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# A phenomenological investigation into the opposing effects of fluid flow on sonochemical activity at different frequency and power settings. 2. Fluid circulation at high frequencies

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ABSTRACT

Sonochemical activity is dependent on flow patterns within the reactor and either no affect or a decrease in activity was observed at 376, 995, and 1179 kHz from overhead stirring. The interaction of fluid flow with ultrasound was further investigated in this study with circulatory flow. The effect of fluid circulation on radical production was investigated at two circulation speeds, with and without surface stabilisation. The sonochemical activity was determined by the yield of hydrogen peroxide, measured by iodide dosimetry. The sonochemically active region was pictured using sonochemiluminescence imaging and the flow fields were visualised with dyed flow videos. At 376 and 995 kHz, an increase in sonochemical activity was observed with the slower flow rate; however at 1179 kHz, the sonochemical activity was either not affected or decreased. The observed changes in sonochemical activity were attributed to an increase in asymmetry of the bubble collapse brought about by fluid motion.



## 1. Introduction

Literature reports of sonochemical activity measurements under the influence of fluid flow have conflicting results [1–9]. Although there is general agreement that at low frequencies, fluid flow is able to reduce the aggregation of bubbles and increase sonochemical activity. Furthermore, evidence suggests at low frequencies that an optimum flow rate exists for sonochemical activity for a reactor with a given power and given frequency [1]. This was confirmed in our previous paper at 40 kHz [10]. Then at high frequencies (above 100 kHz) a variation of trends with respect to sonochemical activity was observed [4,5,8,10]. The additional sonochemical activity at high frequencies was attributed to additional nucleation sites and enhanced mixing [5,8]. However the retardation of activity was not elucidated nor was the consideration of the effect of fluid flow at high frequencies where additional nucleation sites were minimised. In our previous paper [10], the provision of additional nucleation sites was minimised and different trends were observed at the two different input power settings at three frequencies, 376, 995 and 1179 kHz. A decreasing trend in sonochemical activity with an increase in overhead stirring speed was observed at the lower input power setting, and then at the higher power setting, there was no apparent dependence of sonochemical activity on flow rate. The response to the overhead stirrer was attributed to several possible factors; reduction in the active sonochemical area, disturbance and relocation of the ultrasonic intensity, and reduction of the standing wave portion. The reduction of the standing wave portion was theorised to be counteracted from an increase in transient cavitation. Therefore it was hypothesised that fluid flow, which does not interfere with the propagation of the travelling wave would increase or retain sonochemical activity. This hypothesis was tested by introducing fluid circulation at a high and low speed into the travelling wave field at 376, 995 and 1179 kHz in the present contribution.

## 2. Methodology

Experiments were carried out in an ultrasonic reactor (Meinhart Ultraschalltechnik) as described elsewhere [10] with frequencies 376, 995 and 1179 kHz. Potassium iodide (0.1 M) solution was pumped into the bottom of the reactor via a two speed pump placed in a reservoir beaker at 414 and 34 ml $min^{-1}$. The flow out of the reactor from its upper portion returned to the reservoir beaker and the diameter of the inlet and outlet for flow was 0.9 cm. A total volume of 1 L was used for all circulation experiments and 0.5 L for still experiments. The height in the reactor for still experiments and experiments with circulation was kept constant at

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15.5 cm from the transducer plate. Experiments were conducted with and without surface stabilisation in order to reflect the ultrasonic wave [11–13]. Surface stabilisation was achieved with a lid made of foam and coated in parafilm, shaped to float on the surface of the reactor solution. The sonochemical activity was measured as hydrogen peroxide yield determined via iodide dosimetry [14]. Sonoluminescence images and calorimetric power values were recorded as described previously, according to the literature [1,14,15]. Sonochemical activity and calorimetric experiments were repeated 4–7 times, and averages and standard deviations are reported.

The images of the flow patterns were taken by introducing a red dye into the reservoir beaker during circulation and sonication of distilled water. The flow pattern was video recorded using a Digital Single-Lens Reflex (DSLR) camera (Lumix). Videos were recorded at different reactor and flow settings and still images at various time intervals were captured using Picassa software.

## 3. Results and discussion

The results were considered with regards to the hypothesis that flow which does not interfere with the propagation of the ultrasonic wave, could increase or retain the sonochemical activity. The sonochemical activity and the interaction of the acoustic flow with the circulation flow were studied, and the observations were then discussed in regards to sonochemical theory.

### *3.1. Sonochemical activity at different circulation speeds and ultrasound frequencies*

The introduction of circulation increased the yield of hydrogen peroxide at certain speed and power settings for 376 and 995 kHz (Fig. 1). The still experiments with and without surface stabilisation, were reported and discussed in a previous contribution and are shown here for comparison [10].

At 376 kHz circulation at both circulation rates increased the average sonochemical activity at the higher power setting, and at the lower power setting with the slower circulation rate (34 ml $min^{-1}$). At the higher circulation rate, (414 ml $min^{-1}$) and at the higher power, 76 W $L^{-1}$, without surface stabilisation, the hydrogen peroxide yield was increased compared to the still experiment whereas for all the other settings the introduction of circulation did not have a determinable difference on the yield of hydrogen peroxide. Yet, the average value of the yield of hydrogen peroxide was maximised at the slow flow rate, at 76 W $L^{-1}$ with and without surface stabilisation and at 58 W $L^{-1}$ without surface stabilisation.

At 995 kHz the circulation at 34 ml $min^{-1}$ generally increased the yield of hydrogen peroxide (Fig. 1). In contrast, the circulation at 414 ml $min^{-1}$ either did not affect or hindered hydrogen peroxide production. At the ultrasonic power of 72 W $L^{-1}$, without surface stabilisation the flow at 34 ml $min^{-1}$ increased the yield, yet flow at 414 ml $min^{-1}$ did not have a significant effect. At the lower power setting, 52 W $L^{-1}$, without surface stabilisation, the circulation at 414 ml $min^{-1}$ resulted in a lower hydrogen peroxide yield compared to the circulation at 34 ml $min^{-1}$ and the still experiments. In addition, the introduction of a lid resulted in an increase in hydrogen peroxide yield with flow at 34 ml $min^{-1}$ at both ultrasonic powers. In summary the sonochemical activity was maximised at the slower circulation flow rate compared to still experiment and experiments at 414 ml $min^{-1}$ at 376 and 995 kHz.

The observed trend at 1179 kHz did not correspond to the trends for 376 and 995 kHz. At 1179 kHz there was no determinable difference on hydrogen peroxide yield caused by different circulation speeds for all cases. Although, at 75 W $L^{-1}$, the average yield of hydrogen peroxide decreased with an increase in circulation speed with and without surface stabilisation (Fig. 1). Therefore, the different response to circulation at 1179 kHz indicated other mechanisms were involved.

These results were considered with regards to the attributes of the ultrasonic fields. Firstly the ultrasonic field alters with frequency, as was discussed in the preceding submission. In brief; a higher frequency results in an increased number of cavitational events, leading to more sonochemical activity. However a reduced time period of the ultrasonic wave at higher frequencies results in smaller bubble sizes, and hence the participation of the bulk solution in cavitation is reduced, reducing sonochemical activity. Hence sonochemical activity increased from 376 to 995 kHz but was reduced at 1179 kHz .

In this case at each frequency the travelling wave was the primary wave responsible for the production of sonochemical activity since the addition of surface stabilisation reduced the yield of hydrogen peroxide. The effect of surface stabilisation is to increase the standing wave component of the field [11–13,16] and was discussed in our previous paper [10] with respect to the observations with and without stabilisation at each frequency. The travelling wave and acoustic streaming are known to increase with an increase in frequency and intensity [17]. The attenuation of the intensity leads to a pressure gradient as the distance from the transducer increases which in turn causes acoustic streaming. Intensity, *I*, in the reactor is dependent on the attenuation coefficient and the distance, *d* from the transducer;

$$I = I_0 e^{-\alpha d}$$

where $I_0$ is the intensity and $\alpha$ is the attenuation coefficient. A modified attenuation coefficient was proposed based on theoretic predictions and experimental data [18], given by:

$$\alpha = \frac{8\mu\pi^2 f^2}{3\rho C^3}$$

where $\mu$ and $\rho$ are density and viscosity, *C* and *f* are speed of sound and frequency. Therefore attenuation increases with an increase in frequency which increases the pressure gradient which in turn leads to an increase in acoustic streaming velocity. In addition the presence of cavitational activity was demonstrated to contribute to the attenuation of ultrasound and subsequent streaming [19]. Moreover acoustic streaming can be reflected by walls or liquid surfaces [5] which may reduce the overall streaming force. Consequently the acoustic streaming was stronger without surface stabilisation at the higher input power for frequencies, 995 and 1179 kHz. This was due to the increased attenuation coefficient at 1179 kHz and the increased cavitational activity which in turn increased the attenuation at 995 kHz. Then the acoustic streaming was weakest at 376 kHz, at 58 W $L^{-1}$ with surface stabilisation.

The threshold of cavitation was also considered. An increase in power will increase the amplitude of the ultrasonic wave and the incidence and severity of cavitation. Moreover a minimum power or intensity exists for sonochemical activity to be observed, known as the cavitational threshold [20]. As the intensity of the ultrasound increases, the ratio of the maximum radius of the bubble to the minimum ratio increases. Hence at higher intensities a higher active volume of cavitation is achieved [21]. A linear increase in activity with dissipated power was reported [14] and the cavitation threshold increases with an increase in frequency due to the decreased time period of the ultrasonic wave [17]. Since the starting conditions with respect to the geometry and the physicochemical properties of the irradiated solution are the same for each scenario, the lowest cavitational threshold is at 376 kHz and the highest at 1179 kHz.