

Micromixing Experiments in the Undergraduate Curriculum

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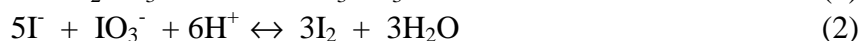
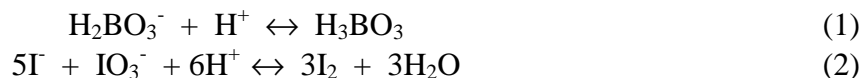
Abstract

An issue that is not typically covered reactor design courses is mixing and reactions. In the chapter on multiple reactions in the standard chemical reaction engineering text by Fogler¹, it is assumed that the reactions are slow compared to the mixing of species. The classic examples for parallel reactions and series reactions are given, but these examples do not cover the basic concept of micro-mixing with respect to the reactants. Only in the final chapter of this text is the concept of micro-mixing introduced using a mathematical theory that is relatively complex for undergraduates. We believe that it is important for undergraduates to have a concept of the importance of micro-mixing on chemical reactions in industrial reactors. This paper describes a series of experiments designed to introduce the concept of micro-mixing in an undergraduate chemical reaction engineering course. These experiments will give the basic problems associated with this phenomenon and illustrate the limitations of the ideal reactor models.

Introduction

In practice the issue of mixing and chemical reactions is very important in economic aspects of chemical reaction engineering. A major priority in industrial reactors is to optimize the yield of desired products. This optimization is a function of reactor geometry, the chemical and physical characteristics of the reacting system, the degree of mixing and the mode of supplying the reactor with reagents. Bourne and Gablinger² have shown how process chemistry developed in the laboratory can go awry when scaled to industrial reactors. An excellent example of the classic series-parallel reaction using an azo dye chemistry is presented by Bourne and Gholap.³ The chemist will optimize the reaction to obtain very high reaction rates for the desired reaction. However, in the industrial reactor, micro-mixing is a limiting factor, negatively impacting the process chemistry.⁴ However, as explained by Etchells⁵, a typical undergraduate reactor design course focuses on ideal reactors and would overlook the impacts of mixing on the reaction chemistry and the formation of trace byproducts. The goal of the experiments described here is to demonstrate to the student the practical limitations of the idealized models.

Baldyga and Bourne⁶ summarize a number of experimental examples of product distributions sensitive to mixing. Examples of parallel or competitive reactions include Diazo coupling with simultaneous reagent decomposition⁷ and Iodate/iodine reaction with neutralization.⁸ Examples of parallel – series reactions or competitive-consecutive reactions include Diamines with isocyanates or other acylating agents, nitrations of dibenzyl, durene, and alkyl benzenes and diazo couplings. The experiments described in this paper involve this pair of parallel competitive reactions:



The first reaction is essentially instantaneous. The rate of the second, in the forward direction, is fast but orders of magnitude slower than that of the first.^{9,10} Thus, when H^+ is added as the limiting reagent, a perfectly mixed system would produce essentially no I_2 . Production of a significant quantity of I_2 is attributed to a local excess of H^+ ; a condition in which all $H_2BO_3^-$ in a region is consumed and H^+ remains to react with I^- and IO_3^- .

Any I_2 formed in solution will react further with I^- :



The concentration of the I_3^- ion can be measured accurately with spectrophotometry and Beer's law. Thus, the yield of reaction 2 is readily determined. Consequently, this reaction was deemed suitable for an undergraduate experiment because it meets several important criteria:

- The reagents are cheap and reasonably safe, with water acting as the solvent.
- Quantitative results can be obtained with a fairly simple analytical method.
- The kinetics are known¹⁰.
- Imperfect mixing has an effect on product distribution that is straightforward to quantify and explain.

The experiment will be integrated into a junior course on Chemical Reaction Engineering in the Spring 2002 semester. It is intended to illustrate the concept of micro mixing to the students so that they have a first-hand awareness of the limitations of the ideal reactor models.

Apparatus

A team of undergraduate students assembled apparatus and developed an experimental procedure during the Fall 2001 semester, as an Engineering Clinic¹¹ project. There are two distinct experimental setups: one uses a 2 L reactor with baffles and a Lightnin Mixer as shown in Figure 1, the other an ordinary 600 mL beaker with a magnetic stirring bar. In the first setup a syringe pump is used to add the limiting reagent, sulfuric acid, at a controlled, known rate. In the second setup an Eppendorf pipet is used to add the acid. Both experiments require stock solutions as summarized in Table 1.



Figure 1: Mixer and 2 L Reactor

Table 1: Reagents

Reagent	Concentration (mol/l)	MW (g/mol)
H_3BO_3	0.606	61.83
NaOH	1.0	40.0
KIO_3	0.0233	214
KI	1.167	166
H_2SO_4	0.50	98.04

Experimental Procedure

The experimental procedure developed for the Lightning Mixer is as follows. The impeller speed of the mixer is left unspecified as that is the parameter the students vary; actual values will span the range defined by Figure 3.

- 1) Fill reactor with the 1080ml of DI water.
- 2) Add 225ml of the H_3BO_3 solution.
- 3) Add 30ml of the NaOH solution.
- 4) Add 150ml of the KIO_3 solution.
- 5) Start mixer at 500 rpm (regardless of experimental speed) and allow solution to mix thoroughly.
- 6) Add 15ml of the KI solution. Let solution mix for several minutes to insure homogeneity.
- 7) Reset mixer **to experimental** speed.
- 8) Inject 10ml of the 1N sulfuric acid with the syringe pump. Use the calibration curve for the pump to determine the proper addition time.
- 9) Wait approximately 2 minutes (to insure homogeneity of the solution) then turn OFF MIXER!
- 10) Take sample from the same height as the impeller

The procedure for the beaker-stirring bar system is analogous. The proportions of all reagents added are the same, with the total solution volume 300 mL rather than 1.5 L as in the Lightning Mixer.

The analytical procedure for either experimental setup is as follows:

- 1) Be sure the spectrophotometer (Spec220) is on and has warmed up for at least 15 minutes.
- 2) Set the wavelength to 353nm, the sensitivity to high, and the mode to Absorbance.
- 3) Fill one quartz cuvet with DI water and set the absorbance to zero on the Spec220.
- 4) Take 1 mL of sample using Eppendorf pipet (do not depress purple button on pipet when aspirating sample) and inject into 10 mL volumetric flask. Fill the remainder of the 10 mL volume with DI water (mix well).
- 5) Pour the diluted sample into quartz cuvet. Take to Spec220 and read the absorbance (reading should be between 0 and 1.999).

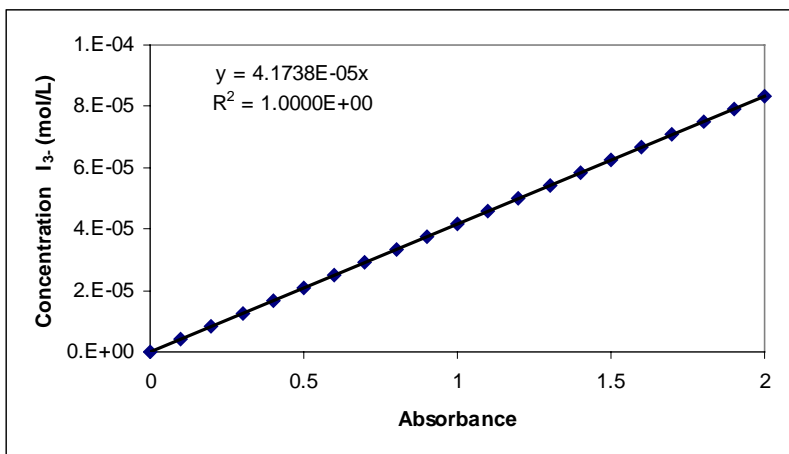


Figure 2: Calibration Curve for I_3^- Ion Concentration

Data Analysis

A calibration curve relating I_3^- concentration to absorbance has been prepared and is shown in Figure 2. Students will thus measure the I_3^- concentration by applying Beer's law

$$C_{I_3^-} = \frac{A}{\epsilon \ell} \quad (4)$$

and deduce the I_2 and I^- concentrations from the following known equilibrium relationship for reaction (3).¹²

$$\text{Log}(K_{eq}) = 555/T(K) + 7.355 - 2.575 * \text{Log}(T(K)) \quad (5)$$

Thus, by applying standard chemical reaction engineering principles of species balances and equilibrium relationships, students can compute the fraction of H^+ ions that reacted by reaction 1 and the fraction that followed reaction 2. This fraction is a function of the rate of micro-mixing.

Students will quantify the product distribution using the same method as Guichardon and Falk.⁹

Two limiting conditions are identified:

Perfect Mixing in which the system acts like the perfectly mixed CSTR familiar to the students by this point in the Reaction Engineering course. In this system, the yield of reaction 2 is essentially zero if the system is perfectly mixed.

Total Segregation describes a system in which micro mixing is infinitely slow, so both reaction rates are essentially instantaneous by comparison. In this situation the rates of reaction 1 and 2 will be in proportion with the local concentrations of $H_2BO_3^-$ and I^- .

Guichardon and Falk characterize the system by dividing the total volume of the reactor into a "perfectly mixed volume" V_{PM} and a "totally segregated volume" V_{TS} . The "micromixedness ratio" α , is defined as V_{PM}/V_{TS} . Details of calculating α for this system are given in their paper.⁹

Procedure to determine alpha:

The following equation is the species mass balance:

$$C_{I^-} = C_{I_0^-} - \frac{5}{3}(C_{I_2} + C_{I_3^-}) - C_{I_3^-} \quad (6)$$

And the combination of this equation with the equilibrium equation yields the following quadratic:

$$0 = -\frac{5}{3}(C_{I_2})^2 + (C_{I_0^-} - \frac{8}{3}C_{I_3^-}) * C_{I_2} - \frac{C_{I_3^-}}{K_{eq}} \quad (7)$$

From this equation we can now calculate the concentration of I_2 . This is valuable, since we now know how much H^+ went to the Dushman reaction (reaction 2), rather than the acid-base neutralization (reaction 1). We now need some way of standardizing our results. When the reactor is poorly mixed and there is local excess of certain reactants, we say there is segregation,

so to quantify micromixing, a segregation index was developed (X_s). At perfect mixing, $X_s = 0$, and at total segregation, $X_s = 1$. This can be defined as $X_s = Y/Y_{ts}$, where $Y = [\text{moles of } H^+ \text{ consumed by the } I_2 \text{ rxn (Reaction 2)}]/[\text{moles of } H^+ \text{ injected}]$, and Y_{ts} is the maximum value of Y . These are related to the species concentrations as follows:

$$Y = 2 \frac{V_{\text{tank}} * \frac{C_{I_2} C_{I_3^-}}{C_{H_0^+}}}{V_{\text{inject}}} \quad (8)$$

$$Y_{ts} = \frac{6 * \frac{C_{IO_3^-}}{C_{H_2BO_3}}}{(6 * \frac{C_{IO_3^-}}{C_{H_2BO_3}} + 1)} \quad (9)$$

We now assume that the total volume is made up of two separate volumes, a perfectly mixed volume (V_{pm}) and a totally segregated volume (V_{ts}). If one performs a mass balance on this we see that:

$$(V_{pm} + V_{ts}) X_s = V_{pm} X_{\text{perfectmixing}} + V_{ts} X_{\text{totalsegregation}} \quad (10)$$

But, we already defined $X_{\text{perfectmixing}}$ as 0, and $X_{\text{totalsegregation}}$ as 1. So, this reduces to the following:

$$(V_{pm} + V_{ts}) X_s = V_{ts} \quad (11)$$

The micromixedness ratio (α) is defined as:

$$\alpha = \frac{V_{pm}}{V_{ts}} \quad (12)$$

Combining Equation 11 with Equation 12, we get

$$\alpha = \frac{(1 - X_s)}{X_s} \quad (13)$$

Figure 3 illustrates the relationship between α and the impeller speed in revolutions per second for both experimental setups, as determined in trial runs conducted in the Fall of 2001. Data produced by the Reaction Engineering class should be similar. Note that in both systems α increases with increasing impeller speed. Thus, the influence of improved mixing on product distribution is both demonstrated and quantified.

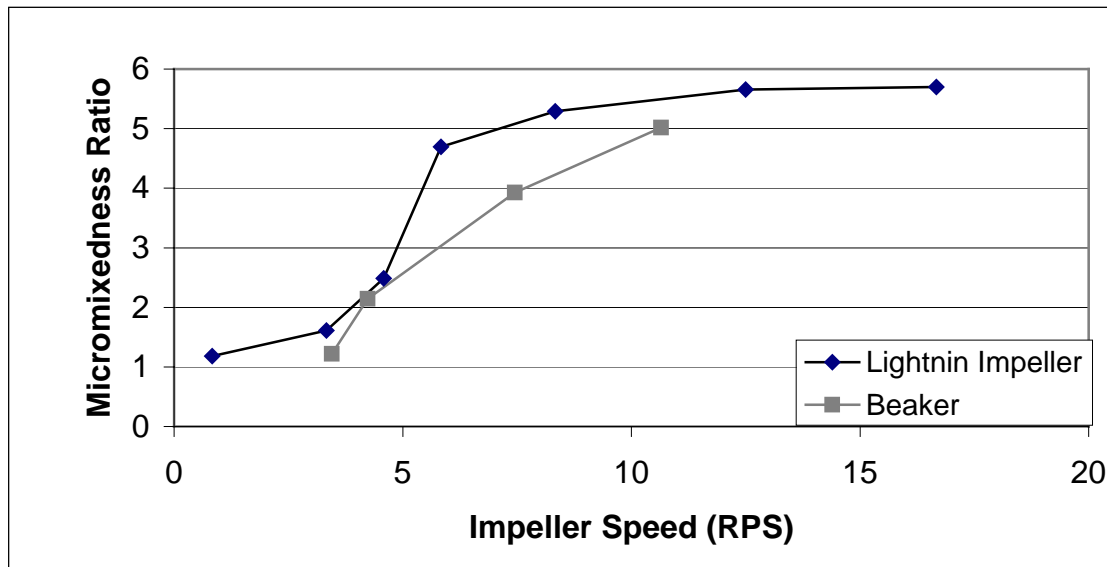


Figure 3: Experimental Results – Effect of Impeller Speed on Micromixedness Ratio (α)

Conclusion

An experiment intended to introduce the concept of micromixing to undergraduate students has been developed and tested. It will be integrated into a junior-level Chemical Reaction Engineering course in the Spring 2002 semester. The presentation will detail results and student response.

Acknowledgements

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BIOGRAPHICAL INFORMATION

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