Ultrasonics Sonochemistry 32 (2016) 68–78

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

The effects of ultrasound on micromixing

Jeroen Jordens [a,b], Bram Bamps [a], Bjorn Gielen [a,b], Leen Braeken [b], Tom Van Gerven [a,*]

[a] KU Leuven, Department of Chemical Engineering, Celestijnenlaan 200F, B-3001 Leuven, Belgium
[b] Research Group Lab4U, Faculty of Industrial Engineering, KU Leuven, Universitaire Campus gebouw B bus 8, 3590 Diepenbeek, Belgium

ARTICLE INFO

Article history:
Received 6 October 2015
Received in revised form 12 February 2016
Accepted 18 February 2016
Available online 18 February 2016

Keywords:
Micromixing
Process intensification
Sonochemistry
Villermaux–Dushman
Microstreaming
Sonolysis
Modeling
Cavitation

ABSTRACT

The Villermaux–Dushman reaction is a widely used technique to study micromixing efficiencies with and without sonication. This paper shows that ultrasound can interfere with this reaction by sonolysis of potassium iodide, which is excessively available in the Villermaux–Dushman solution, into triiodide ions. Some corrective actions, to minimize this interference, are proposed. Furthermore, the effect of ultrasonic frequency, power dissipation, probe tip surface area and stirring speed on micromixing were investigated. The power and frequency seem to have a significant impact on micromixing in contrast to the stirring speed and probe tip surface area. Best micromixing was observed with a 24 kHz probe and high power intensities. Experiments with different frequencies but a constant power intensity, emitter surface, stirring speed, cavitation bubble type and reactor design showed best micromixing for the highest frequency of 1135 kHz. Finally, these results were used to test the power law model of Rahimi et al. This model was not able to predict micromixing accurately and the addition of the frequency, as an additional parameter, was needed to improve the simulations.

1. Introduction

Mixing on a molecular scale (micromixing) plays an important role in several chemical reactions like precipitation, neutralization, combustion or polymerization reactions [1–4]. It increases the selectivity of competitive reactions where the reaction rate of interest is limited by diffusion. Additionally, micromixing improves the reaction rate of mixing sensitive reactions by reducing the micromixing time below the reaction time [5,6].

Ultrasound has shown drastic improvements of this micromixing, up to ca. 50% compared to silent conditions [2,7–10]. Three main mechanisms are proposed to explain these enhancements. First, the collapse of cavitation bubbles is thought to create micro-jets, shockwaves and micro-streaming which generate turbulence in the liquid and hence improve mixing on the molecular scale [2,5,8,10,11]. These effects are mainly attributed to transient cavitation bubbles as these implode more violently compared to stable ones [8]. Secondly, micromixing can be improved by oscillating stable cavitation bubbles. These bubbles will vibrate around their resonance radius and hence cause convective circulation in the surrounding liquid which creates turbulences in the liquid and consequently improve micromixing [10]. Finally, the mechanism of acoustic streaming is proposed in literature [8,12,13]. This macroscopic streaming is generated when ultrasound energy is dissipated by viscous stress and results in steady vortices and time independent circulation which improve micromixing [14]. This effect is more pronounced at higher acoustic frequencies as attenuation of sound waves will be higher at these frequencies and hence more energy is dissipated compared to lower frequencies [15]. It is still not clear to which extent these mechanisms contribute to micromixing and if there is a dominant one.

Although ultrasound showed significant enhancements compared to silent conditions, the ultrasonic parameters which optimize micromixing are not clear. Lee et al. for example observed less micromixing with a 647 kHz plate transducer compared to a 20 kHz probe [4]. Also, Monnier et al. had a similar observation; a 20 kHz probe created better micromixing compared to 540 or 955 kHz transducers [1]. Rahimi et al., Parvizian et al. and Faryadi et al. in contrast, found that their 1.7 MHz transducers created better results than a 24 kHz probe [10,11,13]. Furthermore, they compared their results with the ones of Monnier et al. and observed that, at a constant ultrasonic intensity per unit volume, their 1.7 MHz reactor created better micromixing than the 20 kHz probe and cup probe of Monnier et al. [11]. No explanation for this discrepancy was given. However, from their papers one could notice that several parameters differ during their experiments.

First, the reactor geometry used among the different papers varies considerably. Monnier et al., Lee et al., Rahimi et al. and Parvizian et al. used reactors of respectively 100, 165, 360 mL

* Corresponding author.
E-mail address: tom.vangerven@cit.kuleuven.be (T. Van Gerven).

http://dx.doi.org/10.1016/j.ultsonch.2016.02.020
1350-4177/

and 2 L [4,5,10,11]. From literature, it is known that the reactor geometry significantly influences the ultrasound field [7,16]. Hence, different levels of acoustic streaming or cavitation characteristics can be created which consequently impact micromixing.

Secondly, ultrasonic probes with small diameters of 12 to 20 mm are compared with ultrasonic transducers with larger diameters up to 45 mm. The former are more likely to create a non-uniform acoustic field and transient cavitation bubbles while the latter favor a uniform acoustic field and stable bubbles [13,17–19]. Again, these differences can impact micromixing behavior.

Furthermore, the ultrasonic power is not always compared in a similar way. Monnier et al., Parvizian et al. and Rahimi et al. applied a constant electrical power to the ultrasound sources while Lee et al. kept the power inside the reactor constant. The latter was done by calorimetric measurements which allow, according to literature, a much fairer comparison between different frequencies [20–23].

Finally – besides these different geometries, bubble types and power levels – also the positioning of the ultrasonic source differs. All probes are introduced from the top of the reactor while most transducers are placed at the bottom. Therefore, the direction of the ultrasound waves will be opposite and the acoustic properties like the proportion of standing and travelling waves and reflected power will differ [24]. These acoustic properties influence the cavitation structures and therefore also micromixing [16,25]. All these parameters together make it difficult to investigate solely the effect of frequency on micromixing and do not allow to draw a univocal conclusion.

The effect of ultrasonic power or intensity on micromixing, in contrast, is very clear. Higher ultrasonic powers lead to better micromixing [2,5,8,10,26]. This is straightforward as higher powers lead to more violent collapse of cavitation bubbles and more acoustic streaming. Rahimi et al. even proposed a model to simulate the effect of ultrasonic energy dissipation (ε) on the micromixing time (t_m) [26]. The following power law was used to correlate both parameters to each other:

$$t_m = a\varepsilon^b \tag{1}$$

In this equation, a and b are fitting parameters which need to be defined experimentally. The micromixing times were plotted in function of the energy dissipation ratios (W/kg) for each operating condition. Power law trend lines were fitted through these points and from the equations of these trend lines, the values for a and b were obtained. Different trend lines, and therefore different values for a and b, were obtained for acid concentrations of 0.5, 0.75 and 1 M and sonicated and silent conditions. The power law model was used to predict the micromixing time under silent and sonicated conditions for a given acid concentration in their reactor setup. It showed a very good correlation between simulated and measured values with errors of less than 8%. This model was, however, developed for their reactor configuration and frequency of 42 kHz.

The Villermaux–Dushman or iodide–iodate reaction is one of the most used techniques to characterize micromixing due to its easy implementation, cheap reagents and well established reaction kinetics [1,2,5,6,8,10,26–30]. The degree of micromixing is measured by the amount of triiodide (I_3^-) produced by the iodide–iodate reaction. The worser the micromixing, the more I_3^- produced. The reader is referred to Section 2.2 for a detailed description of the reactions and reagents. This Villermaux–Dushman method is also commonly used to study the effect of ultrasound on micromixing [1,2,4,5,8,11,26]. All of the papers referred to in the previous paragraph, for example, used this method. However, when looking deeper in literature, one can find that potassium iodide, which is excessively available in the Villermaux–Dushman buffer solution, is oxidized by reactive species such as ·OH radicals and hydrogen peroxide formed by collapsing cavitation bubbles [31,32]. The generation of these reactive species in sonicated water is often referred to as the sonolysis of water. These reactive species will oxidize the available iodide ions to iodine which subsequently reacts with the excess of iodide to triiodide according to the following reaction scheme [31,32]:

$$\cdot OH + I^- \rightarrow I + OH^-$$

$$I + I^- \rightarrow I_2^-$$

$$2I_2^- \rightarrow I_2 + 2I^-$$

$$I_2 + I^- \rightarrow I_3^-$$

In fact, these reactions are commonly used in the field of sonochemistry during the "Iodine release method" to characterize the cavitational activity [33]. This sonolysis reaction can, however, interfere with the Villermaux–Dushman reaction as both reactions produce triiodide ions. In this way, the amount of triiodide produced by the Villermaux–Dushman reaction will be overestimated and hence the micromixing underestimated. To the authors' best knowledge, no reports are present in literature which investigated this possible interference or proposed any corrective actions.

In the present work, the effect of sonolysis on the Villermaux–Dushman reaction will be studied and some corrective actions will be proposed. Furthermore, the effect of ultrasonic frequency on micromixing will be studied in a single reactor geometry with a constant probe tip surface area, similar power dissipations, the same stirring speed and cavitation bubble type. Moreover, the effect of stirring speed, ultrasonic intensity and power on the micromixing efficiency will be investigated. Finally, the power law model of Rahimi et al. will be tested among different frequencies and ultrasonic powers. The addition of the frequency, as an additional parameter, in the micromixing model will be investigated as well.

2. Materials and methods

2.1. Experimental setup

Fig. 1 shows the experimental setup which consists of a jacketed glass cylinder without top or bottom plate and an ultrasound transducer. This transducer is placed at the bottom of the reactor and clamped to the cylinder to allow proper sealing of the reactor. By clamping different transducers to the bottom, each operating at their own resonance frequency, it is possible to use the same reactor over a wide frequency range. The temperature was fixed at 25 °C by a Julabo MP thermostatic bath. A Cole Parmer ultra compact mixer with axial blade impeller of 30 mm diameter was used to stir the solution at different stirring rates. The stirrer was always placed in the center of the reactor at 1 cm from the bottom. An Ismatec REGLO-Z Digital gear pump was used to add the sulfuric acid solution to the reactor. The tubing from this pump had an inner diameter of 1 mm, was located at a radial distance of 2 cm from the impeller and was immersed 3 cm in the reactor solution. This location was fixed during all experiments. The tubing was immersed just before the addition of the acid and a check valve was installed between the outlet of the pump and the tubing to avoid release of acid before the start of the experiment. Also, the height of the pump and reactor were adjusted to minimize hydrostatic pressure differences which could lead to uncontrolled acid release.