study of mixing at the molecular scale (micromixing) gives an indication of the best way to carry out important processes such as polymerization, crystallization and competing fast chemical reactions. Rotating packed bed (RPB), in which gravity is replaced by a centrifugal force, plays an important role on intensification of mixing and transfer. In this study, by means of the diazo coupling and iodide–iodate test reactions, the micromixing efficiency of RPB was characterized at various operational conditions (e.g. rotational speed, liquid flow rate and reagent concentration). With a special configuration RPB which can achieve sampling along the radial position, the importance of inlet region of packing in RPB was experimentally confirmed firstly. Compared with other mixing devices, RPB is superior in improving micromixing efficiency.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Micromixing; Rotating packed bed; Iodide–iodate; Diazo coupling

1. Introduction

In industrial practice, some processes (i.e. precipitation, polymerisation, etc.) consist of mixing two liquid streams which react in certain reactors. It is well known that the way in which reagents are mixed can have a large influence on the selectivity, yield and quality of final products of a chemical reaction [1]. Micromixing, or mixing at the molecular scale, has been shown to be primarily responsible for this influence. Thus, it is important to develop experimental methods in order to characterize micromixing. Due to indistinguishability and instrumental limitations, the experimental methods employed for characterizing micromixing efficiency based on physical phenomena (e.g. optical and conductometric methods), have been deemed limited. Hence, chemical methods were used to characterize the micromixing efficiency. By taking advantage of the sensitivity and flexibility of chemical reactions, the micromixing efficiency, furthermore the expression for the characteristic mixing time can be determined. A good test reaction should fulfill several conditions: simple reaction scheme in order to avoid analysis of many products; easy analysis of reaction products; known reaction kinetics, faster than mixing rate; good sensitivity and reproducibility [2]. The most current systems diazo coupling and iodide–iodate test reactions satisfy these criteria pretty well.

Rotating packed bed (RPB) is also known as HIGEE, an acronym for high gravity. It has been over two decades since the first patent on RPB was filed by Ramshaw and Mallison, Imperial Chemical Industried, U.K. [3]. The height equivalent of a theoretical plate (HETP) of RPB can be as low as 1–2 cm and that a volume reduction by 2–3 orders of magnitude compared to that of conventional packed columns can be attained [4]. So the miniaturization of equipment stimulated great interest in RPB unit. RPBs have been applied to processes such as desorption, absorption, distillation, and ozone oxidation, etc [5–8]. In recent years, there has been an emerging trend towards the applications of the RPB for the synthesis of drug nanoparticles and inorganic nanoparticles [9,10]. These pioneering efforts open up the great potential future for RPB as a novel reactor for specific chemicals and advanced materials as well as nanodrugs.

However, although gained great successes in various applied fields, the elementary studies on RPB are still limited, which restrict its further application. Furthermore, the inlet region that lies within the inner periphery of the packing in RPB has long been considered to play a crucial role on influencing mixing and mass transfer [11]. In this work, in order to validate the importance of inner periphery of the packing in RPB, a special

---

[*] Corresponding author. Tel.: +86 10 64446466; fax: +86 10 64434784.
E-mail address: chenjf@mail.buct.edu.cn (J.F. Chen).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.04.010

Nomenclature

a	volumetric ratio
E	total absorption
k_2	rate constant of Dushman reaction ($\mathrm{mol^{-4}\,L^4\,s^{-1}}$)
K_B	equilibrium constant ($\mathrm{L\,mol^{-1}}$)
N	rotational speed (rpm)
R	radial distance of the vertical-axis RPB (mm)
T	temperature (K)
V	flow rate ($\mathrm{L\,min^{-1}}$)
X_S	segregation index
$[Z]$	concentration of reactant Z ($\mathrm{mol\,L^{-1}}$)

Greek letters

δ	path length of spectrophotometer (m)
ε_R, ε_S	extinction coefficients of product R and S at wavelength λ ($\mathrm{m^2\,mol^{-1}}$)
μ	ionic strength ($\mathrm{mol\,L^{-1}}$)

configuration of RPB was designed to achieve radial sampling. Additionally, by adoption the diazo coupling and iodide–iodate test reactions, respectively, micromixing efficiency in RPBs was characterized qualitatively. The effects of operational conditions (e.g. rotational speed, flow rates, reagent concentrations) on micromixing efficiency (indicated by segregation index X_S) were investigated.

2. Experimental

2.1. Experimental set-up

The RPB unit generally consists of rotor (with packing attached on it), casing, liquid inlet or distributor, liquid outlet, gas inlet and gas outlet, motor etc [12]. Fig. 1 shows sketches of two RPB units (parameters of the PRB units are given in Table 1), one having a rotor with a horizontal axis and the other having a rotor with a vertical axis. Corresponding to them, experiments were carried out with the diazo coupling and iodide–iodate test reactions respectively. In order to validate the importance of the inlet region, the vertical-axis RPB was designed to achieve sampling along the packing radius. The experimental flow chart and the operating parameters are shown in Fig. 2 and Table 2, respectively.

Table 1
Specification of RPB used in this study

Horizontal-axis RPB	
Inner diameter of rotor (mm)	50
Outer diameter of rotor (mm)	150
Diameter of casing (mm)	180
Axial height of packing (mm)	50
Diameter of Injection (mm)	A Ø6, B Ø6
Material of packing	Wire mesh
Voidage of packing	97%
Wire cross section ($\mathrm{mm^2}$)	0.3 × 0.7
Vertical-axis RPB	
Inner diameter of rotor (mm)	60
Outer diameter of rotor (mm)	446
Diameter of casing (mm)	780
Axial height of packing (mm)	50
Diameter of Injection (mm)	A 3 × Ø1.5, B 4 × Ø3
Material of packing	Wire mesh
Voidage of packing	97%
Wire cross section ($\mathrm{mm^2}$)	0.3 × 0.7

Table 2
Operating parameters adopted in this study

Horizontal-axis RPB with diazo coupling system	
Volumetric flow rate ($\mathrm{L\,min^{-1}}$)[a]	0.35–2.45
Flow rate ratio	20–80
Rotational speed (rpm)	600–1500
Vertical-axis RPB with iodide–iodate system	
Volumetric flow rate ($\mathrm{L\,min^{-1}}$)	6.83–10.25
Flow rate ratio	7.2–12
Rotational speed (rpm)	600–1200

[a] Volumetric flow rate is the total flow rate of the two reagent streams.

2.2. The diazo coupling test

In 1980, the team of Bourne in Zürich proposed a first test with the 1-naphthol, based on a system of concurrent consecutive reactions of diazo-coupling between 1-naphthol and diazotized sulphanilic acid [13]. The test may be written as:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{R} \tag{1}$$

$$\mathrm{R} + \mathrm{B} \xrightarrow{k_2} \mathrm{S} \tag{2}$$

where A, B, R, S are 1-naphthol, diazotized sulphanilic acid, monoazo dye and bisazo dye, respectively. At $T = 298$ K and pH 10.0, the rate constants of these reactions k_1 and k_2 are: $k_1 = 7300\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$, $k_2 = 1.56\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$. The reaction products R and S can be quantitatively analyzed by spectrophotometry. Product mixtures were analyzed by assuming that R and S absorb independently and that the Lambert–Beer law is valid at the concentration levels used. Thus, at a given wavelength, the total absorption over a path length δ is:

$$E = \varepsilon_R[\mathrm{R}]\delta + \varepsilon_S[\mathrm{S}]\delta$$

$$\frac{E}{\varepsilon_R\delta} = [\mathrm{R}] + [\mathrm{S}]\frac{\varepsilon_S}{\varepsilon_R}$$

By measuring total absorption E at various wavelengths, a plot or a linear regression of $E/\varepsilon_R\delta$ against $\varepsilon_s/\varepsilon_R$ is prepared. [R] and [S] follow as intercept and slope of the plot. The segregation index (X_S) was defined as the selectivity of secondary product S:

$$X_S = \frac{2[\mathrm{S}]}{2[\mathrm{S}] + [\mathrm{R}]}$$

In the following years, the system has been improved and took the more complex final form of a coupling of two systems: a system of two competitive parallel reactions and a system of two competitive consecutive reactions [14]. To void the large error in the estimation of X_S which caused by ill-conditioned matrix

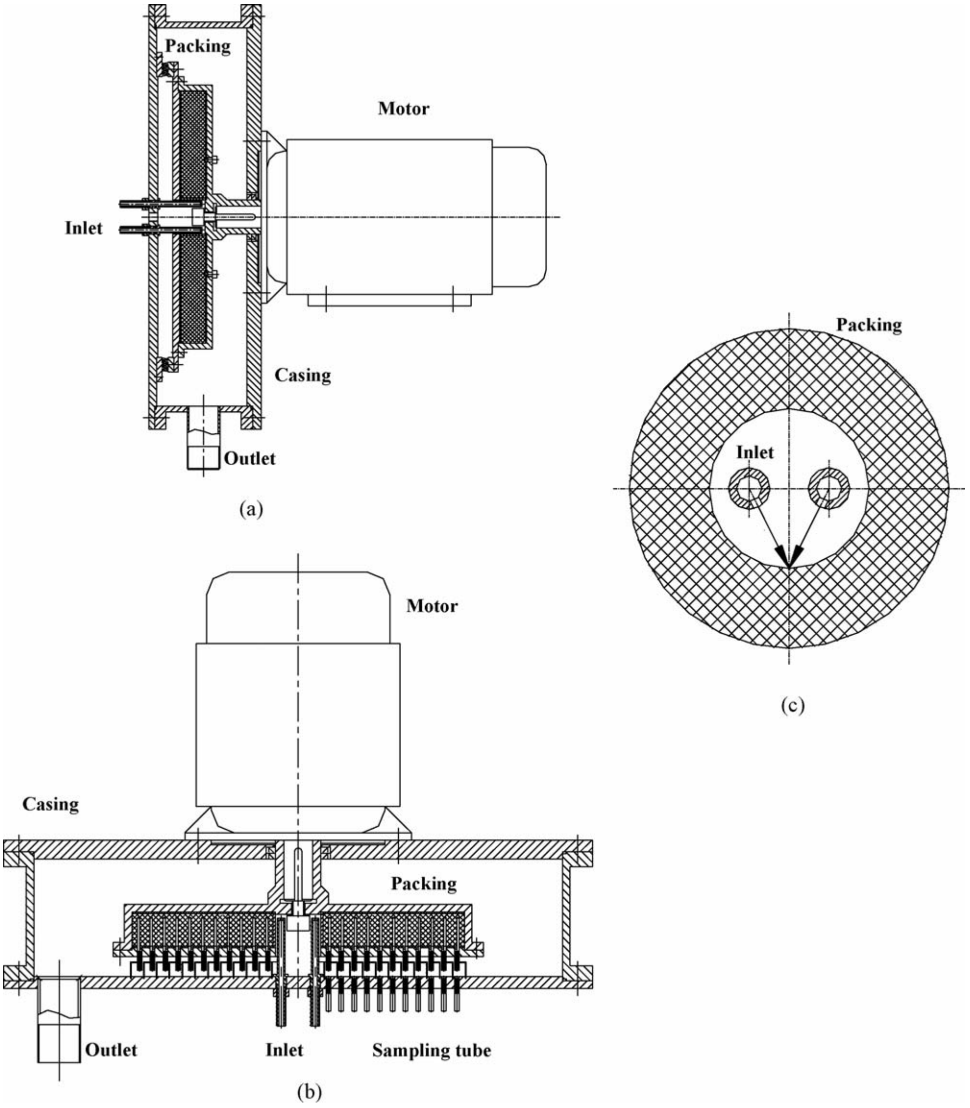

Fig. 1. Sketch of RPB units: (a) horizontal-axis RPB (assessed with diazo coupling test); (b) vertical-axis RPB (assessed with iodide–iodate test); (c) enlarging of the injection zone.

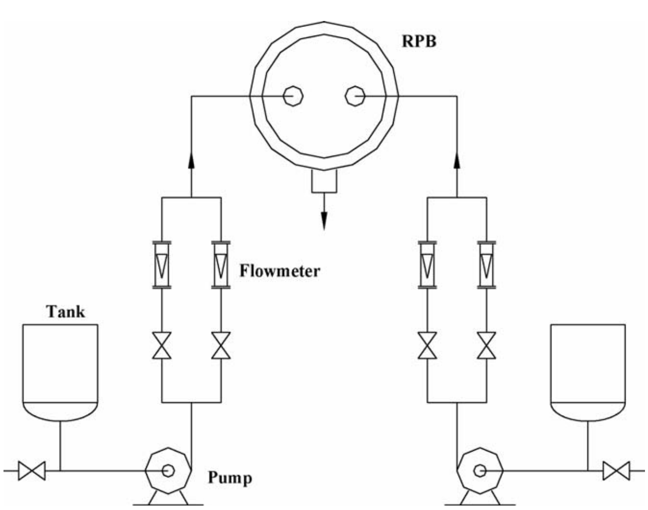

Fig. 2. The experimental flow chart.

system [15], The diazo coupling between 1-naphthol alone and diazotized sulphanilic acid was still adopted in this study.

In this work, the reagents concentration adopted ranged between 0.0125 mol/m^3 and 0.075 mol/m^3 and the stoichiometric ratio of A and B was 1.0.

2.3. The iodide–iodate test

The iodide–iodate test was developed by Villermaux's group (Nancy Cedex, France) and first presented in detail by Fournier et al. in 1996 [2]. From then on, the test was adopted widely to assess the micromixing efficiency in various reactor configurations. The iodide–iodate test consists of the following three chemical reactions.

$$H_2BO_3^- + H^+ \Leftrightarrow H_3BO_3 \tag{3}$$

$$5I^- + IO_3^- + 6H^+ \Leftrightarrow 3I_2 + 3H_2O \tag{4}$$

$$I^- + I_2 \Leftrightarrow I_3^- \tag{5}$$

The first reaction is quasi-instantaneous. The rate of the second reaction (i.e. Dushman reaction) is given by

$$R_2 = k_2 C_{I^-}^2 C_{IO_3^-} C_{H^+}^2$$

where k_2 depends on the ionic strength μ of the medium such as

$$\mu < 0.166\,\text{M}, \quad \log(k_2) = 9.28105 - 3.664\mu^{1/2}$$

$$\mu > 0.166\,\text{M}, \quad \log(k_2) = 8.383 - 1.5112\mu^{1/2} + 0.23689\mu$$

The third reaction is an equilibrium reaction and the equilibrium constant can be written as

$$\log K_B = \frac{555}{T} + 7.355 - 2.575 \log T$$

where T is the reaction temperature.

In the experiments, the test procedure consists of adding a small quantity of sulfuric acid (in stoichiometric deficiency) with the concentration of 0.08–0.15 mol L^{-1}, and a mixture of iodate (0.0116 mol L^{-1}), iodide (0.00233 mol L^{-1}) and borate ions (0.0909 mol L^{-1}) into the RPB simultaneously. Under perfect mixing conditions, the injected acid is instantaneously dispersed in the reactive medium and consumed by borates according to neutralization reaction (1), which is infinitely faster than reaction (2). On the other hand, the aggregation of acid involves a local over concentration of acid, which, after complete consumption of local $H_2BO_3^-$, can react with the surrounding iodide and iodate ions to produce iodine. The selectivity of iodine is thus a measure of the fluid segregation state. The amount of produced I_3^- can be detected via the use of the spectrophotometer at 353 nm (UV-2501PC, Shimadzu corporation, Japan). Here, the segregation index (X_S) is defined as:

$$X_S = \frac{Y}{Y_{ST}} \tag{6}$$

with

$$Y = \frac{2(n_{I_2} + n_{I_3^-})}{n_{H_0^+}} \quad \text{and} \quad Y_{ST} = \frac{6(IO_3^-)_0}{6(IO_3^-)_0 + (H_2BO_3^-)_0},$$

where Y is the ratio of acid mole number consumed by reaction (2) divided by the total acid mole number injected and Y_{ST} is the value of Y in total segregation case when micromixing process is infinitely slow. The value of X_S should be $0 < X_S < 1$. $X_S = 0$ and $X_S = 1$ indicate maximum micromixing and total segregation respectively.

In 2001, Guichardon et al. [15] compared the two most current systems using the batch experiments and drew the following conclusions. As regards facility to experimental procedures and analyses, the best system is the iodide–iodate reaction. As regards sensitivity to micromixing effects, the diazo coupling between 1-naphthol alone and diazotized sulphanilic acid is the most powerful in the mixing conditions tested.

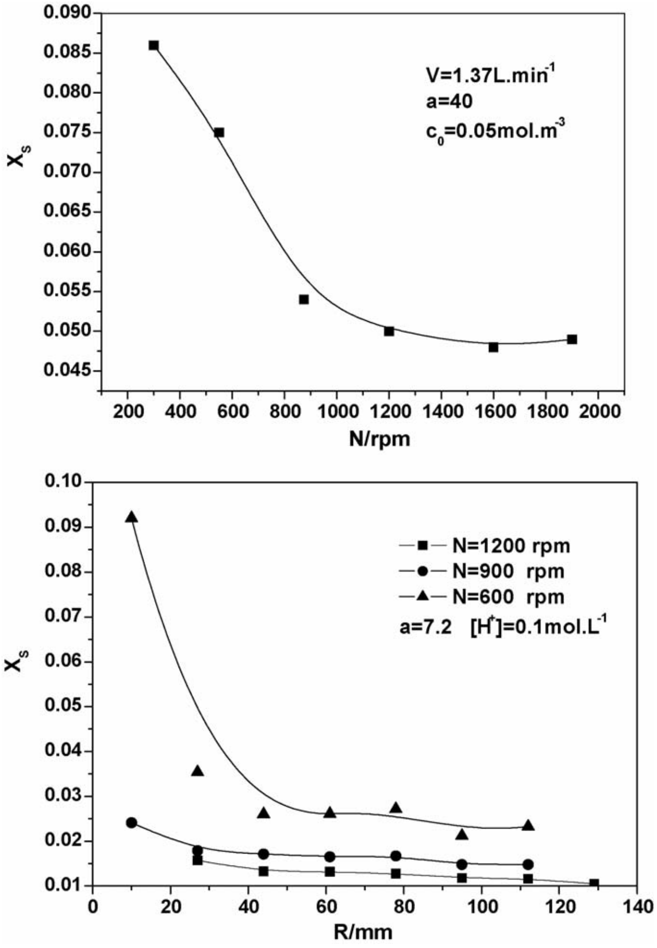

Fig. 3. Effects of rotational speed on X_S: (above) results with diazo coupling test; (below) results with iodide–iodate test.

3. Results and discussion

3.1. Effects of rotational speed on X_S

Fig. 3 illustrates the effects of rotational speed on X_S at two apparatuses with different test reactions. Under a specific condition, with increasing the rotational speed, X_S decreased rapidly and a steady value was reached at about 1000 rpm. The results indicate that a higher rotational speed, namely a larger centrifugal force could enhance micromixing efficiency in the RPB. The reasons can be summarized as follows. First, greater relative velocity among all kinds of liquid elements (e.g. droplet, thread, film) and packing are affected with an augment in rotational speed. Consequently, vigorous impingement and homogeneous dispersion of the liquids will occur, hence resulting in good mixing efficiency (smaller X_S). Second, the residence time distribution (RTD) of the liquid will decrease with an increase in rotational speed [16]. In Burn's visual study [17], the liquid flow in the packing is fan-shaped, hence inferring that it is hard for two liquid elements to collide during the flow in the packing space. Most of the collisions between liquid elements occur when they are captured by the packing. The shorter the RTD, the shorter the time interval needed for the two liquid elements

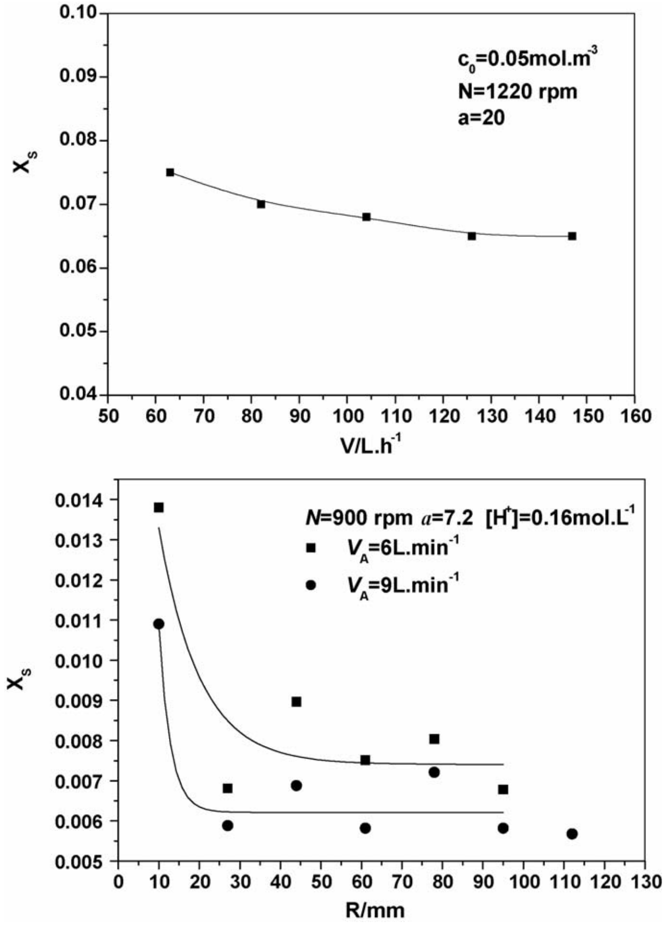

Fig. 4. Effects of liquid flow rates on X_S: (above) results with diazo coupling test; (below) results with iodide–iodate test.

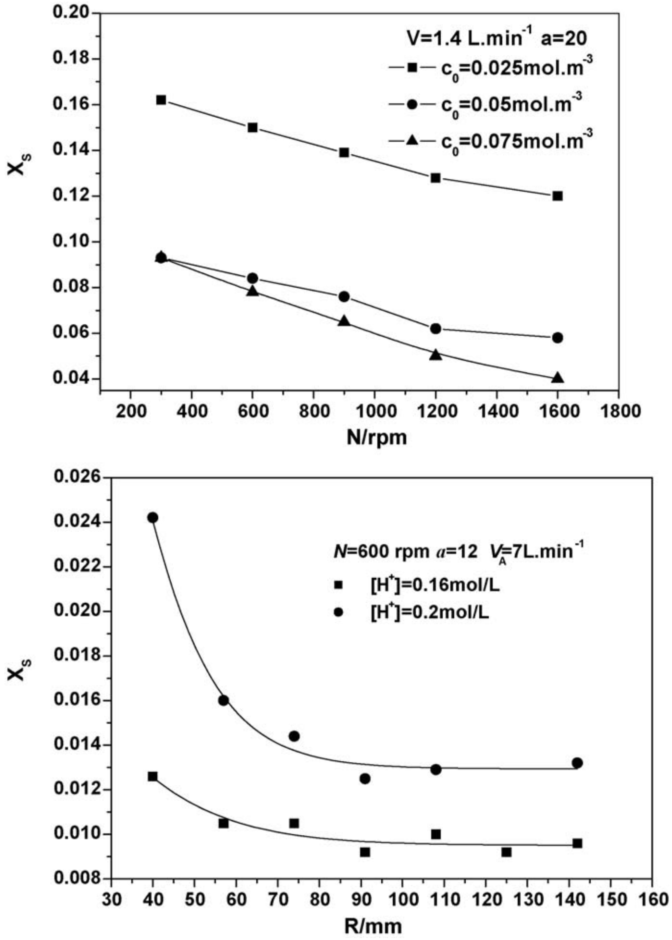

Fig. 5. Effects of reagent concentration on Xs: (above) results with diazo coupling test; (below) results with iodide–iodate test.

to be captured by the packing. So the micromixing rate and coalescence–redispersion frequency of the liquid elements were accelerated.

Furthermore, from Fig. 3, a significant conclusion can be drawn. The inner periphery of the packing in RPB plays a crucial role on the mixing and reaction processes. In this inlet region, the injection flow from the liquid distributors makes contact with the packing, and is then twisted and broken up by the rotary packing. The interaction is violent because of the great relative velocity and induces a homogeneous mixing between liquid elements. The above conclusion has practical applications in industry. By optimizing the thickness of packing, both the cost of packing and the energy consumption can be reduced.

3.2. *Effects of liquid flow rates on X_S*

It is valuable to study the effect of liquid flow rates on micromixing efficiency for increasing reactor's throughput. Fig. 4 shows the influence of liquid flow rates on X_S at different experimental conditions. It can be appreciated that X_S decreases slightly with increasing liquid flow rates. For a specific liquid distributor, a higher liquid flow rates causes a higher injecting velocity, furthermore a larger relative velocity between liquids and packing and a more homogeneous mixing. In addition, the residence time distribution also decreases with increasing liquid flow rates. As analogous to the effect of rotational speed, a shorter RTD will mean an increase in the coalescence-redispersion frequency between liquid elements and micromixing rate. Otherwise, the volumes of liquid elements are enlarged slightly as increasing of flow rates, which delay the mixing process of liquid elements and reduce the mixing efficiency. Integrating the above effects, X_S decreases slightly with increasing liquid flow rates.

3.3. *Effects of reagent concentrations on X_S*

It is surprising that the effects of reagent concentrations on X_S in different test reactions are greatly inconsistent (Fig. 5). With the iodide–iodate test reactions, just similar as other mixers, X_S increases with the increasing of reagent concentration. Upon entry into the packing space, the liquid stream is fragmentized and dispersed into a lot of smaller entities (i.e. droplets). The reactions take place under varying degrees of reactant segregation. Obviously, with the augment of reagent concentration, the local concentration segregations among different reagent entities become worse and X_S increases accordingly. However, with the diazo coupling test reactions, X_S decreases as increasing the reagent concentrations. During flow in the packing, reagent liquids are broken up violently by the rotary packing and dispersed homogeneously as very small entities. So these liquid elements have very large interface. As we all know, most organic compounds have the phenomenon of surface absorption. This is a kind of segregation of small entities. Generally, relationship between absorption quantity and concentration can be described with the absorption equation of Langmuir. As the increasing of reagent concentrations, the absorption quantity increases and reaches a steady value at last. However, the percent of absorption quantities in the total reagent liquid decreases continuously. That is to say, the degree of segregation in the small entities decreases continuously. So X_S decrease as increasing of reagent concentrations.

3.4. Comparison with other mixing devices

The diazo coupling and iodide–iodate test reactions have been used widely since their emergences to assess micromixing efficiency of mixing devices with various configurations. At the similar experimental conditions, X_S of Tee mixer [18] or tubular reactor [19] assessed with the diazo coupling test reactions are generally larger than that of RPBs'. Monnier et al. [20] studied the effect of ultrasound on micromixing in a continuous flow cell by adopting the iodide–iodate test reactions. They found that increasing ultrasound power could improve micromixing efficiency, where X_S varied from 0.03 to 0.07 were obtained. In this study, with the same reactant concentrations and liquid flow ratio, our experimental results show that X_S can be as low as 0.01, depending on the rotational speed. From above discussion, we can conclude that the RPB, with the aid of the centrifugal force, could improve micromixing efficiency significantly. Meanwhile, as a continuous mixer or reactor, the large throughout of RPB will further widen its applications in the chemical industry and other industrial domains.

4. Conclusions

This work characterized the micromixing efficiency in RPB qualitatively by adopting the diazo coupling and iodide–iodate test reactions. Through a throughway method with specially designed RPB configuration, the importance of inlet region in RPB packing was experimentally confirmed firstly. The effects of different operating conditions on segregation index (X_S) show that: X_S decreases distinctly with increasing rotational speed but decreases slightly as the augment of flow rates; the effects of different test reactions on X_S appear inconsistent because of the surface absorption of organic reagents. Compared with other mixing devices, RPB has a distinct advantage in improving micromixing efficiency, and maybe of many novel applications in the chemical and related industries.

Acknowledgement

This work was supported by the National Natural Science Foundation of People's Republic of China (Nos. 20236020 and 20325621).

References

[1] J. Baldyga, R. Pohorecki, Turbulent micromixing in chemical reactors-a review, Chem. Eng. J. 58 (1995) 183.

[2] M.C. Fournier, L. Falk, J. Villermaux, A new parallel competing reaction system for assessing micromixing efficiency-experimental approach, Chem. Eng. Sci. 51 (1996) 5053.

[3] C. Ramshaw, R.H. Mallinson, Mass Transfer Process, U.S. Patent 4,283,255 (1981).

[4] C. Ramshaw, "HiGee" distillations – an example of process intensification, Chem. Eng. 2 (1983) 389.

[5] R. Fowler, A.S. Khan, VOC Removal with a rotary air stripper, AIChE Annual meeting, New York, USA, 11 (1987) 15-17.

[6] C.C. Lin, W.T. Liu, C.S. Tan, Removal of carbon dioxide by absorption in a rotating packed bed, Ind. Eng. Chem. Res. 42 (2003) 2381.

[7] Y. Kelleher, J.R. Fair, Distillation studies in a high-gravity contactor, Ind. Eng. Chem. Res. 35 (1996) 4646.

[8] C.C. Lin, W.T. Liu, Ozone oxidation in a rotating packed bed, J. Chem. Technol. Biot. 78 (2003) 138.

[9] J.F. Chen, M.Y. Zhou, L. Shao, Y.H. Wang, Y. Jimmy, Nora Y.K. Chew, H.K. Chan, Feasibility of preparing nanodrugs by high-gravity reactive precipitation, Int. J. Pharm. 269 (2004) 267.

[10] J.F. Chen, Y.H. Wang, F. Guo, C. Zheng, Synthesis of nanoparticles with novel technology: high-gravity reactive precipitation, Ind. Eng. Chem. Res. 39 (2000) 948.

[11] K. Guo, F. Guo, Y.D. Feng, J.F. Chen, C. Zheng, C.G. Nelson, Synchronous visual and RTD study on liquid flow in rotating packed-bed contactor, Chem. Eng. Sci. 55 (2000) 1699.

[12] D.P. Rao, A. Bhowa, P.S. Goswami, Process intensification in rotating packed beds (HIGEE): an appraisal, Ind. Eng. Chem. Res. 43 (2004) 1150.

[13] J.R. Bourne, F. Kozicki, P. Rys, Mixing and fast chemical reaction I: test reactions to determine segregation, Chem. Eng. Sci. 36 (1981) 1643–1648.

[14] J.R. Bourne, O.M. Kut, J. Lenzner, An improved reaction system to investigate micromixing in high-intensity mixers, Ind. Eng. Chem. Res. 32 (1992) 949–958.

[15] P. Guichardon, L. Falk, M. Andrieu, Experimental comparison of the iodide–iodate and the diazo coupling micromixing test reactions in stirred reactors, Trans IchemE. 79 (2001) 906–914.

[16] K. Guo, A study on liquid flowing inside the Higee rotor, Ph.D. dissertation, Beijing University of Chemical Technology, 1996.

[17] J.R. Burns, C. Ramshaw, Process intensification: visual study of liquid maldistribution in rotating packed beds, Chem. Eng. Sci. 51 (1996) 1347.

[18] T. Guray, A study of micromixing in Tee mixers, Ind. Eng. Chem. Res. 26 (1987) 1184–1193.

[19] J.R. Bourne, G. Tovstiga, Micromixing and fast chemical reactions in a turbulent tubular reactor, Chem. Eng. Res. Des. 66 (1988) 26–30.

[20] H. Monnier, A.M. Wilhelm, H. Delmas, Effects of ultrasound on micromixing in flow cell, Chem. Eng. Sci. 55 (2000) 4009.