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Combined effects of phase-shift and power distribution on efficiency of dual-high-frequency sonochemistry

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ABSTRACT

In an effort to increase the efficiency of sonochemical reactors, this study investigates a single-source, dual-high-frequency ultrasound reactor. Experiments were conducted with a variety of piezoelectric crystals and reactor components, and for each reactor design a range of power distributions and phase shifts between the two frequencies were evaluated. Certain dual-frequency configurations produced up to a threefold increase in sonochemical efficiency, while others yeilded no improvement over a single frequency. These results led to two significant findings. First, phase-shift had a strong effect on sonochemical efficiency for both harmonic and non-harmonic frequency combinations. Second, the most efficient dual-harmonic-frequency waveforms had a single peak per half-cycle, rather than two unique peaks. If dual-frequency, single-source ultrasound reactors are to become more efficient they must be able to consistently control the phase angle of and power distribution between harmonic waves to create an optimal waveform.

1. Introduction

Sonochemistry is the coupling of acoustic and chemical processes [1] and occurs during the ultrasonic irradiation of aqueous solutions [2]. The ultrasonic pressure waves initially cause bubbles to nucleate [3], grow through rectified diffusion and finally quasi-adiabatically collapse [4]. During high-energy bubble cavitation events, the bubble vapor temperature nears 4000 K [5,6] and the bubble interface temperature nears 800 K [7]. The high vapor temperatures drive unimolecular water thermolysis producing H-atoms ($H^{\cdot}$), hydroxyl radicals ($OH^{\cdot}$), and O-atoms ($O^{\cdot}$) [2]. These radicals can diffuse into the bulk aqueous solution and react with solutes.

The sonochemistry generated during high-energy bubble events has been reported to be effective for the degradation of a range of aqueous pollutants [8–10]. The high temperatures and radicals generated have been observed to degrade even the most persistent pollutants such as aromatics [8], chlorocarbons [9], and fluorocarbons [10]. However, even though sonochemistry is effective for recalcitrant chemical degradation, it is not often used in practice due to low energy efficiency. The standard measure of sonochemical efficiency (SE) is moles potassium iodide (KI) oxidized per joule, which typically falls between 10^{-11} and 10^{-9} mol·J^{-1} [11–13]. However, a better measure may be $OH^{\cdot}$ production since I^{-} can be oxidized by mild oxidants. If 100% of the input energy used to generate ultrasonic waves were converted to hydrogen peroxide (H_2O_2) production (a surrogate for $OH^{\cdot}$ production) then an “ideal” SE would be 2.6×10^{-6} mol·J^{-1} [14]. This study used H_2O_2 as the measurement of sonochemical activity because another study utilizing the same equipment verified a strong correlation between H_2O_2 production and degradation of a model pollutant (Table A1).

One strategy to improve sonochemical efficiency is to utilize dual-frequency ultrasound where an aqueous solution is simultaneously insonicated with two different frequencies. For example, dual frequency as compared to single frequency ultrasound at a similar acoustic energy input has been observed to increase p-nitrophenol (PNP) degradation [8], iodide oxidation [15], hydroxyl radical production [16], and H_2O_2 production [17,18]. The majority of previously reported dual frequency ultrasound research has focused on the combination of two low ($<$ 100 kHz) frequencies or a low and a high ($>$ 100 kHz) frequency (see Table A2 [8,15–38]); for the latter, enhanced efficiencies are hypothesized to be due to bubble nucleation by the low frequency and bubble collapse due to the high frequency. However, the most promising results have been observed with the simultaneous insonication of two high frequencies. For example, iodide oxidation rates during second harmonic superposition of 1000 and 2000 kHz or 750 and 1500 kHz have been reported to be increased by more than an order of magnitude over the fundamental at similar applied powers [37]. The second harmonic superposition with the optimal power distribution and

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phase shift yields a waveform that maximizes bubble radial motion enhancing rectified diffusion and in turn the rate and intensity of cavitation events [20].

The mechanism behind dual frequency synergy is an active area of research. Numeric models have shown that dual-frequencies can achieve enhanced sonochemistry by increasing the oscillation amplitude of the bubbles, and thereby making the quasi-adiabatic collapse events more intense, generating higher temperatures [20]. However, this enhancement only occurs with specific power distribution and phase shift combinations [20]. This theoretical prediction is consistent with experiments observing that power distribution and phase shift achieve varying degrees of sonochemical activity [15,27,33]. Various explanations for this synergy have been offered, including that the lower frequency promotes nuclei formation while the high frequency leads to bubble collapse [29,39], the multiple wavelengths cause a new class of bubbles to form that have different properties than the bubbles which form under either single frequency alone [32], and/or inter-bubble interactions occur between bubbles resonating with the two individual frequencies [32]. What is clear from these various results is that the dual-frequency synergy exists, but depends on the specific interactions between the frequencies, which is likely dependent on the specific frequencies, power distributions, and phase shifts.

Most previous studies have used two piezoelectric ultrasound sources to achieve dual-frequency insonication, which increases the complexity of the system and decreases control of the phase-shift between the two frequencies. Harmonic phase shift has a strong effect on sonochemical efficiency [37] and previous studies on the impact of phase shift have utilized a single dual-frequency piezoelectric [40]. However, studies using a single ultrasound source have been minimal: only 2 of the 21 experimental studies summarized in Table A2 [8,15–38] used a single source. Thus, there is fundamentally still a significant amount to be elucidated about single-source dual-frequency ultrasound systems.

Here, we examine three single-source dual-frequency ultrasound reactors to compare sonochemical kinetics of H_2O_2 production by single frequency (370, 450, 740, 770 kHz) dual frequency harmonic (370 and 740 kHz) superposition, and dual frequency non-harmonic (450 and 770 kHz) superposition. The dual frequency experiments were completed over a range of higher frequency phase shifts and fractional applied power versus the fundamental. Single frequency experiments were used to gain insight in the mechanism of enhanced sonochemistry.

2. Experimental methods

2.1. Reactor design

The reactor was a 1.3 L jacketed glass reactor with a clamp to attach one of three circular stainless steel (SS) end-pieces with an attached piezoelectric crystal (Fig. 1). The first SS end-piece was machined from a single piece with a circular inset for attaching the piezoelectric crystal that was 70 mm in diameter and 1.7 mm thick and is referred to as P-1. The second end-piece consisted of two-pieces: an SS seal and a machined disk for piezoelectric attachment that was 127 mm in diameter and 0.5 mm thick. The disk was set into the seal and was held in place by the clamp and is referred to as P-2. The third piece was similar in style (two-piece) to the second piece with the only difference being the disk was machined to be 1.22 mm thick and is referred to as P-3. The thickness of the machined stainless steel pieces was selected to match either a quarter- or a half- wavelength of a piezoelectric crystal resonating at 600 kHz, which was the manufacturer specified resonant frequency of the crystals used. However, as will be discussed below, none of the tested piezoelectric crystals resonated at the manufacturer frequency and all had two resonant frequencies with one below and one above 600 kHz.

2.2. Piezoelectric crystals and ultrasound generation

Ultrasonic waves were generated by cylindrical piezoelectric lead-zirconate-titanate (PZT-840) crystals that were 3.4 mm thick and 50.0 mm in diameter (American Piezo Ceramics (APC) International Ltd). The crystals were attached to the center of the machined steel plates using a colloidal silver-based conductive epoxy (CHO-bond 584) from Parker Chomerics (Woburn, MA). The AC leads were attached to the piezo-crystals by soldering a positive lead to the edge of the crystal using lead free solder (96% Sn, 4% Ag) from Amerway Inc. (Altonna, PA). The ground lead was clamped to the stainless steel frame when the piezo end-piece was attached. The dual frequency waveforms were generated by an arbitrary waveform generator (33522A; Agilent). First the fundamental, or low frequency in the non-harmonic case, was set and then the overall peak-to-peak amplitude (mV) was set. The harmonic, or higher frequency in the non-harmonic, phase shift and percent amplitude as compared to the fundamental were then set. The arbitrary waveform generator output was increased by a RF linear amplifier (2100L; E & I Ltd.; Rochester, NY) that has a linear response over the range of frequencies evaluated here and a total power range of 0–100 W. The output of the linear amplifier was used to excite the piezoelectric crystal generating ultrasonic waves in the aqueous solution.

2.3. Piezoelectric crystal resonant frequency determination and calorimetry

To determine the resonant frequency of the piezoelectric crystals an AC sine wave with amplitude of 300 mV was programmed into the waveform generator (the linear amplification was kept constant) and the output frequency was scanned manually from 200 to 1000 kHz in 5 kHz increments. At each frequency, the transmitted (W) and reflected (W) AC power were recorded from the linear amplifier and the difference between the two was assumed to be total forward AC power (W) applied to the piezoelectric crystal. To validate this assumption, calorimetry was completed for the frequencies where a forward power maxima was observed. Calorimetry experiments were performed by operating the ultrasonic reactor for at least 20 min at a fixed amplitude without cooling. Temperature was recorded every 2 min and the acoustic energy converted to heat was calculated. Calorimetric efficiency was defined as the electrical energy converted to heat as a percentage of nominal power delivered. For each end-piece both resonant frequencies were evaluated.

2.4. Dual-frequency effects on sonochemical oxidation production

For all experiments, the jacketed reactor solution temperature was controlled by a recirculating water bath (Accel 250 LC, Thermo Scientific) at 6 °C. Prior to the start of a reaction, the solution was sparged with 99.999% argon (Airgas, Inc) for 20 min and then continuously during experiment to ensure a constant dissolved gas composition. Once temperature and dissolved argon reached steady state, ultrasound was applied to the target solution. Ultrasound experiments were run for 30 min and at least 6 reactor aliquots were sampled at regular intervals (every ~5 min) for hydrogen peroxide measurement. For each piezoelectric end-piece (P-1/P-2/P-3), control experiments were first run for the two individual resonant frequencies. Then, experiments were completed to determine the optimal dual frequency conditions with the higher frequency at 0, 20, 40, 60, 80, and 100% of the lower frequency AC power level, and at each power ratio the higher frequency was phase-shifted from the lower frequency by 0, 45, 90, 135, 180, 225, 270, and 315 degrees. P-3 was additionally tested with the higher frequency at 10% power of the lower frequency. All combinations of the higher frequency fraction of total power and phase shift was completed with at least three different total powers and then the range of total power values were fit linearly. The slope of the linear fit is the oxidant production as a fraction of applied energy. Error was