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# Optimization of multiple-frequency sonochemical reactors

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**Abstract**

In the present work, the effect of different operating parameters such as frequency of irradiation, intensity of irradiation, initial radius of the cavity, the gas content of the cavity and the operating temperature on the cavitational activity has been studied in a triple-frequency sonochemical reactor using numerical solutions of the cavity dynamics equations. The typical range of these operating parameters has been selected based on the experimental evidences (i.e. most commonly used range of operating parameters in actual practice) so as to get a realistic picture about the likely effect of the operating parameters in the sonochemical reactors. Comparison of the obtained trends in terms of the variation in the cavitational activity with the experimental results (some in the present work whereas some earlier published experimental results) has enabled us to give some recommendations regarding the optimum set of operating parameters. It has been observed that the cavitational activity is maximum when a combination of lower frequencies at higher intensity of irradiation is used as compared to the higher frequencies and lower intensities of irradiation and the operating conditions are such that lower initial size nuclei are generated in the system. Also conditions of lower operating temperature and an optimum gas fraction are suitable for the generation of higher cavitational activity. The present study should help in the efficient design and operation of the multiple-frequency sonochemical reactors for obtaining maximum cavitational efficacies.


*Keywords:* Multi-phase reactors; Optimization; Numerical simulation; Multiple-frequency ultrasonic irradiation; Sonochemistry

## 1. Introduction

Sonochemical reactors have a promising future in different areas of chemical and physical processing such as intensification of chemical reactions/solid–liquid extraction/mass transfer, wastewater treatment, polymer chemistry, biological applications, etc., primarily due to the generation of cavitating conditions with the passage of ultrasound in the liquid medium. Cavitation can be defined as generation, growth and a subsequent violent collapse of the cavities releasing large magnitudes of energy over millions of locations in the reactor simultaneously. The important effects of the cavitation phenomena can be given as the generation of hot spots (very high local temperatures and pressures with overall ambient conditions), release of highly reactive free radicals, turbulence and liquid circulation resulting in enhanced diffusion transfer rates of the species. However, a crucial hindrance in the successful application of sonochemical reactors on an industrial scale (Mason, 2000) has been the lack of suitable large-scale design strategies coupled with the fact that intense cavitational activity is obtained very close to the transducers (device used for generating ultrasound; Dahnke and Keil, 1998), and the existing conventional designs do not give substantial efficacy at larger scales of operation. Multiple-frequency multiple transducer reactors have been used in the recent past with great success (Destaillats et al., 2001; Swamy and Narayana, 2001; Gogate et al., 2001; Sivakumar et al., 2002; Feng et al., 2002; Zhao et al., 2002; Servant et al., 2003) as compared to the conventional designs such as ultrasonic horn or ultrasonic bath and with substantially higher processing capacities (in the range of 1–40 l as against few milliliters in the case of ultrasonic horn/bath). Gogate et al. (2003) reported that the cavitational yields

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(net quantification of the chemical effects) obtained for the degradation of formic acid are order of magnitude higher as compared to the conventional reactors studied in the work, whereas Thoma et al. (1997) reported the beneficial application for the sonochemical destruction of dichloromethane and *o*- dichlorobenzene in aqueous solutions using multiple-frequencies. Though there are few instances where the beneficial aspects for multiple-frequency reactors have been reported, very little design information is available in terms of the effect of the various operating parameters on the cavitational activity (the reported results are specific to the operating conditions as used in the work). Tatake and Pandit (2002) have presented theoretical analysis of a dual-frequency ultrasonic processor along with experimental verification using KI decomposition as a model reaction. It has been observed that the dual-frequency reactors give better control over the cavitational activity and also enhanced reaction rates due to higher resonant bubble growth as compared to the single-frequency reactors. Further, it is best to operate the multiple ultrasound sources with no phase difference as it leads to uniform pressure field distribution in the cavitational reactor and hence maximum cavitational activity. Dual-frequency ultrasonic processor operating with no phase difference between the two frequencies effectively eliminated standing waves, thereby increasing the effective cavitationally active volume of the reactor. It is worthwhile to explore the idea further to triple-frequency reactors, as it is possible that a combination of more frequencies can result in better cavitational effects (higher cavitationally active volume and cavitational intensity to enhance the reaction rates) as observed in the earlier work of Gogate et al. (2003), where degradation of formic acid was investigated in a triple-frequency as well as dual-frequency reactor. The present work aims at investigating the effect of important operating parameters in a triple-frequency reactor, using the theoretical analysis of the cavity behavior during various stages of the cavitation phenomena and subsequent comparison with the experimental results with an aim of optimizing the operating conditions for achieving maximum benefits and possibly minimizing the specific energy consumption for a desired chemical or physical transformation. It should be noted that not all operating parameters could be varied in the available experimental setup and hence for these parameters experimental results from the available literature has been presented. The present work is only a first step and mainly a theoretical effort in the correct direction for modeling the multiple-frequency reactors and further work will be directed towards optimizing the multiple-frequency reactors using a variety of reactions and different set of operating conditions.

## 2. Details of numerical simulations

Simple Rayleigh Plesset equation describing the cavity behavior has been used with the modification of the equation for the fluctuating pressure field under the effect of multiple-frequencies. The details of the numerical simulation for a single cavity system have been explained extensively in the earlier work (Gogate and Pandit, 2000), though for a single-frequency operation. We now discuss the modifications required specifically for a multiple-frequency operation. In the case of multiple-frequency transducer systems, the nature of the acoustic field generated is not uniform. Thus, it is very important to know whether the transducers are driven perfectly in phase or with a constant phase difference or independently.

For the specific case of triple-frequency reactors where three frequencies ($f_1$, $f_2$ and $f_3$) influence the acoustic field simultaneously, the local pressure field due to individual frequency of irradiation can be given by

$$P_{\mathrm{An}} = P_0 - P_A(\sin 2\pi f_n t), \quad n = 1, 2, 3,$$

where, $P_0$ is the ambient pressure, $P_A$ is the pressure amplitude due to the ultrasonic intensity of irradiation considered as same for all the operating frequencies, given as

$$P_A = \sqrt{2I\rho_l C},$$

where $I$ is the intensity of ultrasound ($\mathrm{W/m^2}$), $\rho_l$ the density of the medium ($\mathrm{kg/m^3}$) and $C$ the velocity of sound in that medium (m/s).

The resultant time-dependent pressure as a result of all the three driving frequencies is thus given by

$$P_t = P_0 - P_A[\sin(2\pi f_1 t) + \sin(2\pi f_2 t) + \sin(2\pi f_3 t)]. \quad (1)$$

Studies indicate that in a multiple-frequency system (Tatake and Pandit, 2002), the best results are obtained when the phase difference is zero, which has been attributed to the existence of uniform pressure/acoustic field in the cavitational reactor as compared to the case where there is some phase difference between the operating frequencies. Therefore, in the present work, only a sin–sin–sin combination, which is also an optimised operating combination, has been considered.

Well-known Rayleigh–Plesset Noltingk Neppiras equation (which also considers the effects of the medium physicochemical properties) has been used to explain the cavity dynamics under the influence of acoustic field and has been represented in the following form:

$$R\left(\frac{\mathrm{d}^2R}{\mathrm{d}t^2}\right) + \frac{3}{2}\left(\frac{\mathrm{d}R}{\mathrm{d}t}\right)^2 = \frac{1}{\rho_l}\left[p_i - \frac{4\mu}{R}\left(\frac{\mathrm{d}R}{\mathrm{d}t}\right) - \frac{2\sigma}{R} - p_\infty\right], \quad (2)$$

where $p_i$ is the pressure inside the bubble at time $t$, $R$ is the instantaneous cavity radius, $\mu$ is the viscosity of the liquid, $\sigma$ is the surface tension of the liquid medium, $p_\infty$ is the driving local pressure field (it will be equal to $p_t$ as represented by Eq. (1) for the present case). The equation is a second-order nonlinear differential equation, which can be solved by the fourth-order Runge–Kutta–Nystrom method and is valid up to the point when cavity wall velocity ($dR/dt$) is less than the velocity of sound in the cavitating media due to the assumption of incompressible nature of the liquid (for the present study, water is considered as cavitating media and velocity of sound is 1500 m/s) and hence the collapse of the cavity has been assumed to be complete when the cavity wall velocity exceeds 1500 m/s. The various assumptions involved in the solution of the cavity dynamics equation (Eq. (2)) are as follows:

(1) Spherical geometry of the cavity during the entire lifetime and the presence of the single cavity in isolation.
(2) Uniform cavity interior i.e. no pressure and temperature gradients within the bubble.
(3) The liquid is incompressible.
(4) Body forces such as gravity force have been neglected.
(5) There is a constant volumetric fraction of gas and vapor in the bubble interior during its oscillations.
(6) The partial pressure of the gas inside the bubble is predominant and the effect of the medium vapor pressure is negligible.

At any given set of the operating parameters, the numerical simulations were terminated when the instantaneous bubble wall velocity becomes greater than 1500 m/s as stated earlier and the pressure pulse was calculated using the instantaneous values of the radius and the bubble wall velocity. The equation used for the calculation of the collapse pressure pulse is

$$P_{\text{collapse}} = \left(p_0 + \frac{2\sigma}{R_0}\right) \times \left(\frac{R_0}{R}\right)^{3\gamma} - \frac{2\sigma}{R} - \frac{4\mu}{R}\left(\frac{dR}{dt}\right). \quad (3)$$

The simulation procedure also yielded the value of the maximum radius reached by the cavity during the growth phase of the cavitation phenomena ($R_{\max}$) at the given set of operating conditions, which is also indicative of the total quantum of the free radicals that are likely to be generated in the sonochemical reactor.

It should be noted that the procedure for numerical simulations used in the present case is only preliminary and can be considered as a first step in the right direction for the theoretical analysis of the multiple-frequency reactors, where cavitational intensity for a single cavity has been predicted irrespective of the exact location of the cavity in the reactor. Further work can be directed in obtaining a more realistic picture of the distribution of the cavitational activity by considering interaction between the cavities, compressible nature of the liquid medium, reflection of waves and existence of standing wave pattern, prediction of the local cavitational activity (dependent on the location inside the reactor also considering the geometry effects), etc.

## 3. Experimental system

For the experimental verification of the obtained trends with the numerical simulations, some experimental studies has also been undertaken considering Weissler reaction as the model reaction (this reaction is generally used for investigating the efficacy of the sonochemical reactors, as the reaction is only induced due to the presence of free $OH^{\bullet}$ radicals generated due to the cavitation phenomena and free radical attack is the controlling mechanism for the propagation of this reaction) in the triple-frequency flow cell (M/s Dakshin, Mumbai, India). Fig. 1 represents the schematic representation of the reactor system used in this work. The reactor has a total capacity of 7.5 l (dimension of the hexagonal side is 10 cm) and can be operated either in the batch mode or in the continuous mode, though in the present work experiments have been performed only in the batch mode (7 l of solution was used). Parallel plate configuration has been used so that standing waves will be formed in the system. Multiple transducers (three in number per side having circular cross-section) having equal power rating of 150 W per side have been mounted. Thus the maximum supplied electric power is 900 W when all the transducers are functional). In all, there are 18 transducers attached to the wall of reactor, which helps in increasing the cavitationally active volume. The two opposite faces of the flow cell have the same irradiating frequency. The operating frequency of transducers is 20, 30 and 50 kHz and can be operated in different combinations either individually or in the combined mode. In the annular position, a quartz tube has been provided, inside which there is a provision for placing the UV tube for simultaneous irradiation (using a simultaneous irradiation of UV and ultrasound is beneficial, though the present work does not aim at investigating this effect).

In the present work, 1% KI solution was irradiated with seven different combinations of frequencies for 30 min. The extent of iodine liberated during the reaction is estimated

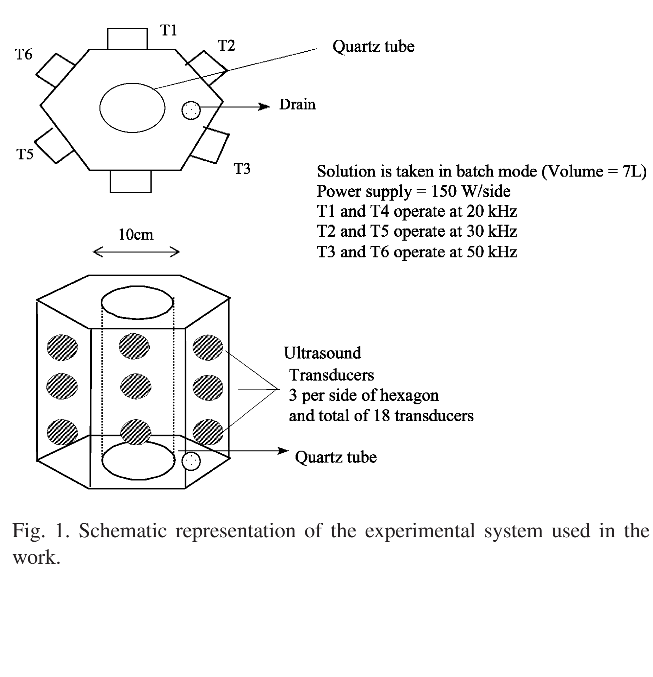


Fig. 1. Schematic representation of the experimental system used in the work.

with the help of UV/VIS spectrophotometer by measuring its absorbance at 355 nm wavelength. Some experiments have been also repeated in the presence of air (introduced using a sintered multi-point air sparger at a flow rate of $1.02\ cm^3/s$) so as to investigate the effect of the presence of external gaseous atmosphere and the dissolved gases in the system. Cavitational yield, which gives the extent of iodine liberation per unit of supplied power, has been quantified and used for the comparison of cavitational efficacy under different set of operating conditions.

Table 1
Effect of frequency combination on the maximum cavity size and collapse parameters

| Frequency combination | $R_{max}/R_0$ | Lifetime of cavity (s) | Collapse pressure (atm) |
|---|---|---|---|
| Single | 128.0 | $3.24 \times 10^{-5}$ | 47171.5 |
| Dual | 205.8 | $3.70 \times 10^{-5}$ | 45169.1 |
| Triple | 262.4 | $4.02 \times 10^{-5}$ | 44961.6 |

## 4. Results and discussion

### 4.1. Effect of frequency of irradiation

The effect of frequency of irradiation has been studied over the range 20–200 kHz and for multiple cases, i.e. single-frequency, dual-frequency and triple-frequency operation. Table 1 gives the representative results for the comparison of single- dual- and triple-frequency combinations for a representative case of frequency of irradiation as 30 kHz, intensity of irradiation as $10\ W/cm^2$ (same for all the frequencies of irradiation in a combination mode of operation), gas fraction of 100% and initial cavity radius as 2 μm. It can be seen that the triple-frequency combination results is about 100% higher $R_{max}/R_0$ ratio as compared to single-frequency and about 30% higher $R_{max}/R_0$ ratio as compared to dual-frequency combination. Also, the cavity lifetime is about 25% higher for the triple-frequency combination as compared to the single-frequency operation and 8% higher as compared to the dual-frequency combination. The collapse pressure due to a single cavity collapse for the triple-frequency combination, however, marginally decreases ($< 5\%$) as compared to the single- and dual-frequency operations at same operating intensity of irradiation for each frequency. Similar trends were also obtained for the simulations of all the other operating frequencies studied in the work. The collapse pressure pulse will play a role when the controlling mechanism is pyrolysis, whereas for free radical attack as the controlling mechanism, quantum of free radicals and hence $R_{max}/R_0$ ratio is important. Thus, on the basis of theoretical analysis, it can be said that the combination of frequencies is strongly recommended for operations with free radical attack as the controlling mechanism as compared to the single-frequency operations (larger influence on the cavitational activity, i.e. both cavitational volume [$\alpha R_{max}^3$] and lifetime of the cavities are enhanced). For pyrolysis as the controlling mechanism, it is expected that the increase in the cavitational lifetime nullifies the negative effect of the decrease in the pressure pulse and hence the combination of frequencies should also be beneficial.

Quantification of the energy efficacy of the cavitational transformation (cavitational yield) estimated for the triple-frequency flow cell (irradiation using different sources of same frequency), for the specific case as described earlier ($1.33 \times 10^{-10}$ g/J), was order of magnitude higher as compared to both the single-frequency operation ($1.056 \times 10^{-13}$ g/J) as well as the dual-frequency operation ($4.14 \times 10^{-13}$ g/J). It can be also seen from the above results that the dual-frequency operation also results in about four times increase in the cavitational yield as compared to the single-frequency operations, whereas it is not possible to conclusively explain the exponential increase obtained for the case of triple-frequency operation which can be possibly attributed to a higher number of cavitational events in the reactor (the estimated collapse pressure pulse is for single cavity, whereas the experimental result is the cumulative effect of all the cavities present in the reactor) and uniform distribution of the pressure/acoustic field as compared to a dual-frequency operation. Swamy and Narayana (2001) have also shown that the combination of two frequencies gives better efficacy in chemical leaching of copper as compared to individual frequencies of irradiation at same operating intensity of irradiation, whereas Servant et al. (2003) have shown using theoretical analysis (no optimization studies of the dual-frequency reactor has been reported; also, no information about the power input into the system for mono-frequency and bi-frequency reactors is available) that the active cavitational volume in the case of dual-frequency reactor is higher and also more intense as compared to the mono-frequency reactor. Thus, the utility of multiple-frequency combination is conclusively established as better cavitational efficacy at same power dissipation has been observed for all the cases except that of Servant et al. (2003), where information on power input is lacking.

The effect of individual frequency was also investigated by changing one frequency in the combination and the results have been depicted in Fig. 2. It can be seen from the figure that, overall, the collapse pressures and the maximum temperatures of the cavity interior show an increase in the magnitude with an increase in the individual frequency (maximum extent of increase is around 30%). However, more significant effect was observed on the $R_{max}/R_0$, which showed a decrease with an increase in the frequency of irradiation, i.e. as we move away from the resonant combination of frequencies (ratio is maximum for the 30–30–30 kHz combination and minimum for the 30–30–200 kHz frequency combination). A specific case has been discussed for better understanding. For the resonant combination of lower

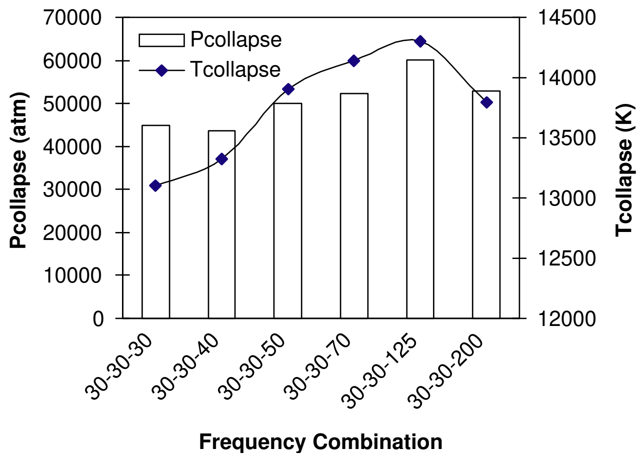


Fig. 2. Effect of individual frequency in triple-frequency combination on the collapse pressure and temperatures.

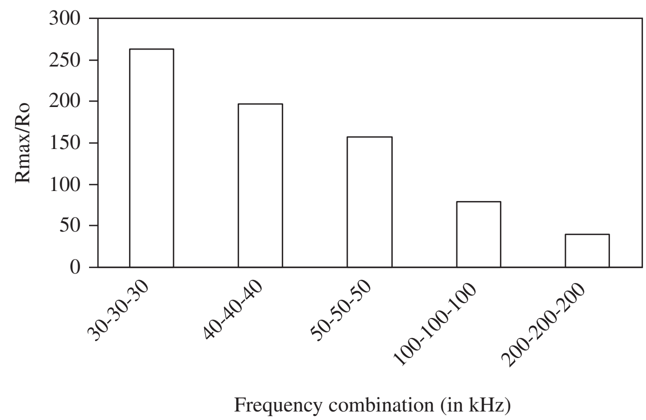


Fig. 3. Effect of resonant frequency combination on the $R_{max}/R_0$ ratio during the cavitation phenomena.

frequencies (30–30–30 kHz combination), $R_{max}/R_0$ value is always 80–100% higher as compared to other frequencies, combinations (30–30–$X$ where $X$ is in the range 40–200 kHz) and minimum value (134.6) is obtained for the 30–30–200 kHz combination. Thus, it is recommended to use a combination of multiple resonant frequencies ($R_{max}/R_0$ value will be maximum and hence recommended for free radical attack as the controlling mechanism) or frequency combination where the individual frequencies differ marginally (for example, a combination of 30–30–40 kHz or 30–30–50 kHz is more favorable as compared to 30–30–90 kHz; collapse pressure will be higher and hence should be beneficial where pressure/temperature pulse is important) depending on the controlling mechanism for the desired application. Thus, it also becomes imperative to check the controlling mechanism, i.e. pyrolysis controlled by the magnitude of the temperature/pressure pulse generated at the collapse of cavity or free radical attack controlled by the cavitational volume (proportional to $R_{max}/R_0$).

It was also thought desirable to check whether a combination of lower resonant frequencies should be used or is it advisable to use a higher frequency resonant combination? Fig. 3 shows the results in terms of the variation of the $R_{max}/R_0$ with the frequency combination. It is observed that the combination of the lower resonant frequencies is much favorable as compared to the combination of the higher frequencies. The collapse pressures and temperatures were almost constant (in the range 45,000–50,000 atm) over the range 30–80 kHz frequency of irradiation, but increased by nearly 100% when the frequency combination was 200–200–200 kHz as compared to 30–30–30 kHz combination. In this case, however, the $R_{max}/R_0$ value decreased from 262 to 39.6 (by about six times) and hence, the overall cavitational effects (combined effect of cavitational volume and cavitational collapse intensity in terms of pressure/temperature pulse generated) will be significantly reduced. Thus, in summary, it can be said that, combination of resonant/near-resonant frequencies with lower magnitudes are best suited in the case of triple-frequency sonochemical reactors. No comparison with the experimental data could be made for this specific case in question due to the absence of the experimental results, but this certainly has to be exploited in future.

Table 2
Effect of intensity of irradiation on the maximum cavity size and collapse parameters at optimized resonant frequency combination (30–30–30 kHz)

| Intensity ($W/cm^2$) | $R_{max}/R_0$ | Lifetime of cavity (s) | Collapse pressure (atm) |
|---|---|---|---|
| 1 | 122.9 | $3.2 \times 10^{-5}$ | 41117.1 |
| 5 | 213.5 | $3.7 \times 10^{-5}$ | 61199.7 |
| 10 | 262.4 | $4 \times 10^{-5}$ | 44961.6 |
| 20 | 319.3 | $5.9 \times 10^{-5}$ | 59463.4 |
| 50 | 409.5 | $6.6 \times 10^{-5}$ | 55236.2 |

## 4.2. *Effect of intensity of irradiation*

The effect of intensity of irradiation has been studied over the range of intensity of 1–50 $W/cm^2$ at an optimized resonant frequency combination (30–30–30 kHz) as discussed earlier and the results have been depicted in Table 2. It can be easily concluded from the values reported in the table that higher intensity of irradiation is more suitable for enhanced cavitationally active volumes in the reactor (both the maximum radius of the cavity as well as cavity lifetime increase with an increase in the operating intensity). Collapse pressure does not show any specific trend at this frequency combination, though the effect is not so significant at lower frequencies of operation (50% variation over the range of intensity considered in the work) as compared to the variation in the maximum radius reached by the cavity (about four times variation over the same range). For the combination of higher resonant frequencies, however, the collapse pressure showed an optima (maximum collapse pressure at an optimum value and this value decreases as the intensity is increased beyond this optimum value) with respect to the intensity of irradiation (magnitude of the optimum value is also dependent on the frequency combination; it increases with an increase in the individual frequency of the triple-frequency combination). Thus, based on the significant dependency on the cavitationally active volume, it is recommended that higher intensities of irradiation, but below the optimum value in the case of higher resonant frequencies should be used. In the experimental setup available with our group, variable power dissipation was not possible and hence the effect of intensity of irradiation could not be verified with the experiments of KI oxidation. However, Feng et al. (2002) and Zhao et al. (2002) have shown that the cavitational activity increases with an increase in the intensity of irradiation over the range considered in the work (1–20 $W/cm^2$). Swamy and Narayana (2001) have also observed that the efficacy of bi-frequency ultrasound in chemical leaching of copper increases with an increase in the intensity of irradiation over the range of intensity studied in the work (0–2 $W/cm^2$). Thus it can be stated that, generally, higher intensity of irradiation is preferred, but in some cases an optimum intensity of irradiation may be observed where the controlling mechanism driving the application under question is decided by the temperature/pressure pulse generated due to the collapse of the cavities (for example, chemical reactions driven by pyrolysis mechanism).

### 4.3. Effect of initial cavity radius

The variation in the initial cavity radius has been investigated over the range 2–10 μm for optimized-frequency combination 30–30–30 and an operating intensity of 10 $W/cm^2$. The results have been shown in Table 3. It can be clearly seen from the table that lower initial radius of the cavitating nuclei results in higher cavitational activity as indicated by the higher growth of the cavity as well as higher collapse pressures and temperatures. As it is not possible to directly control the initial radius of the cavity in the reactor, an optimum combination of liquid-phase physicochemical properties has to be selected so as to achieve cavities of lower initial size. The recommendations for the selection of the liquid physicochemical properties are the use of low vapour pressure, viscosity, surface tension and use of optimum quantity of the dissolved gases/impurities, which can act as nucleation sites. No experimental evidences were observed in the literature for the dependency of the cavitational activity on the initial cavity size in the case of multi-frequency reactors, whereas no techniques for the exact measurement of the initial cavity size are available with our group to verify the obtained trends.

### 4.4. Effect of gas fraction used

The effect of gaseous cavities on the collapse characteristics has been investigated at the optimized conditions as discussed earlier and over a range of gas fraction from 0% to 100% (vaporous to gaseous cavity). The results have been shown in Table 4. It can be seen that the growth of the cavity is unaffected by the presence or the absence of gas inside the oscillating cavity but the collapse pressure and temperature shows an optima at gas fraction of 30%, beyond which these parameters show a decrease in the value with an increase in the gas fraction. Experiments with sparging of air at a particular flow rate (1 $cm^3/s$ through a porous sparger) indicated that the cavitational yield in terms of iodine liberation is about 30% higher as compared to that in the absence of aeration. It should be noted that these results in terms of the dependency of the cavitational activity on the presence or the absence of gas are only indicative in nature and much work needs to be done in terms of varying the type and the quantity of the dissolved gas, both in the theoretical analysis as well as in its experimental verification (effect of flow rate of the gas and the type of the distributor can also be investigated) before any firm recommendations can be made. At this stage, it can be said that the presence of gaseous species at low concentrations is beneficial for the multiple-frequency sonochemical reactors. This recommendation is also supported by the fact that the number of cavities will also be higher due to the introduction of the gas initially as the presence of gas will act as additional nuclei for the generation of the cavities. But at higher gas sparging, the quantity of ultrasonic energy transferred into the system decreases due to the gas envelope shielding effect and hence beneficial effects may not be observed. Some design information about the effect of gaseous species on the efficacy of mono-frequency sonochemical reactors can be obtained from the work of Hart and Henglein (1985), Entezari et al. (1997), Gondrexon et al. (1997) and Wakeford et al. (1999).

Table 3
Effect of initial cavity size on the maximum cavity size and collapse parameters at optimized resonant frequency combination (30–30–30 kHz) and intensity of 10 $W/cm^2$

| $R_0$ (m) | $R_{max}/R_0$ | $P_{collapse}$ (atm) | $T_{collapse}$ (K) |
|---|---|---|---|
| $2 \times 10^{-6}$ | 262.4424 | 44961.6 | 13163.7 |
| $5 \times 10^{-6}$ | 105.5457 | 30251.4 | 11754.6 |
| $10 \times 10^{-6}$ | 53.1097 | 19145.2 | 10314.3 |

Table 4
Effect of gas fraction on the maximum cavity size and collapse parameters at optimized resonant frequency combination (30–30–30 kHz), intensity of 10 $W/cm^2$ and initial cavity size of 2 μm

| Gas fraction % | $R_{max}/R_0$ | $T_{collapse}$ (K) | $P_{collapse}$ (atm) |
|---|---|---|---|
| 0 | 262.1035 | 27532.0 | 47904.7 |
| 30 | 261.8997 | 42307.0 | 59589.2 |
| 50 | 262.1342 | 27872.3 | 47786.8 |
| 70 | 262.2752 | 20059.0 | 46388.0 |
| 90 | 262.3896 | 14875.4 | 45140.2 |
| 100 | 262.4424 | 13163.7 | 44961.6 |

Table 5
Effect of operating temperature on the maximum cavity size and collapse parameters at optimized resonant frequency combination (30–30–30 kHz), intensity of $10\,W/cm^2$ and initial cavity size of $2\,\mu m$

| Temperature (°C) | $R_{max}/R_0$ | Lifetime of cavity (s) | $T_{collapse}$ (K) |
|---|---|---|---|
| 20 | 262.35 | $4.011 \times 10^{-5}$ | 16483.3 |
| 30 | 262.44 | $4.013 \times 10^{-5}$ | 13163.7 |
| 40 | 262.51 | $4.015 \times 10^{-5}$ | 12614.5 |
| 50 | 262.56 | $4.016 \times 10^{-5}$ | 10761.0 |
| 60 | 262.61 | $4.018 \times 10^{-5}$ | 9973.8 |

### 4.5. Effect of operating temperature

The effect of temperature has been investigated over the range of operating temperature as 20–60 °C. The results have been depicted in the Table 5. It can be seen from the table that an increase in the operating temperature does not have any effect on the growth of the cavity as well as on the total lifetime of the cavity. However, a significant effect on the collapse temperature is observed (collapse temperature decreases with an increase in the operating temperature). These simulations indicated that the lower operating temperatures are beneficial. It should be noted that higher operating temperatures result in the presence of higher fraction of volatile components in the cavity (which is not considered in the current theoretical simulations), which will increase the rate of cavitational reactions. Also, higher operating temperatures should lead to a higher number of cavities in the system as the ease of generation of cavities is higher at higher vapor pressures due to an increase in the temperature. In this case, an optimum operating temperature might exist beyond which an increase in the operating temperature might result in reduced cavitational efficacy for the desired applications. Many sonochemical reactions such as isomerisation of maleic acid exhibit this behavior, i.e. maxima with respect to the operating temperature (Mujumdar and Pandit, 1998). Thus, it can be said that for non-volatile components, operation at lower temperature is beneficial, whereas for chemical processing application involving volatile species, an optimum operating temperature needs to be established using laboratory-scale studies for the desired application.

## 5. Conclusions and recommendations for optimum design

The present work involving the theoretical simulations of the cavity behavior under the influence of triple-frequency sonochemical reactor and subsequent comparison with the experimental results obtained in the work as well as with that reported in the literature has allowed to establish the following useful design information:

1. With the addition of another frequency using additional transducers, cavity sizes as well as the lifetime of the cavity are enhanced considerably with a relatively marginal drop in the collapse pressures and temperatures. Therefore, triple-frequency sonochemical reactors show considerably higher overall cavitational activity as compared to the single- and dual-frequency sonochemical reactors at equivalent power dissipation levels.
2. The best efficacy of the multiple-frequency sonochemical reactors will probably result from resonant combinations or with combinations where the individual frequencies differ marginally from each other. Also, lower frequency combinations are preferable.
3. Generally, higher intensity of irradiation is preferred but in some cases an optimum intensity of irradiation may be observed, where the controlling mechanism driving the application under question is decided by the minimum temperature/pressure pulse generated due to the collapse of the cavities and required for the propagation of chemical reactions similar to the concept of the activation energy (for example, chemical reactions driven by pyrolysis mechanism).
4. Lower initial cavity size is preferred, which can be adjusted by optimizing a set of liquid phase physicochemical properties.
5. Lower operating temperature and the presence of gas fraction at optimized value (30% as observed in the present work) are recommended, though much work needs to be done both on the theoretical front as well as the experimental front to arrive at firm recommendation on the type and the concentration of the gaseous species.

The present study has helped us in establishing the guidelines for the selection of the optimum set of operating parameters for maximum cavitational activity and hence maximum benefits for the desired application, which should help in the efficient design and operation of the multiple-frequency large-scale sonochemical reactors, which appears to be a near technological feasibility. The setup depicted in the present work also gives an idea regarding the actual experimental design to be used in the case large-scale multiple-frequency sonochemical reactors.

## Notation

| | |
|---|---|
| $C$ | velocity of sound, m/s |
| $(\mathrm{d}R/\mathrm{d}t)$ | cavity wall velocity, m/s |
| $(\mathrm{d}^2R/\mathrm{d}t^2)$ | cavity wall acceleration, $m/s^2$ |
| $f_1, f_2, f_3$ | operating individual frequency of ultrasound, kHz |
| $I$ | intensity of irradiation, $W/m^2$ |
| $p_i$ | pressure inside the cavity at time $t$, $N/m^2$ |
| $P_A$ | pressure amplitude due to the ultrasound, $N/m^2$ |
| $P_{An}$ | local pressure field due to individual frequency of irradiation, $N/m^2$ |
| $P_{collapse}$ | collapse pressure of the cavity, atm |
| $P_0$ | ambient pressure, $N/m^2$ |

| | |
|---|---|
| $P_t$, $p_\infty$ | time-dependent resultant pressure driving the cavity dynamics, $N/m^2$ |
| $R$ | radius of the cavity at time $t$, m |
| $R_0$ | initial radius of the cavity, m |
| $R_{max}$ | maximum radius reached by the growing cavity during different stages of cavitation phenomena, m |
| $t$ | time, s |
| $T_{collapse}$ | collapse temperature of the cavity, K |
| $X$ | individual frequency in the triple frequency combination, kHz |

*Greek letters*

| | |
|---|---|
| $\gamma$ | gas constant |
| $\mu$ | viscosity, Pa s |
| $\rho_l$ | density of the liquid medium, $Kg/m^3$ |
| $\sigma$ | surface tension, N/m |

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