Micromixing in a Rotor–Stator Spinning Disc Reactor

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ABSTRACT: This paper presents the micromixing times in a rotor–stator spinning disc reactor. Segregation indices are obtained at different rotational speeds performing the Villermaux–Dushman parallel-competitive reaction scheme. Consequently, the corresponding micromixing times are calculated using the engulphment model, while considering the self-engulphment effect. It was found that the segregation index decreases with an increasing disc speed. Furthermore, for the investigated operational conditions, the estimated micromixing times are in the range of $1.13 \times 10^{-5}$ to $8.76 \times 10^{-3}$ seconds, in agreement with the theoretical dependency on the energy dissipation rate of $e^{-35}$. In a rotor–stator spinning disc reactor it is thus possible to further continue the theoretical trend of decreasing micromixing times with very high levels of energy dissipation rates that are unattainable in traditional types of process equipment.

INTRODUCTION

The worldwide population has grown dramatically over the last century, and with it the need for transformation of raw materials into finished products. Process Intensification (PI) is considered to be the framework under which to achieve the required increase in production capacities, while simultaneously converting traditional processes into their more innovative, decentralized, and more sustainable counterparts. Under process intensified conditions, processes become less hazardous, more environmentally friendly, and more profitable while maintaining or even increasing quality. This can be achieved by designing novel types of process equipment that overcome classical limitations with regard to heat and mass transfer. In that way, new process windows open up at elevated pressures and temperatures in which reactions can be performed at their intrinsic kinetic conditions.1

A novel type of chemical reactor that significantly increases mass and heat transfer rates is the rotor–stator spinning disc reactor (rs-SDR). This device, schematically depicted in Figure 1, utilizes centrifugal forces in a high-shear environment to intensify single and multiphase processes. The reactor consists of a rotating disc enclosed by a fixed cylindrical housing (the stator), with a distance between them of only a few millimeters. The high rotational speed of the disc, up to 2000 rpm, generates a large velocity gradient in the narrow rotor–stator gap. As a result, a high amount of energy is transferred from the rotor to the reactor contents, involving high levels of turbulence intensity, which in turn increases the heat and mass transfer coefficients.2 Simultaneously, the high shear forces in the reactor fluid lead to the very fine dispersion of droplets and bubbles with a large specific surface area. It is the combination of the high surface area and increased mass/heat transfer coefficients that lie at the heart of the rs-SDR’s performance. Previous investigations have shown that the values for the overall gas–liquid mass transfer coefficient per unit volume of gas in an rs-SDR are a factor 40 higher compared to conventional bubble columns.34 A factor 25 increase in the liquid–liquid mass transfer coefficient was similarly observed in comparison with packed columns,5 while liquid–solid6 and heat transfer7 were also enhanced. By overcoming heat and mass transfer limitations, the rs-SDR is thus exceptionally well suited for performing highly exothermic or dangerous reactions in short residence times using a small but efficient reactor volume, making processes inherently safer.

Since reaction rates of mixing controlled reactions are significantly increased in an rs-SDR, the quality of mixing becomes relevant in determining selectivity. When reagents compete for a limiting reactant, the micromixing time should be lower than the reaction time in order to promote the progression of the fastest reaction. Also, for extremely exothermic reactions, a poor micromixing time may lead to local hot spots and loss of selectivity. A thorough understanding of the mechanism behind micromixing and the effect of hydrodynamics are thus of paramount importance in designing and developing rs-SDR systems. Hinrichsen and Jacobsen (2012)8 performed measurements of micromixing times in a more traditional type of spinning disc reactor. In this configuration a spinning disc is freely rotating in a larger container, while an impinging liquid feed flows radially off the disc in a thin boundary layer. The reported micromixing times are of the order of milliseconds. Later in 2015, Haseidl et al. studied the performance of an rs-SDR,9 and their results indicate that better mixing is achieved at higher rotational speeds.

H$_2$BO$_3$ + H$^+$ $\rightarrow$ H$_3$BO$_3$

IO$_3^-$ + 5I$^-$ + 6H$_2$O $\rightarrow$ 3I$_2$ + 3 H$_2$O

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speeds, and by injecting the limiting reactant at a radial position far from the center of the disc.

This paper experimentally investigates micromixing in a rotor–stator spinning disc reactor in relation to the hydrodynamics in the rotor–stator cavity. The structure of the paper is as follows: First, the theoretical background that supports this work is discussed, starting with a description of the method used for the characterization of the micromixing times (the Villermaux–Dushman system), followed by the hydrodynamics in an rs-SDR, and the estimation of the energy dissipation rate. Subsequently, a description of the experimental setup is presented, followed by the method used to analyze the collected data. Next, the results are presented and discussed and the final section concludes the paper with some summarizing remarks.

■ THEORY

Characterization of Micromixing. In 1995, Fournier et al. proposed a new system of parallel competing reactions that allows the study of micromixing in chemical reactors. It consists of an acid–base neutralization reaction competing with the Dushman reaction for the limiting amount of acid protons. After the initial publication of the method, a lot of research attention was given to the exact kinetics of the system, so as to determine the best set of concentrations, and operating conditions in which to work. With this kinetic data, it became possible to accurately model the system, and so determine micromixing times and mixing efficiency as a function of process conditions in various types of industrial equipment.11–14

\[
\text{H}_2\text{BO}_3^- + \text{H}^+ \rightarrow \text{H}_3\text{BO}_3
\]

\[
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}
\]

The neutralization reaction (eq 1) is assumed to be instantaneous in comparison to the micromixing, while the Dushman reaction (eq 2) although very fast, takes place in the same time range as the micromixing.11 The method relies on the addition of acid to the system in a stoichiometric defect, so that the acid proton becomes the limiting reactant. Under perfectly micromixed conditions, the acid is fully consumed by the first reaction. On the other hand, when the mixing is less than perfect, the acid starts to be consumed by the Dushman reaction, leading to the formation of iodine. The amount of iodine that is formed is thus a direct measure for the level of segregation, or “unmixedness”, in the fluid.

The system initially consists of a premixed solution of iodide and iodate ions in a $\text{H}_3\text{BO}_3^-/\text{H}_2\text{BO}_3$ buffer to which acid is added. The iodine that is subsequently formed reacts in a second step with the iodide anion to yield triiodide, in a quasi-instantaneous equilibrium reaction:15

\[
\text{I}_2 + \Gamma = \text{I}_3^-
\]

The equilibrium reaction stated above has an equilibrium constant $K_B$ that depends on the temperature of the system $T$ (K), according to

\[
K_B = \frac{[\text{I}_3^-]}{[\text{I}_2][\Gamma]}
\]

The triiodide species is UV active at a wavelength of 353 nm, so that its concentration can conveniently be measured by UV–vis spectrophotometry.

Although the reaction rate of the neutralization is too fast to be quantified accurately, it is believed to be in the range of $10^{11}$ L mol$^{-1}$s$^{-1}$ which is comparable to similar bimolecular acid/base neutralization reactions in aqueous solutions.16 The kinetics of the Dushman reaction have been studied since 1888, resulting in several empirical kinetic models.17–20 In this study, the fifth order rate law (eq 6) was adopted because it is commonly used in literature for micromixing studies, as it allows for a qualitative comparison of mixing devices. As shown below, the kinetic rate law does not depend on temperature, but is a function of the ionic strength $I$:

\[
r_2 = k_2[\text{IO}_3^-][\Gamma]^2[\text{H}^+]^2
\]

where $k_2$ is given by

\[
I = \frac{1}{2} \sum C_{\text{z}}^2
\]

\[
I < 0.166, \quad \log_{10}(k_2) = 9.281 - 3.664I^{1/2}
\]

\[
I > 0.166, \quad \log_{10}(k_2) = 8.383 - 1.511I^{1/2} + 0.237I
\]
In eq 7, \( C_i \) denotes the concentration of ionic species \( i \), and \( z_i \) is its corresponding ionic charge.

The mixedness on the microscopic level can be expressed by the segregation index, \( X_S \). When \( Y \) is defined as the experimentally observed ratio of acid consumed by the Dushman reaction divided by the total acid injected, and \( Y_{ST} \) as the value of \( Y \) for infinitely slow mixing, the segregation index can be expressed as

\[
X_S = \frac{Y}{Y_{ST}}
\]

(10)

\[
Y = \frac{2(n_{1+} + n_{1-})}{n_{1+}^2} = \frac{2V_{\text{total}}([I_2] + [I_3])}{V_{\text{injection}}[H^+],_0}
\]

(11)

\[
Y_{ST} = \frac{6[I_{2+}]_0}{6[I_{3+}]_0 + [H_2BO_3]^-_0}
\]

(12)

In literature, one of the most common approaches to determine the micromixing times from the experimental segregation indices, consists of solving a set of differential equations describing the mass balances for each species in a growing eddy over time. The volume of this eddy is modeled according to the Engulfment Model proposed by Baldyga and Bourne in 1989, according to

\[
E \simeq 0.058 \left( \frac{\nu}{ \nu_{\text{K}} } \right)^{1/2}
\]

(13)

in which the modeled engulfment parameter, \( E \), has the units of \( s^{-1} \). On the basis of the assumption that the viscous-convective process of engulfment controls mixing at the smallest scales, the characteristic time for micromixing is then calculated as

\[
\tau_E = \frac{1}{E}
\]

(14)

The complete derivation for the rate of engulfment \( E \), as well as the theoretical background is described in Chapter 8 of Baldyga and Bourne (1999). Because of the empirical nature of the kinetic models available for the Dushman reaction, the method is reliable for qualitative results for characterization of micromixing, a fact that was further highlighted by Bourne (2008) in a short communication on the method. Furthermore, the investigated regime in which the empirical relationship was established does allow for a good comparison between micromixing times in different technologies.

**Hydrodynamics in an rs-SDR.** The models describing micromixing behavior in parallel-competitive reactions all require that, at least locally, the turbulence is homogeneous and isotropic. Under these conditions, the size of the smallest eddies and their corresponding turnover times are of the order of the Kolmogorov microscales:

\[
\tau_K = \left( \frac{\nu}{ \nu_{\text{K}} } \right)^{1/2}
\]

(15)

\[
\eta_K = \left( \frac{\nu}{ \nu_{\text{K}} } \right)^{1/4}
\]

(16)

Consequently, the micromixing time is linearly proportional to the Kolmogorov time, albeit an order of magnitude larger. For simple situations, such as a Rushton stirrer, \( t_{\text{mix}} \) is most commonly given by

\[
t_{\text{mix}} = \tau_E = 17.3 \tau_K
\]

(17)

The topic of flow in the presence of a rotating disc has historically received much attention starting with Von Kármán for the case of an infinite rotating disk in a fluid at rest at infinite distance from the rotor. Von Kármán showed that the flow field comprises a Von Kármán boundary layer containing a radial outflow, while the azimuthal velocity decreases from the speed of the disc to zero while moving away from the disc. In the reversed configuration, a fluid with constant angular velocity at an infinite distance from an infinite stationary wall forms a Bödewadt type boundary layer. In this type of boundary layer, fluid is flowing radially inward while the azimuthal velocity increases from zero to match the rotational motion at infinity while moving away from the disc.

In rotor–stator flows, the flow field can intuitively be thought of as a combination of these two fields in which a Von Kármán boundary layer is attached to the rotating disc, while the stator hosts a Bödewadt layer. For large rotor–stator distances, the two boundary layers are mutually noninterfering and are separated by a region with constant angular and zero radial velocity. When the gap spacing is reduced, the boundary layers start to interfere by their close proximity.

The different types of flow regimes that can occur were first delineated on the basis of the gap spacing and Reynolds number by Daly and Nece (1960). A graphical representation of these regimes in a flow map was made by Djaoui et al. (2001). Adhering to their definitions, the work presented in this paper was performed in Regime III: turbulent torsional Couette flow.

Both numerical and experimental analysis of these types of flow have shown that large velocity gradients exist close to the rotor and the stator, leading to a high degree of shear in the fluid.

**Energy Dissipation Rate.** Kinetic energy from the largest length scale in the flow field is transmitted via the kinetic energy of all the velocity fluctuations to the smallest vortices in which the energy is dissipated. Because of the conservation of energy in this cascade, the torque exerted by the spinning disc can be used as a measure for the dissipation rate at the Kolmogorov scale, determined by eq 16.

The local energy dissipation rate, as a function of radius, can be estimated via the method presented by de Beer et al. (2016). In that study, it was found that the contribution from the pressure drop to the total energy dissipation rate is very small compared to the mechanical energy transferred from the rotating disc, allowing the following approximation:

\[
E_{\eta} \approx \omega \tau
\]

(18)

in which \( \tau \) is the measured torque exerted to the liquid. The local energy dissipation rate as a function of radius is then calculated by assuming a proportionality between the local dissipation rate and \( r^{1/4} \). Details and a derivation of this method can be found in de Beer et al. (2016).
0.145 m, resulting in a radial clearance of \( \omega = 1 \times 10^{-2} \) m between the rotating disc and the stationary shroud. The axial distance between the disc and the stators was equal to \( h_1 = 3 \times 10^{-3} \) m, and \( h_2 = 2 \times 10^{-3} \) m, for the bottom and top parts, respectively. With these reactor dimensions, the total reactor volume was given by \( V_R = 762 \times 10^{-6} \) m\(^3\).

A schematic representation of the setup is shown in Figure 2. The bulk solution was fed into the reactor at the top, near the axis, through “Inlet 1”, at a constant flow rate of \( F_{vis} = 7.5 \times 10^{-6} \) m\(^3\) s\(^{-1}\) using a calibrated gear pump regulated by a Bronkhorst Cori-Flow mass flow controller (MS5). The acid was injected via “Inlet 2”, through a tube in the bottom stator with an inner diameter of \( d_a = 0.5 \times 10^{-3} \) m. The inlet of the acid was located near the rim of the disc at a radial position of \( R_a = 0.130 \) m. A KNAUER Smartline Pump 1050 was used to inject the acid solution at a constant flow rate of \( F_{vis} = 1.5 \times 10^{-7} \) m\(^3\) s\(^{-1}\).

The rotor had a maximum rotational speed of \( \omega_{max} = 209 \) rad s\(^{-1}\) (2000 rpm), provided by a motor SEW-Eurodrive CFM71M. The heat of dissipation caused by the motion of the disc could significantly increase the reactor temperature if left uncontrolled. Under the described experimental conditions, a disc speed of 180 rad s\(^{-1}\) could potentially lead to a temperature increase of around 10 °C, if left uncontrolled. The outlet of the reactor was recirculated from a double walled feed vessel of 5 L, connected to a Lauda ECO RE 630 to maintain isothermal conditions.

Real-time measurement of the triiodide concentration at inlet 1 and the outlet was performed using in-line UV–vis spectrophotometry. Optical fiber cables were used to connect the flow cells with an optical length of 5 \times 10^{-3} \) m to a Dual channel AvaSpec-2048-2-USB2 spectrophotometer, using an Avalight DH-S light source with a wavelength of 353 nm. Measurements were recorded every 0.1 s, with an integration time for the UV–vis spectrocope of 1.1 × 10^{-3} s.

The absorbance, \( A \), in each flow cell was calculated in accordance with eq 19, in which \( N \) is the number of counts in the flow cell, \( N_0 \) is the number of counts corresponding to the dark reference, that is, with the light source turned off, while \( N_{ref} \) is the number of counts measured for the reference sample, demineralized water.

\[
A = -\log \frac{N - N_0}{N_{ref} - N_0}
\]  

(19)

At concentrations of triiodide below 1 \times 10^{-4} \) M, the absorbance as measured via UV–vis is directly proportional to the concentration.

For each set of experiments 5 L of bulk solution was prepared with the concentrations shown in Table 1. All the solutions were made with demineralized water. In order to prevent the undesired formation of iodine when preparing the bulk solution, a specific procedure needed to be followed. First, a two-liter buffer solution was made by dissolving sodium hydroxide (Merck) and boric acid (Sigma-Aldrich), creating a buffer solution of pH = 9.14. At this moderately caustic condition, the formation of iodine is suppressed. Consecutively, two separate solutions of one liter each were added, one containing dissolved potassium iodide (VWR Chemicals), and the other one dissolved potassium iodate (Merck). Finally, water was added to increase the total volume to 5 L.

Although sulfuric acid is typically used in measuring micromixing performance with the Villermaux–Dushman reaction, there is a systematic problem associated with it. The second proton that can be dissociated from sulfuric acid is not nearly as acidic as the first one (\( pK_{a1} = -3 \), \( pK_{a2} = 1.99 \)), making the data unreliable for short micromixing times, as shown by (Köbl and Schmidt-Lehr, 2010).\(^{33} \) It was therefore chosen to use perchloric acid as the proton supplier in the reaction scheme as it is a very strong monoprotic acid (\( pK_a = -9.24 \)). Technical grade perchloric acid (VWR Chemicals) was carefully diluted with water to obtain three different concentrations, as shown in Table 1.

<table>
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<th>Table 1. Set of Concentrations Used for the Experiments</th>
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<tr>
<td>bulk solution</td>
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<tr>
<td>sodium hydroxide</td>
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<tr>
<td>boric acid</td>
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<tr>
<td>potassium iodate</td>
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<tr>
<td>potassium iodate</td>
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<tr>
<td>acid</td>
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<tr>
<td>perchloric acid</td>
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Data Analysis. Experiments were performed using the operational conditions described in the previous section, and following the Villermaux–Dushman method. By varying the concentration of perchloric acid, it is expected that different segregation indices will be observed, as it is a function of the acid concentration. However, for a given disc speed, the micromixing time should be independent of concentration according to the engulfment model as it only depends on dissipation and viscosity. Therefore, a model that relates the segregation index to the theoretical micromixing time is required.

Assuming micromixing by pure engulfment as the dominating mechanism but taking self-engulfment into account, the mass balances and the reaction rates from the Villermaux–Dushman system were adapted into a model that results in a relation between micromixing and segregation index at a given experimental condition. The resulting dependency between $X_S$ and $t_{mix}$ as predicted by this model are given in Figure 3.

To have sufficient accuracy, only the log–linear range is considered in Figure 3 for the determination of the micromixing time. For the range $0.0005 < X_S < 0.15$ it was thus found that

![Figure 3. Variation of the segregation index versus micromixing time, for the operational conditions described in the Experimental Section. Segregation indices are calculated using the engulfment model.](image)

![Figure 4. The effect of calculated segregation index, $X_S$, with varying rotational speeds, $\omega$, for different acid concentrations.](image)
RESULTS AND DISCUSSION

Figure 4 shows the experimental segregation index versus the rotational speed. In accordance with the model, a higher concentration of acid leads to a higher value for the segregation index. In line with theory, the segregation index decreases with an increasing disc speed. This trend has also been observed in other similar devices, by applying the same method for characterization of micromixing.

For the lowest concentration of acid (0.02 M), the measured iodine concentrations were too low to result in accurate predictions, and are thus omitted from further analysis. The same situation occurred for the highest rotational speeds and an acid concentration of 0.06 M. In the following discussion on micromixing times, these points were consequently omitted.

From eqs 20, 21, and 22, the micromixing time corresponding to each measured segregation index is estimated and plotted in Figure 5 versus the local energy dissipation rate at the orifice.

According to the data in Figure 5, the obtained micromixing times are in line with theory, matching the theoretical values relatively well when comparing them with eq 17.

From Figure 5, it can be seen that the micromixing times obtained for energy dissipation rates below $10^2$ W/kg are comparable to the theoretical micromixing times for a Rushton turbine, as reported by Assirelli (2002). In that study, a comparison with other results in the literature was presented, demonstrating that faster micromixing is achieved with faster stirring and by locating the acid feed at a very turbulent region. In addition this trend is shown to hold, even for significantly larger values of energy dissipation rates as observed in an rs-SDR.

In relation to other studies, Rousseaux et al. (1999) investigated the micromixing efficiency of a sliding-surface mixing device, reporting micromixing times ranging from $1.0 \times 10^{-2}$ to $1.0 \times 10^{-1}$ s for the studied operational conditions. In a freely spinning disc reactor which is not enclosed by a narrow encasing, Boodhoo and Al-Hengari (2012) investigated the micromixing efficiency for a range of hydrodynamic conditions, and reported improved micromixing behavior (lower segregation index) at high rotational speeds and high feed flow rates. Moreover, they compared the results with a stirred tank at similar conditions, showing improved micromixing at comparable energy inputs. For a similar setup, Jacobsen and Hinrichsen (2012) not only presented a similar trend but also estimated the micromixing times to lie in the range of $1.0 \times 10^{-1}$ to $1.0 \times 10^{-2}$ s. More recently, Haseidl, Schuh, and Hinrichsen (2015) modified their setup to apply the rotor–stator principle, and they reported an improvement in the micromixing efficiency. Additionally in that study, it was shown that better mixing can be achieved when the acid feed is located closer to the rim of the disc.

CONCLUDING REMARKS

The micromixing time of a rotor–stator Spinning Disc Reactor is determined to range between $1.13 \times 10^{-4}$ to $8.76 \times 10^{-3}$ seconds for rotational speeds between 10 and 188 rad/s. Furthermore, when plotting the micromixing times as a function of the energy dissipation rate, it was found that the theoretical trend for Rushton stirrers can be extended deep into the region of high energy dissipation rate. The rs-SDR will thus be able to rapidly homogenize its contents under process intensified conditions and increased reaction rates.
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