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Modeling aspects of dual frequency sonochemical reactors

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Abstract

The dual or multi-source irradiation with same or different operating frequency has proved to be a new dimension to the sonochemical reactors. In the present work, the model developed earlier [P.A. Tatake, A.B. Pandit, Modeling and experimental investigation into cavity dynamics and cavitational yield: influence of dual frequency ultrasound sources, Chem. Eng. Sci. 57 (2002) 4987] using Rayleigh–Plesset equation has been made more realistic by incorporating the effect of liquid phase compressibility. The aim has been to study the bubble dynamics under the influence of dual frequency acoustic field and explain the superiority of the same as compared to the single frequency irradiations. The effect of intensity and dual-frequency on the bubble dynamics and the conditions of the cavity collapse has been investigated. The numerical results have been compared with the previous experimental trends under similar operating conditions. The simple model developed in the present work seems to quite satisfactorily explain the experimental results obtained using dual frequency sonication system. Thus, the methodology adapted in the present work is a useful starting point for the modeling and designing large scale multiple frequency reactors. Recommendations have also been made for developing realistic bubble dynamics model which should help in optimization of multiple frequency sonochemical reactors.
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Keywords: Sonochemical reactors; Bubble dynamics; Dual frequency operation; Acoustic field; Intensification

1. Introduction

The spectacular effects of cavitation generated using ultrasound have been observed in almost every field of chemical and physical processing. However, some unresolved engineering problems have restricted the applications on a commercial scale. The main problems associated with the efficient design and operation, are the non-uniform cavitational activity, lack of suitable scale up strategies in terms of optimization of the operating and design parameters, and a strong dependence of cavitational activity on the system under consideration. The problems, associated with scale up and design of commercial sonochemical reactor, have been discussed in some of the earlier works [1–3]. The possible path forward has been pointed out to be the use of multiple frequency reactors. Many researchers found that the use of multiple frequency system can increase the active cavitational volume and maximum utilization of the supplied energy can be achieved [2,4–7]. Specifically, the dual frequency sonochemical reactors have been reported to be more efficient than a single frequency sonochemical reactor [7,8–12].

The cavitational bubbles under the influence of two superposed ultrasound waves may have a totally different dynamics as compared to single frequency ultrasound source [12]. A new acoustic field is generated when the traveling waves intersect. This acoustic field differs in properties than those for individual traveling waves [11]. Swamy and Narayana [11] have pointed out that when the amplitudes of the two waves traveling in opposite direction is not equal then the net resultant displacement of particles does not fall to zero. Energy density of standing wave, in this case, is twice that of the individual progressive wave. Thus, it is required to develop a bubble dynamics model for the multiple frequency reactors and predict the cavitational intensity generated in the reactor. The developed model, after comparison with the trends obtained with the experimental illustrations, should aid in optimization of the operating parameters. We now discuss some of the earlier experimental and theoretical approaches in the case of dual frequency reactors in details.

2. Previous work

Tatake and Pandit [12] investigated the use of dual frequency sound source experimentally as well as theoretically. They compared the numerical results of bubble dynamics for dual frequency source to that of a single frequency source at equal level

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Nomenclature

C	velocity of sound in the medium (m/s)
f_a	frequency of first ultrasound source (kHz)
f_b	frequency of second ultrasound source (kHz)
I	intensity of irradiation (W/m^2)
p_{go}	initial gas pressure in the bubble (N/m^2)
p_v	vapour pressure (N/m^2).
P	collapse pressure at bubble wall (N/m^2)
P_A	driving pressure amplitude of ultrasound (N/m^2)
P_{A1}	time varying pressure field due to first sound wave (N/m^2)
P_{A2}	time varying pressure field due to second sound wave (N/m^2)
P_i	initial pressure inside the bubble (N/m^2)
P_t	resultant time varying pressure field due to two waves (N/m^2)
P_0	ambient pressure (N/m^2)
p_1, p_2	initial and final pressures during each simulation step respectively (N/m^2)
P_∞	pressure in the surrounding liquid (N/m^2)
r	radius of cavity/bubble (m)
$\dot{r}$	($\mathrm{d}r/\mathrm{d}t$), bubble wall velocity (m/s)
$\ddot{r}$	($\mathrm{d}^2r/\mathrm{d}t^2$), bubble wall acceleration (m/s^2)
r_{max}	maximum radius of the bubble/cavity (m)
r_0	initial radius of the bubble/cavity (m)
R	radial distance from the bubble wall (m)
t	time (s)

Greek letters

γ	specific gas constant
μ	viscosity of liquid (N s/m^2)
ρ	density of the liquid medium (kg/m^3)
σ	surface tension of liquid (N/m)
ϕ	phase difference between the two sound waves

of energy dissipation per unit volume. They have demonstrated the advantages of dual frequency sound source over a single frequency sound source, over a relatively narrow range of the operating parameters, numerically as well as experimentally. Also, Rayleigh–Plesset equation was considered in the work which is a simplistic approach and may not be applicable to all the reactors in industrial applications.

Servant et al. [2] modified the CAMUS code (cavitating medium under ultrasound) originally developed for a single frequency sonication to include the dual frequency sonication effects. They have numerically shown that active volume of cavitation or volume fraction of cavitational bubbles is higher for dual frequency sonoreactors than mono frequency sonoreactors. They have also pointed out that the dual frequency sonication involves more intense cavitation bubble field, though at a fixed set of operating parameters.

Gogate et al. [6] experimentally found 4–8 times more transfer of the input electrical energy and subsequent utilization for cavitational events as compared to the single frequency operation. They also observed 1.5–20 times more cavitational yield as compared to the conventional reactors, i.e. ultrasonic bath and horn respectively. For the degradation of *p*-NP, Sivakumar et al. [7] have experimentally proved that the energy efficiency as well as cavitational effects for dual frequency sonication is higher than the single frequency sonication. Swamy and Narayana [11] have reported better metal recovery in leaching process using dual frequency ultrasonic irradiation as compared to the single frequency operation. They have also observed the reduced irradiation time in the case of dual frequency ultrasound source for maximum metal recovery as compared to a single frequency ultrasound source. Zhu et al. [9] carried out ultrasonic irradiation at 28 kHz combined with 0.87 MHz sound sources and reported that the dual source irradiation resulted into more iodine liberation than the arithmetic sum of the quantity produced by two individual sonication modes.

Most of the previous work, either theoretical or experimental, using dual frequency ultrasound has been carried out over a limited range of operating parameters. In the present numerical investigation, wide range of operating parameters (intensity and frequency), over which sonochemical equipments are generally operated has been considered. The aim has been to recommend optimum set of operating parameters to maximize the cavitational effects in dual frequency reactors. The effect of the operational intensity and dual frequency irradiation on the collapse pressure and/or r_{max}^3/t_c ratio of cavity (r_{max} is the maximum radius of bubble and t_c is the collapse time of bubble) have been investigated. The r_{max}^3/t_c ratio gives a qualitative idea about the amount of the free radicals generated at the end of collapse of cavities. Thus, the trends established in the present work are equally applicable to both the governing mechanisms of sonochemical reactors, viz. pyrolysis and free radical attack. It is well established that cavitational yield strongly depends on the ratio r_{max}/r_0 (r_0 is the initial radius of bubble). The cavitation bubbles possess maximum potential energy at its maximum size, r_{max}. This potential energy, during bubble collapse, is partly converted into chemical reactions (i.e. formation of radicals and ions) and partly into mechanical energy, heat and light emission. Higher the r_{max}, higher will be the potential energy available and higher will be the amount of energy converted into chemical reactions. Indeed, many other researchers [13–14], considering heat and mass transfer effects have explained the trends in cavitation yield on the basis of r_{max}/r_0. They have numerically as well as experimentally explored this fact. In the present work as well as in the earlier work [12], we have extended this concept by considering r_{max}^3/t_c (by considering 't_c' we have also incorporated the rapidness of collapse). When t_c is very less (and thus higher r_{max}^3/t_c ratio), the vapors do not get sufficient time to escape from the bubble and more amount of vapor dissociates resulting in higher amount of radicals formation. Thus, to correlate the ratio r_{max}^3/t_c with the amount of radicals qualitatively is indeed justified.

The numerical results obtained have been also compared with the experimental results obtained by the earlier investigators with an aim of explaining the intensification obtained due to the use of the dual frequency irradiations. It should be also noted here that the geometry, shape and size of the reactor and or/transducer will play a part in deciding the final cavitational yield and hence exact matching of the data is not expected. The current work is only a starting step in the modeling of multiple frequency reactors and should qualitatively match the trends obtained using dual frequency irradiations over a wide range of operating parameters. More work is indeed required, as discussed in detail later, to approach a realistic situation.

3. Numerical scheme

3.1. Model equations and methodology

The model proposed by Tatake and Pandit [12] for dual frequency sound source has been used in the present work with the consideration of the compressibility of the liquid medium. It is very important to consider the compressibility effects in industrial scale operations as the predictions of the cavitational intensity differ significantly under conditions of large energy input into the system [15], especially due to the spatial non-uniformity.

When two sound waves, with a phase difference of ϕ, having frequencies f_a and f_b, pass through a cavitating liquid medium, the time varying pressure field of each wave can be expressed as

$$P_{A1} = P_0 - P_A(\sin 2\pi f_a t) \quad (1)$$

$$P_{A2} = P_0 - P_A(\sin 2\pi f_b t + \phi) \quad (2)$$

where P_0 is the ambient pressure, and P_{A1} and P_{A2} are the time varying pressure field due to first and second sound wave, respectively.

The pressure amplitude P_A of ultrasound is given as

$$P_A = (2I\rho c)^{1/2} \quad (3)$$

where I is the intensity of ultrasound in W/m^2, ρ the density of the cavitating medium, kg/m^3 and c is the speed of sound in the cavitating medium (1500 m/s for water).

The resultant time dependant pressure for two irradiating waves is thus given by

$$P_t = P_0 - P_A[(\sin(2\pi f_a t) + \sin(2\pi f_b t + \phi)] \quad (4)$$

For two waves having phase difference of zero, the resultant time varying pressure field is given by

$$P_t = P_0 - P_A[(\sin 2\pi f_a t + \sin 2\pi f_b t)] \quad (5)$$

For the two waves having different acoustic pressure amplitude the above equation can be written as

$$P_t = P_0 - P_a(\sin 2\pi f_a t) - P_b(\sin 2\pi f_b t) \quad (6)$$

where P_a and P_b are the pressure amplitude of first and second wave, respectively. From Eqs. (1), (5) and (6), it can be seen that for the combination of the two acoustic waves the fluctuating pressure field is different than the single acoustic wave of higher intensity. Thus, in the case of dual source sonication operation, the new acoustic wave pattern is created depending on the phase angle between the two waves and the operating pressure amplitudes and the frequencies used.

Previous numerical investigation [12] has reported that the case of zero phase difference between the two waves is most beneficial for the sonication operation as more uniform acoustic field is associated with such type of sonication operation. Although the case of zero phase angle is purely from the mathematical point of view it can be created in actual sonochemical reactor with proper locations of transducers, electronics and operating frequencies. Thus, in the present study, only sin–sin wave combination has been investigated.

First at any specified intensity pressure amplitude has been obtained from Eq. (3). For a single source operation, this pressure amplitude has been substituted in the Eq. (1) in order to obtain the time varying acoustic pressure field, whereas for the dual source operation it has been substituted in the Eq. (5). Thus, the total power input has been distributed in the case of dual source operation. When the intensities of the dual sources are different [as considered in the Section 4.3(a)] then Eq. (6) has been considered. In this case P_a and P_b depending on the intensities of the two sources have been obtained from Eq. (3) and the resulting P_a and P_b have been substituted in the Eq. (6) to obtain the time varying acoustic pressure field.

P_t as obtained from Eqs. (5) or (6), can be substituted for P_∞ in the following Rayleigh–Plesset equation, describing the cavity dynamics:

$$r\frac{d^2r}{dt^2} + \frac{3}{2}\left(\frac{dr}{dt}\right)^2 = \frac{1}{\rho}\left[P_i - P_\infty - \frac{2\sigma}{r} - \frac{4\mu}{r}\left(\frac{dr}{dt}\right)\right] \quad (7)$$

where r is the radius of cavitational bubble at any time, μ the viscosity of the liquid medium, N s/m^2, σ the surface tension, N/m, P_i the pressure inside the bubble, N/m^2 and P_∞ is the pressure in the liquid far from the bubble, N/m^2.

The collapse pressure at bubble wall is estimated as

$$P = \rho\left[r\frac{d^2r}{dt^2} + \frac{3}{2}\left(\frac{dr}{dt}\right)^2\right] \quad (8)$$

The effect of mass and heat transfer on the general trends of bubble dynamics with operating parameters in the cavitation phenomena is usually not significant [14,16,17]. It should be noted that the inclusion of the heat and mass transfer effects [18,19], leading to a realistic situation, might change the absolute values of the predicted collapse pressure but definitely will not change the predicted trends including the quantitative variation of the maximum radius as well as the collapse time. Qualitative matching of the observed experimental trends and qualitative recommendations for the operating parameters is the main aim of the present work. Thus effect of mass and heat transfer has been neglected to develop a simplistic model for explaining the superiority of the dual frequency reactors.

For the bubble wall velocity, less than the speed of sound, a simplistic Rayleigh–Plesset equation is applicable to predict the relative trends in terms of effect of operating parameters in single as well as dual frequency reactors. A more realistic approach for quantitative matching and to develop design correlations would be to use a rigorous model not based on the assumption of uniform bubble interiors and not considering polytropic approximation. Considering the main objectives of the present work, Rayleigh–Plesset equation has been used till bubble wall velocity equal to the velocity of the sound in the medium.

When bubble wall velocity is greater than the sound velocity it is important to consider the compressibility of the cavitating medium and hence the following equation proposed by Tomita and Shima [20], which accounts for the liquid phase compressibility (second order) has been considered:

$$r\ddot{r}\left(1-\frac{2\dot{r}}{C}+\frac{23\dot{r}^2}{10C^2}\right)+\frac{3}{2}\dot{r}^2\left(1-\frac{4\dot{r}}{3C}+\frac{7\dot{r}^2}{5C^2}\right) +\frac{1}{\rho}\left[p_\infty(t)-p_{2(R=r)}+\frac{r}{C}(\dot{p}_\infty(t)-\dot{p}_{1(R=r)}) +\frac{1}{C^2}\left\langle -2r\dot{r}(\dot{p}_\infty(t)-\dot{p}_{1(R=r)})+\frac{1}{2}(p_\infty(t) -p_{1(R=r)}\left(\dot{R}^2+\frac{3}{\rho}(p_\infty(t)-p_{1(R=r)})\right)\right\rangle\right]=0 \qquad (9)$$

where the p_1 and p_2 are functions of R and are given as follows:

$$p_{1(R=r)}=p_{\text{v}}+p_{\text{go}}\left(\frac{r_0}{r}\right)^{3\gamma}-\frac{2\sigma}{r}-\frac{4\mu}{r}\dot{r} \qquad (10)$$

$$p_{2(R=r)}=p_{1(R=r)}-\frac{4\mu}{3\rho c^2}(\dot{p}_{\infty(t)}-\dot{p}_{1(R=r)}) \qquad (11)$$

The physical properties of water at 298 K, which are supplied to the numerical code are—density (ρ) = 1000 kg/m^3, viscosity (μ) = 0.0009 N s/m^2 and surface tension (σ) = 0.072 N/m. Fig. 1 shows the flow diagram of numerical solution scheme used in the present work.

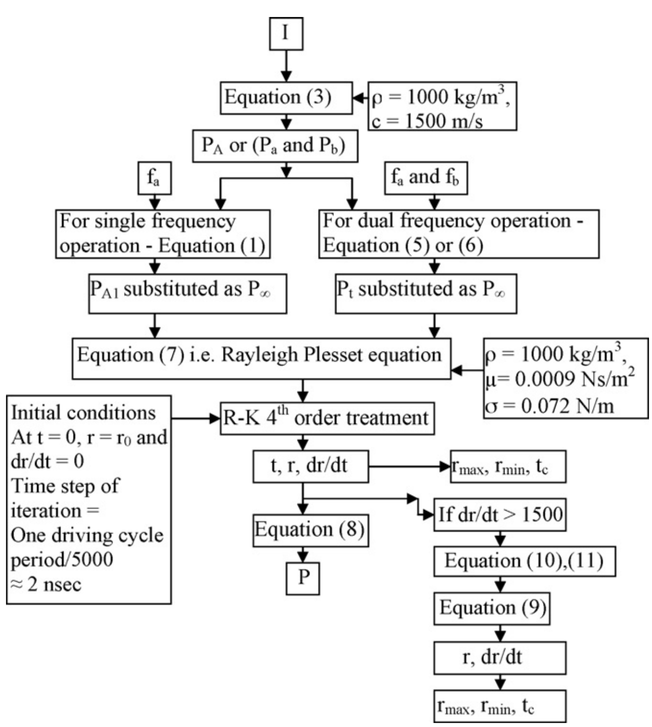

Fig. 1. Flow diagram of numerical solution scheme.

3.2. Assumptions made

The following assumptions have been made in the present study:

1. The bubble has been considered to be spherical in shape through out the life-time (although bubble loses its spherical shape especially during final stages of collapse, for a single bubble dynamics it is a general accepted approximation).
2. Uniform spatial pressure and temperature within bubble (this simplified approach does not change a single bubble dynamics significantly [14] in terms of explaining the observed trends in a qualitative manner).
3. Heat and mass transfer effects have not been considered in bubble dynamics (previous numerical investigation [14] indicates that r_{max} and r_{min} do not change significantly with the inclusion of these effects).
4. Initial radius (r_0) of the bubble is assumed to be 5 and 10 μm (previous experimental studies [21,22] have reported above mentioned range of initial size for most of the bubbles for the range of irradiation frequencies considered in the present study).

It should be noted here that the simplistic model developed in the present work is specific and suitable for explaining the trends in a qualitative manner. For a perfect quantitative matching and development of the design equations for the prediction of cavitational intensity as a function of operating parameters, a more rigorous model is required. In particular, the assumptions 2 and 3 stated earlier may be relaxed to approach the realistic situation. A more rigorous bubble dynamics equation such as Keller Miksis equation [23] may also be used, though the simplistic models such as the one used in the present work also explain the observed trends satisfactorily.

4. Results and discussion

The effect of the ultrasound frequency and the intensity on bubble dynamics for dual ultrasound waves has been investigated numerically through the solutions of Eqs. (7) and (9). The compressibility of the liquid medium has been considered to obtain more realistic picture. The simulations have been terminated when r/r_0 ratio reached 0.1 (0.3 in some cases), on the assumption that for sonochemical processing, the collapse of the bubble is rapid and violent and at the collapse, bubble breaks apart dispersing the contents of the bubble into the liquid [14,17]. The above mentioned values of r/r_0 are the minimum attained in 1–3 oscillations of the bubble depending upon the operating intensity and the frequency of sonication. The cavitational bubble, in most of the cases, under strong acoustic forcing, collapses in few acoustic cycles. However, under some specific conditions (at high frequencies), it may oscillate (rebound) for some period after a first strong partial collapse. In such cases, during rebounds, the bubble does not attain its original maximum size reached during the first growth phase. This is known as stable cavitation and in general, the collapse of the bubble is not as severe as in transient cavitation [16]. Thus, in this study the few expansions and the subsequent collapse of the cavitational bubble have been considered, neglecting the stable multiple-oscillations of the bubble. Again a more realistic solution process might consider these oscillations, though it will necessarily not affect the predictions of the maximum radius values and also the observed trends in terms of effect of operating parameters. Preliminary results with modification of the simulation procedure did confirm this fact. The exact predictions of the collapse pressure/temperature might be marginally affected but more work in this direction is required to clearly establish the usefulness of the consideration of multiple bubble oscillations.

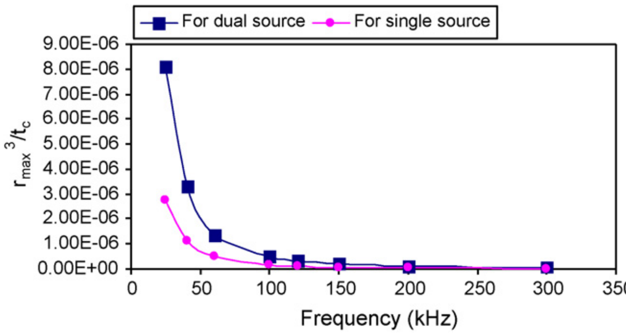

Fig. 3. Variation in r_{max}^3/t_c with dual frequency for $I = 10\,W/cm^2$.

4.1. Effect of dual frequency sonication

The effect of dual frequency on the collapse pressure of the cavity, using Eqs. (7) and (9), has been considered over the frequency range of 25–300 kHz, typically used in industrial sonochemical equipments. Tatake and Pandit [12] have considered different combinations of dual frequencies, e.g. 25–25, 25–40, 25–50 kHz, etc. They observed that the combination of same frequency results in the higher bubble growth and hence higher subsequent collapse pressure of the bubble. So, in the present study, similar combination of frequencies over a much wider range has been considered.

From Fig. 2, it can be seen that as the operating frequency of the ultrasound is increased, the r_{max}/r_0 ratio decreases significantly and so is the collapse pressure of the cavity. The net collapse time of the cavity (t_c = time from r_{max} to r_{min} during the collapse) was also found to decrease with an increase in the frequency of ultrasound, when operated in dual source mode. Similar results have been obtained even for different initial cavity size, i.e. $r_0 = 5\,\mu m$. From Fig. 3, it can be found that as the frequency of sound increases, the r_{max}^3/t_c decreases. Tatake and Pandit [12] and Sivakumar et al. [7] have indicated the importance of r_{max}^3/t_c. It should be noted that the formation of the radicals not only depends on the collapsing conditions of the bubble but also on the heat and mass transfer effects, at the bubble–liquid interface, during the expansion and the collapse of the bubble. During the expansion, the water vapors transfer into the bubble due to evaporation and during the collapse phase these vapors partly undergo condensation while some part dissociates into radicals. For higher r_{max}, more water vapor transfer into the bubble is expected. If t_c, net collapse time, is less, then entrapment of the vapors is more and thus, at the end of the collapse, higher quantity of the vapors dissociates resulting in more amount of radicals. Although, in the present work, heat and mass transfer effects are neglected, r_{max}^3/t_c could be an indicative of these effects qualitatively. Thus, for higher r_{max}^3/t_c ratio, higher collapse pressure and greater number of radicals can be expected. This factor not only gives the idea of the severity of the cavity collapse (through t_c) but also the cavitationally active zone (through r_{max}^3) for radical formation inside the collapsing cavity (quantitative discussion has been given in the Section 4.3). Thus, it can be concluded, on the basis of single bubble dynamics, that combination of the lower frequency of sound ($f < 100$ kHz) operated in a dual source mode would give higher cavitational yield as compared to combination of higher irradiation frequency. At this stage it should be mentioned that this conclusion is based on a single bubble numerical investigation. In actual sonication operations, for higher irradiation frequencies, greater number of effective cavitation events per unit time can be generated and in that case higher effective bubble population along with the collapse conditions of bubbles can play a major role in the overall sonochemical activity.

From Fig. 3, it can be also seen that there is a significant difference between r_{max}^3/t_c for dual and single frequency operation at any specified frequency (<100 kHz) for the same operating irradiation intensity. It can be observed that for dual frequency operation r_{max}^3/t_c is greater than that for a single frequency operation. For the dual frequency operation at 25 kHz (two sources with half the power both operating at 25 kHz), this factor is 2.7 times greater than that of a single frequency operation at 25 kHz with same cumulative power. For 40 kHz it is three times greater than that of single frequency operation. This clearly indicates the advantage of the use of dual frequency ultrasound source over a single frequency source. At the higher frequencies, the difference is small indicating that at higher operational frequencies, multiple source operation may not be significantly advantageous. However, this conclusion is only based on the single cavity consideration. Multiple sources (non-interfering) will result into higher number of cavitational events and thus may still prove beneficial.

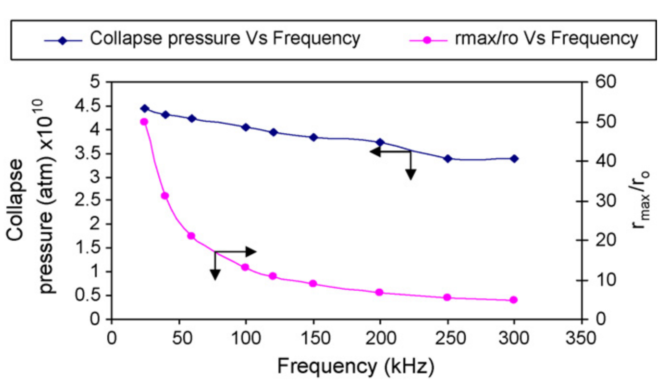

Fig. 2. Variation in the collapse pressure with dual frequency (25/25 kHz, 50/50 kHz, etc.) for $I = 10\,W/cm^2$ and $r_0 = 10\,\mu m$.

4.2. Effect of intensity of irradiation

The effect of intensity on the collapse pressure of the cavity has been numerically investigated, using Eq. (9), for dual sound source. The constant simulation parameters were $f_a = f_b = 25$ kHz and $r_0 = 10$ μm. It should be noted that in the case of dual source, the power intensity was equally distributed over the two transducers, thus the overall power dissipation per unit volume in the system was the same. For example, when total intensity was 10 W/cm^2, for dual source operation, 5 W/cm^2 was substituted in Eq. (3) and the resulting P_A (which will be less) was substituted in Eq. (5). From Fig. 4, it can be seen that for both the single and dual sources operating at the same frequency, as the intensity of irradiation is increased over the range of 10–300 W/cm^2 (equally distributed in the case of dual frequency source), the collapse pressure of the cavity (as estimated using Eq. (8)) is also found to increase initially and then remains almost constant. It can be seen that for dual source there is an optimum value of intensity, i.e. 60 W/cm^2. It is due to the higher growth and rapid collapse of the cavity at the operating intensity of 60 W/cm^2 than for the other values of intensity. Over the range of 10–300 W/cm^2, it can be found that the cavity collapse pressure for dual source is always greater than for a single source operation. It was observed that the maximum growth of the cavity before collapse, as indicated by the value of r_{max}/r_0 ratio, was substantially greater for dual source than for a single source. Again, it can be concluded that over the considered range of intensity, dual sound source is more efficient than a single source in terms of generating higher collapse pressure and thus possibly the cavitational yield.

Fig. 5 gives the variation in the collapse pressure (using Eq. (9)) of the cavity as a function of the operating intensity for dual source of 25–25 kHz and with $r_0 = 5$ μm. It can be observed that the optimum value of intensity is now 80 W/cm^2 for $r_0 = 5$ μm. Thus, the initial size of cavity influences the optimum value of intensity. From Fig. 6, it can be seen that for $r_0 = 2$ μm, there is marginal increase in the collapse pressure of the cavity beyond an intensity value of 100 W/cm^2. Thus, for dual source operation it can be concluded that as the initial size of the cavity increases (medium with higher vapour pressure or lower surface tension or higher operating temperature) the optimum value of intensity of ultrasound to get maximum cavitational growth and/or effect decreases.

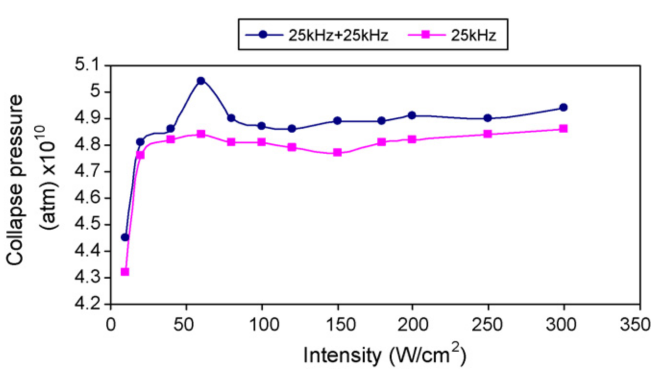

Fig. 4. Variation in the collapse pressure with intensity and for $r_0 = 10$ μm.

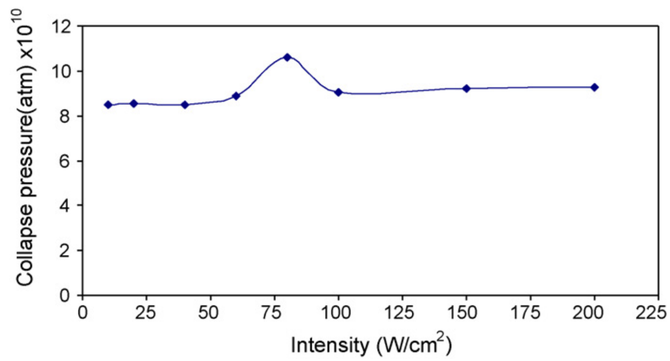

Fig. 5. Variation in the collapse pressure with intensity and for $r_0 = 5$ μm.

4.3. Comparison with the previous experimental results

4.3.1. Feng et al. [5]

Feng et al. [5] have pointed out that for dual source operation (one operating in kHz range and the other in MHz range), transducer frequency in the kHz range is responsible for the observed sonication effects and the other transducers operating in the MHz range acts as an assistant to accelerate mass transfer and enhance the cavitation. On the basis of the above fact, Zhu et al. [9] have carried out experiments with different sonication equipments. We now compare some of their experimental results with the trends obtained from our numerical simulations. Zhu et al. [9] have performed the KI decomposition under 28 kHz sonication in combination with 0.87 MHz ultrasonic irradiation. In their study, the output of 28 kHz ultrasound was fixed at about 58 W/cm^2 and the intensity of 0.87 MHz ultrasound was varied over a range of 4–10 W/cm^2. They found that when the intensity of 0.87 MHz source was increased in the range of 4–7 W/cm^2, the cavitational yield (i.e. iodine released) of the combined irradiation was equal to 1.9–3.4 times the sum of the yields given separately by the two sources operating independently. The numerical results obtained in the present study (using Eq. (8)), for the same operating parameters, resemble their experimental results. In the present numerical analysis, the intensity of the 28 kHz ultrasound was fixed and that of 0.87 MHz was varied. From Fig. 7, it can be seen that there is a significant difference between the values of r^3_{max}/t_c for 28 kHz and the combined irradiation (i.e. 28 kHz + 0.87 MHz). Over the considered range of intensity, the values of r^3_{max}/t_c are 6–8 times greater for combined irradiation, corresponding to 1.9–3.4 times

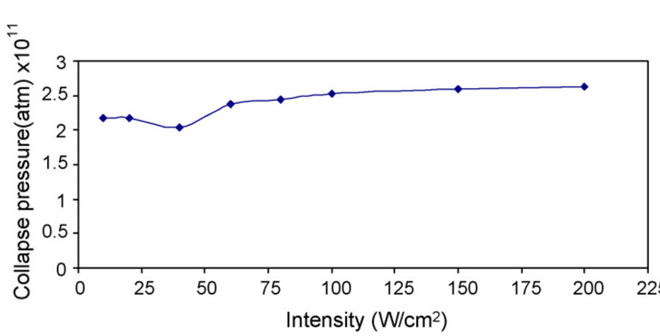

Fig. 6. Variation in the collapse pressure with intensity and for $r_0 = 2$ μm.

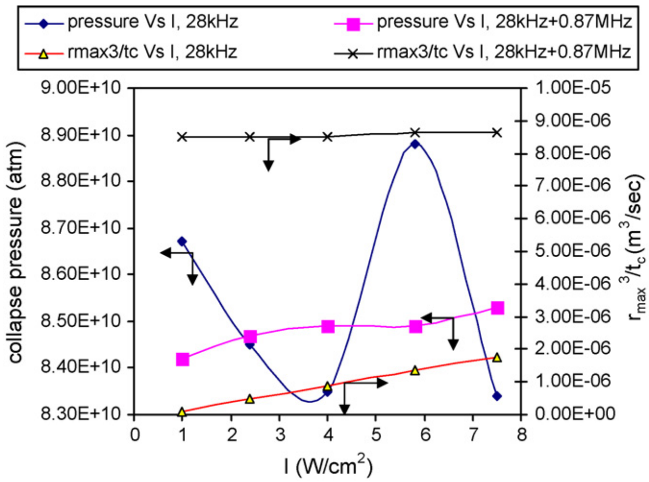

Fig. 7. Variation in r_{max}^3/t_c and collapse pressure with intensity for $r_0 = 5$ μm and for 28 kHz, 28 kHz + 0.87 MHz.

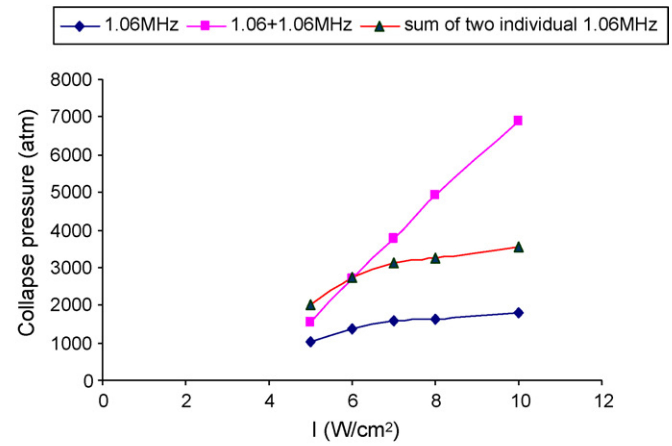

Fig. 8. Variation in the collapse pressure with intensity and for $r_0 = 5$ μm and MHz frequencies.

increase in the iodine liberation yield observed by Zhu et al. [9]. There is no significant difference (varies within ±7%) in the collapse pressure of the cavities for combined irradiation but irregular variation has been observed for 28 kHz irradiation as can be seen in the Fig. 7. It should be noted here that even though at some values of intensities, for 28 kHz irradiation, the collapse pressure is higher (this may be due to small variation in final r/r_0 values), the r_{max} values for combined irradiation were significantly higher than for only 28 kHz irradiation. The net collapse time was less for 28 kHz irradiation than the combined irradiation. The ratio r_{max}^3/t_c thus, represents the combined effect of maximum cavity growth and net collapse time of the cavity (i.e. the violence as well as the active volume of the collapse). Thus, r_{max}^3/t_c is indicative of the cavitational yield due to ultrasonic irradiation. Hence, here again the advantage of dual source ultrasonic irradiation (operating even at different frequencies) over a single frequency irradiation has been justified numerically and in qualitative manner. A more rigorous model with rigorous simulation procedure might also result in quantitative matching of the extent of intensification obtained due to the use of dual frequency reactors.

4.3.2. *Zhu et al. [10]*

Zhu et al. [10] also generated cavitating conditions using dual beam orthogonal 1.06 MHz pulse ultrasonic irradiation. For the values of intensity greater than 4.7 W/cm^2, they found that the cavitational yield of dual beam pulse ultrasound irradiation was about three times the sum of the yield of the two individual pulse ultrasonic irradiation. In the present case, simulations have been done at the above-mentioned operating parameters and for an assumed $r_0 = 5$ μm. The simulations were terminated when r/r_0 reaches 0.3 instead of 0.1 as at higher frequency, cavities undergo many oscillations (number of partial collapses) and r/r_0 does not reach 0.1. In this particular simulation, condition of compressibility (bubble wall velocity greater than the velocity of the sound in the liquid medium) was never reached. In this particular case, it was not possible to calculate r_{max}^3/t_c ratio due to multiple oscillations of the cavity. From Fig. 8, it can be seen that the collapse pressure (obtained using Eq. (8)) for the combined irradiation is significantly greater than a single (1.06 MHz) and sum of two individual 1.06 MHz irradiations. Over the range of intensities of 7–10 W/cm^2, the collapse pressure for combined irradiation is 1.2–1.9 times greater (corresponding to three times increase in the iodine liberation observed by Zhu et al. [10]) than the sum of the collapse pressure of the two individual irradiation again indicating the applicability of the present numerical scheme and the interpretation of the results through the parameters such as the collapse pressures and r_{max}^3/t_c. It appears that there is no quantitative correspondence between the predictions of the numerical simulations (up to two times increase) and experimental results (up to three times increase). This indicates that the cavitational yield (quantification of the cavitational effects in terms of experimental output) and the cavitational intensity (quantification of collapse temperature/pressure pulse and/or quantum of free radicals) are related by some mathematical relationship as discussed in our earlier work [24]. A simplest form of the mathematical relationship can be given as follows:

$$\text{cavitational yield} = K(\text{cavitational intensity})^n$$

where K and n depends on the type of the reactor and the type of the desired transformations.

It is worth mentioning that the cavitational yield depends on the temperature and pressure conditions associated with bubbles as well as on the size and shape of the reactor, geometric arrangement of the transducers (which governs the wave propagation patterns and the associated pressure fields in multiple transducer system), and the type of reaction being carried out. The exponent "n" in the above equation can be related to all these factors in the form of a lumped parameter.

4.3.3. *Swamy and Narayana [11]*

Swamy and Narayana [11] in the case of leaching of metal, found that single frequency ultrasound either with 20 or 40 kHz

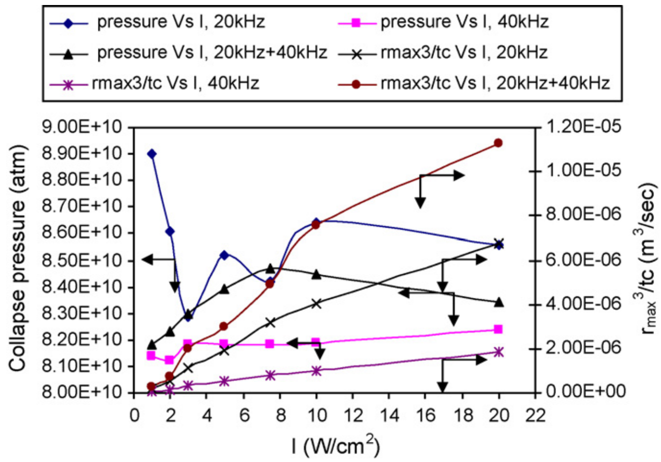

Fig. 9. Variation in r_{max}^3/t_c and collapse pressure with intensity and for $r_0 = 5$ μm and for 20, 40, 20 + 40 kHz.

frequency with 2 W/cm^2 intensity of irradiation for 20 min yielded maximum metal recovery of 51.5% and 62.5%. While the combination of these two ultrasound waves at the same intensity (same power output) and for same irradiation period resulted in 92% metal recovery. Here again, simulations have been carried out at the above mentioned operating conditions assuming $r_0 = 5$ μm (using Eqs. (8) and (9)). From Fig. 9, it can be seen that at an intensity of 2 W/cm^2, the r_{max}^3/t_c value for (20 + 40) kHz combination is 1.3 and 4.3 times greater than 20 and 40 kHz individual sonication, respectively. It can be noted that in the case of a single 20 kHz irradiation, there is an irregular variation in the collapse pressure (within ±7%). The r_{max}^3/t_c is an indicative of the cavitational yield as discussed earlier. This clearly indicates an increase in the cavitational activity in the case of dual ultrasound source.

Thus, from the above discussion and as suggested and demonstrated by Tatake and Pandit [12] and Swamy and Narayana [11], it can be concluded that it is more beneficial to distribute the total power (intensity) in two or possibly more transducers located coaxially in opposite direction (to provide interference of the sound waves irradiated by each transducer) instead of supplying the same power through a single transducer. When the same amount of power is distributed between the two transducers located coaxially in opposite direction, higher energy density could be created due to larger amplitudes. An optimum value of intensity, for the collapse pressure has been observed but no such optima for r_{max}^3/t_c. In the case of leaching of metals by sonication for maximum copper recovery, Swamy and Narayana [11] have observed the optimum value of intensity. This may be due to the different system parameters and the fact that in actual experiments, decoupling of ultrasound from the cavitating liquid may take place as correctly pointed out by Ondruschka et al. [25] at very high operational intensities.

It should be noted that the number of active bubbles could also play a major role in previously observed enhancement in the cavitational activity for dual frequency irradiations. At this stage, we can only predict the possibility of active number of bubbles depending on operating parameters and it is very difficult to incorporate this part in the modeling of bubble dynamics, partly because of the unknown number of bubbles and partly because of bubble–bubble interactions.

In the present work, air-bubble has been considered. Thus, the presence of polyatomic molecules, such as O_2, N_2, H_2O are expected within a bubble. The heat transfer from the collapsing bubble to the surrounding liquid medium can be expected due to the thermal conductivity of the different species within the bubble. The pressure inside the bubble also depends on these heat transfer effects and which may lead to the change in the collapse pressure in someway. However, in the present study, the heat transfer from the chemical species and gaseous material within a bubble to the surrounding liquid (due to thermal conduction) have been neglected. However, the qualitative trends obtained (with the effect of intensity and frequency) are not expected to change with or without the inclusion of these effects. However, for a specific quantitative matching, inclusion of heat and mass transfer effects are recommended.

In the present study the initial size of the bubble, r_0, is considered as 5 and 10 μm on the basis of previous experimental investigations [21,22]. It should be noted that in actual sonication operation bubbles with different initial size exist depending on the system geometry and set of operating parameters. The obtained trends in terms of superiority of the dual frequency reactors and/or effect of operating parameters would not change for different initial sizes of the bubble.

The present model is simple yet the obtained trends in the previous experimental results can be explained with it. The difference observed in the results obtained numerically and experimentally could be explained on the basis of different system parameters, for example, initial size of nuclei in the reacting volume, geometry of the equipment, physical properties of the cavitating media, etc. It should be noted that the present mathematical scheme is based on the one-dimensional wave equation and as suggested by Servant et al. [2], there is spatial variation in the pressure field inside the reactor. Thus the present model only gives an idea about the cavitational activity inside the reactor due to dual source acoustic field and it may not give actual quantitative data as the present model only considers a simple case of zero phase difference. Indeed, there could be very different mechanism of acoustic field due to multiple sources as suggested by Servant et al. [2].

It should be also noted that the actual sonication operation involves multiple bubbles, bubble–bubble interactions, nonuniform size of the bubbles and heat and mass transfer effects. The present model does not include the heat and mass transfer effects. However, the formation of radicals strongly depends on these effects. Also, the bubble collapse temperature and pressure depend on the partial pressure of the non-condensable gas in the bubble in addition to the vapor, which is assumed to be constant in the present study as the rectified diffusion has not been considered. Thus, the scope of the present model is not the estimation of the radicals but it can predict, qualitatively, the experimentally observed trends on the basis of bubble dynamics for the case of multi-frequency, multi source operations. The inclusion of heat and mass transfer effects and the estimation of formation of radicals under the dual frequency irradiation is a logical extension of this work. Still, the present model can explain the results of the earlier experimental investigations on the qualitative basis and can be considered as a starting point in the numerical modeling of multiple frequency/source sonochemical reactors.

5. Conclusions

The effect of intensity and frequency of dual source of ultrasound on the bubble dynamics and the collapse conditions of a single cavitational bubble has been numerically investigated. The dual source sonication has been found to be significantly better than a single ultrasound source at same net power dissipation level. For dual frequency sonication, there exists an optimum value of the intensity depending upon the initial size of the cavity. The dual source ultrasound sonication was more efficient compared to the single source sonication, in the lower range of operating frequencies compared to the higher range of operating frequencies. On the basis of the present study, it is recommended to use the transducers with lower range of frequencies (<100 kHz) for achieving more efficient cavitational activity using dual source sonochemical reactors. There is a strong qualitative correspondence in the results obtained in this numerical study and the earlier experimental investigations. Thus, the model developed here is a very effective tool to study the bubble dynamics under the influence of dual ultrasound source operating with similar or different frequencies. The use of multi-frequency transducers can offer a new dimension in sonochemical synthesis, which is relatively easy to scale-up considering the engineering viewpoint as compared to single ultrasound source sonochemical reactors. In order to make the sonochemical reactors commercially feasible, multi-frequency sonication appears to be a way forward. More study of multiple source and/or frequency sonication systems is further recommended both on the theoretical front (present work should serve as a starting point for this) as well as on the experimental front considering different systems and applications.

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