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Review

Design aspects of sonochemical reactors: Techniques for understanding cavitational activity distribution and effect of operating parameters

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ABSTRACT

Cavitation is a phenomenon having enormous potential for intensification of physical and chemical processing applications such as chemical synthesis, industrial wastewater treatment, cell disruption for release of intracellular enzymes, crystallization, extraction and leaching. However, the dynamic behavior of cavitational activity, especially in sonochemical reactors based on the use of ultrasonic irradiations, creates problems in proposing reliable design and operating strategies. The present work presents an overview of different techniques to understand the cavitational activity distribution in the reactor, highlighting the basic aspects, its applicability and relative merits/demerits. A detailed analysis of the literature has also been made with an aim of explaining the dependency of the cavitational activity on the design of sonochemical reactors and also the operating parameters. Recommendations for optimum operating parameters and design of reactor based on the experimental as well as theoretical analysis have been reported. Some trends in the future reactor designs useful in large scale applications have also been discussed.

1. Introduction

Cavitation is a phenomenon of nucleation, growth and subsequent collapse (quasi-adiabatic) of micro bubbles in a liquid medium. Cavitation results in generation of high temperature (in the range 1000–15,000 K) and pressure (in the range 500–5000 bar) locally but at millions of locations in the reactor [1]. In addition to generation of hotspots, cavitation also results in strong acoustic streaming (liquid circulation), high shear stress near the bubble wall, formation of micro-jets near the solid surface (due to asymmetric collapse of bubbles), generation of highly reactive free radicals and turbulence resulting in enhanced transport properties of the species [2–4]. These effects can be effectively used for the intensification of physical and chemical processing applications such as chemical synthesis (in homogenous and heterogeneous reaction systems in terms of acceleration of the rate of reaction, increase in reaction yield, use of less forcing conditions, reduction in induction time, switching of reaction pathway to have better selectivity), wastewater treatment (degradation of biorefractory or complex chemicals such as p-nitrophenol, rhodamine B, phenol, dichloromethane, etc.), textile processing (enhancing the efficacy of dyeing technique), biotechnology (homogenization, water disinfection and cell disruption for release of intracellular enzymes and foam control in bioreactors), crystallization, polymer chemistry (degradation of polymers and initiation of reactions), extraction, emulsification and petrochemical industries (determination of composition of coal extracts), etc.[5–8]. However, it should be noted that in spite of extensive research and vital potential applications proven on laboratory scale, there are limited number of chemical processing applications being carried out on an industrial scale owing to the lack of expertise required in diverse fields such as material science, acoustics, chemical engineering etc. for scaling up successful laboratory scale processes and also due to the lack of suitable reactor design and scale-up strategies. Rate of sonochemical reactions is not only influenced by frequency and intensity of ultrasonic irradiations but also by the shape of reactor, operating power density, fraction of dissolved gases, physicochemical properties of liquid medium, surrounding pressure field in the sonochemical reactor and operating temperature [8,9]. The major problems in efficient design and operation of sonochemical reactor are:

1. Cavitation is a dynamic phenomenon and its effects strongly depend on the operating parameters and geometry of the reactor system. The reaction mechanism and the overall yields of sonochemical reactions are influenced by the bulk temperature, the acoustic intensity or the static pressure in the fluid. A small change in the temperature or gas content in the liquid medium may alter the conditions dramatically leading to a completely different cavitational effect and hence the yield and selectivity

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of the reaction [10,11]. Because of this strong nonlinear behavior, it is difficult to effectively operate a sonochemical reactor. A possible solution to this problem is the quantitative determination of the parameters such as pressure field intensity and local temperature over the entire range of operation as a function of different operating parameters and possible disturbances. Accurate measurements of cavitational activity in the reaction medium quantitatively can also aid in optimizing the reactor volume for given operating conditions [12–14].

2. It has been observed that the cavitational activity in sonochemical reactor is non-uniform in nature. For low frequency operation, maximum energy gets dissipated near to the irradiating surface in a cone like structure. Due to this, there is maximum cavitational activity very near to the irradiating surface and wide variation in the energy dissipation rates in the remaining bulk of liquid.
3. Another problem is the attenuation of sound wave in the bulk of liquid or near the sonicator surface. Cavitation is induced in a liquid by the passage of ultrasound, which is produced by transducers converting electrical energy into mechanical vibration energy. These transducers may be strategically located on the reactor sidewall or at the bottom of the tank or can be directly immersed in the liquid. As the sound wave propagates through the liquid bulk, intensity of sound decreases with an increase in the distance from transducer, generally described as attenuation of sound wave. Attenuation occurs due to reflection, refraction and absorption of incident sound wave and also contributes to spatial variation of the cavitational activity. It is imperative to understand the effect of these changes on the cavitational activity with an objective of possibly eliminating the active and passive zones in the reactor.
4. Cavitational activity in sonochemical reactor is also a function of location of transducers in the reactor/reaction medium, frequency of ultrasound, dimension of reactor, height of liquid medium in the reactor, power density and surface area of the irradiating element. Thus, it is important to understand the dependence of the cavitational activity on these parameters.

Characterization of the cavitational phenomena and its effects in sonochemical reactors are generally described through mapping. Mapping of sonochemical reactor is a stepwise procedure where cavitational activity can be quantified by means of primary effect (temperature or pressure measurement at the time of bubble collapse) and/or secondary effect (quantification of chemical or physical effects in terms of measurable quantities after the bubble collapse) to identify the active and passive zones. It mainly deals with determination of behaviour of sonochemical reactor over the entire range of operation. We now present an overview of the various techniques available for understanding the cavitational activity distribution, highlighting the basic aspects of each technique, their applicability and merits/demerits.

2. Overview of techniques for measuring cavitational activity distribution

The available techniques can be classified into two groups viz., experimental techniques for measurement and theoretical predication of the cavitational activity distribution. Depending on different effects generated by cavitation, experimental techniques can be further classified into techniques based on quantification of primary effects and secondary effects (Fig. 1). The effects generated at the same time as the bubble collapse are called as primary effects such as temperature pulse, pressure pulse, generation of free radicals (in the cavity) and micro-circulation in the vicinity of bubble. The effects generated after the bubble collapse are called as secondary

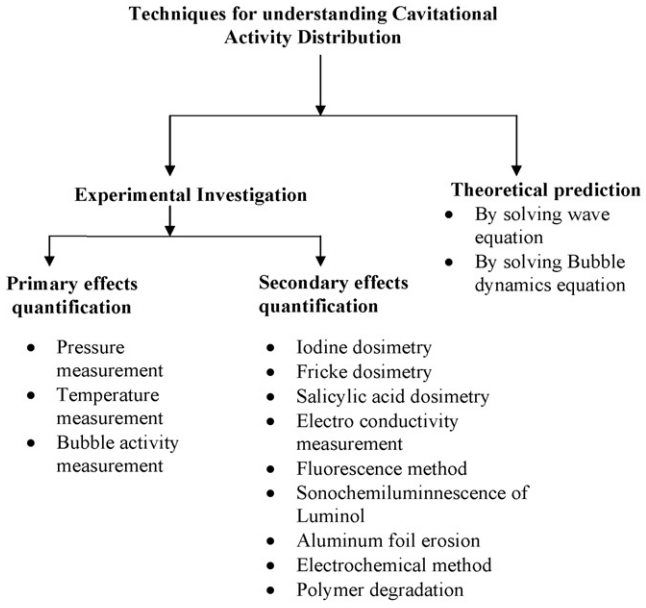


Fig. 1. Classification of different types of mapping techniques.

effects such as oxidation reactions, intensification of mass transfer coefficients, enhanced electrochemical effects, etc. Also it should be noted that, even though generation of free radicals is considered as primary effects, they are usually utilized in chemical reaction after bubble collapse.

2.1. Experimental investigations

2.1.1. Primary effect quantification

2.1.1.1. Pressure measurement. Pressure intensity generated by cavitation in a liquid medium can be quantified using a hydrophone. Hydrophones are electronic devices, which measures the acoustic pressure intensity in the liquid medium with better spatial resolution, bandwidth, excellent directional characteristics (omnidirectional in axial and radial plane) and sensitivity. These properties of hydrophone usually depend on the shape and size of the hydrophone. The active element which senses the pressure intensity is embedded in materials such as silicon rubber, chloroprene rubber, polymer resin, etc. and kept in cylindrical body to avoid erosion. The support body of the hydrophone should have high corrosion resistance and very good antifouling properties. It is generally made up of Copper–Nickel or Aluminium–Bronze alloy. Different types of hydrophones used in the literature illustrations are piezoelectric (needle device, membrane device, liquid electrode hydrophone and reflector-type hydrophone) and optical fibre-tip hydrophone. Table 1 [15–20] indicates the use of different types of hydrophone and type of analyzer which can be used to get the desired information about the cavitational activity distribution.

Some of the difficulties associated in the measurement of pressure intensity using hydrophone are as follows:

- The liquid medium gets disturbed due to the presence of external hydrophone which can affect the cavitational activity distribution, depending on the relative size of hydrophone and reactor.
- The obtained signals can be converted in Pa or atm with the help of calibration charts provides by the manufactures. However it should be noted that the response of hydrophone sometimes becomes sluggish with time, which necessitates the need for frequent calibration. For accurate measurement, the signals need to

Table 1
Different types of hydrophones used in investigations related to mapping of sonochemical reactors.

S. No.	Reference	Type of hydrophone	Frequency of irradiation	Analysis of signal
1	Koch and Jenderka [15]	Optical fibre tip hydrophone with titanium coating(single-mode fibre 125 lm in diameter was used with a cut off wavelength of 600 nm)	Driving frequency of 45 kHz	Heterodyne interferometer is used to detect change in optical path due to sound field
2	Kanthale et al. [16]	Bruel and Kjaer 8103, hydrophone (length of 50 mm and diameter of 9.5 mm)	Driving frequency of 20 kHz	Signals were fed to Fast Fourier transform (FFT) based spectrum analyzer through a charge amplifier and output was measured in terms of mili volts (mV)
3	Hodnett et al. [17]	Sonar type hydrophone	Up to 201 kHz frequency	Output signals were determined using a HP 3589A Spectrum Analyzer. They also used A prototype signal processing acoustic cavitation monitor, called ACAM II to display the fundamental frequency, the sub harmonic, and broadband components of the received signal.
4	Hodnett et al. [18]	Bruel and Kjær type 8103 hydrophone with cylindrical piezoelectric element of height 8 mm and diameter 6.35 mm, with the acoustic center located 6.4 mm from the bottom of the hydrophone.	frequency range of 120–250 KHz	HP4395A Spectrum Analyzer to determine the frequency of signals. They also reported use of Lab View 6.1 software programme for signal analysis and processing.
5	Kumar et al. [19]	Hydrophone (Bruel and Kjaer 8103 of length 50 mm and diameter 9.5 mm)	36 KHz and combination of 20, 30, 50 kHz	Signals from hydrophone were feed to cavitation Activity Indicator which quantifies cavitational intensity in terms of sound pressure levels (dB)
6	Campos-Pozuelo et al. [20]	Hydrophone (Bruel and Kjaer 8103)	20 and 45 kHz	Signals are measured in milivolt

be converted with oscilloscope, fast Fourier transform (FFT) or use of the data acquisition software, which at times can be quite expensive.
- It measures the total pressure intensity including the noise generated by sub harmonically (f/n), harmonically (nf) and ultra harmonically ($((2n+1)f/2)$ oscillating bubbles with fundamental driving frequency 'f'. It should be noted here that all these oscillating bubbles does not result in transient cavitation which is an essential requirement in applications such as chemical synthesis or wastewater treatment of pollutants.

2.1.1.2. Temperature measurement. Propagation of sound wave through the liquid medium results in lowering of the amplitude of sound wave due to absorption and scattering effects of the incident sound wave. In a homogeneous liquid medium, the energy loss due to scattering is usually negligible and absorption of sound wave results in change in thermal conductivity, bulk viscosity and other molecular processes. This energy transfer results in increase in the local temperature of the liquid medium, which can also be used to provide quantitative information about the local cavitational activity. The change in local temperature can be measured by discrete temperature measurement based on the use of thermocouple or thermister at any position in the reactor [21,22]. It should be also noted here that changes in the bulk temperature can also be used to get information about the total amount of energy entering the reactor, and has been widely used for quantifying the efficacy of sonochemical reactor in terms of energy transfer.

The expected difficulties in the use of temperature measurements for understanding the local cavitational activity distribution are:

- Sensor might be damaged due to the collapsing bubbles.
- Reproducibility and sensitivity of the method is low.
- In discrete method, simultaneous measurement of temperature at different locations in a reactor makes measurement technique complex and cost intensive.
- Local temperature of the cavity reached during collapse is high as compared to the surrounding liquid temperature. Measurement of local temperature within short time (life time of cavity is of the order of few microseconds) requires sophisticated instruments such as thermocouples/thermister with very low response time. Farahmand and Kaufman [23] have developed an apparatus to measure temperature of air having response time 54 ± 3 ms but its applicability for sonochemical reactors needs to be tested.

2.1.2. Secondary effect quantification

Magnitude of the temperature and pressure pulse generated during cavitational events depends on the type of cavitation, i.e. transient cavitation (violent bubble collapse) or stable cavitation (oscillating bubbles). In transient cavitation, high temperature and pressure pulse is generated on collapse resulting in dissociation of water vapor inside the bubbles to give free radicals such as $OH^{\bullet}$ radicals, $O^{\bullet}$ radicals and $H^{\bullet}$ radicals. Recombination and further radical reactions might also generate additional oxidant species such as H_2O_2 or ozone. The free radicals can also diffuse into the surrounding liquid and oxidize solutes if present. If volatile solutes are dissolved in the liquid (such as acetone, chloroform), they enter the bubbles by evaporation, dissociate and generate free radicals leading to a series of reactions. Also at lower frequencies of irradiation, bubble collapse results in generation of physical effects such as strong liquid circulation coupled with turbulence, erosion of solid surfaces such as aluminum foil etc. Depending on the utilization of these effects, techniques based on experimental measurements can be further classified into subgroups as chemical methods and physical methods. From chemical processing view point, characterization methods based on the chemical reactions are more representative of the cavitational environment. There are some reactions which proceed only by the action of cavitational effects such as decomposition of KI, Fricke solution, salicylic acid etc. and can be successfully used for investigation of cavitational activity in the sonochemical reactor.

2.1.2.1. Chemical methods.

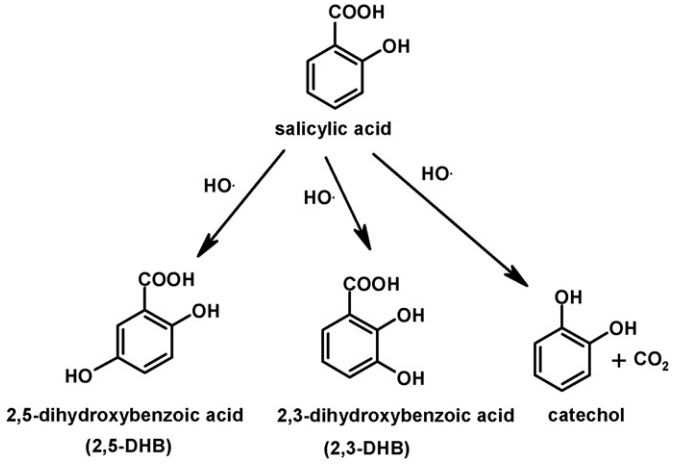
1. Iodine release method
   When aqueous solution of potassium iodide (KI) is irradiated, oxidation occurs and I^- ions are oxidized to give I_2^-. The excess I^- ions present in solution react with I_2 to form I_3^-. The amounts of I_3^- ions can be quantified by UV spectrophotometer in the range of 350–360 nm wave length [9,24–27]. In this method, determination of cavitational activity is based on the fact that iodine ions in KI aqueous solution can be transformed into iodine molecules under ultrasonic irradiation.
2. Fricke dosimetry
   Fricke dosimetry is based on the formation of free radicals and hydrogen peroxide. When sound waves are passed through Fricke solution, Fe^{2+} ions in the solution are oxidized to Fe^{3+} ions as follows:

$$Fe^{2+} + OH^{\bullet} + H^+ \rightarrow H_2O + Fe^{3+}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow H_2O + Fe^{3+} + OH^{\bullet}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{\bullet}$$

   The amount of Fe^{3+} ions can be then quantified using UV spectrophotometer at 304 nm wavelength [9,24].
3. Salicyclic acid dosimetry
   Salicylic acid dosimetry, i.e. monitoring the hydroxylation of salicylic acid [28–30], has been also used to quantify cavitational activity in terms of the extent of hydroxyl radical production rate. The dosimetry based on salicylic acid is very specific to cavitational activity and the reaction products are exclusively caused by the hydroxyl radical oxidation reaction. There is usually addition of the hydroxyl radical to the aromatic ring, leading to formation of 2,5- and 2,3-dihydroxybenzoic acid along with some minute quantities of catechol as depicted schematically below:



In these cases, it is commonly said that the hydroxyl radicals have been trapped and hence the dosimeter can be described as a radical trap. The reaction products of salicylic acid dosimetry can be determined using HPLC with greater sensitivity than the spectrophotometrical measurements used with iodide and Fricke dosimeter.

In general, some of the difficulties associated with chemical methods are as follows:

- The chemical methods can have large measurement errors.
- In this method, cavitational activity is measured in terms of ions formed after collapse of mainly transient cavitation bubbles. However, the cavitational activity generated by oscillating bubbles is not considered in the chemical measurements, but can contribute to the overall effects depending on the specific application under question (more specifically to physical processing applications).

2.1.2.2. Electroconductivity measurement. In this method, ultrasound is passed though known amount of water under the given set of operating conditions. Water contains a small amount of dissolved N_2 and O_2 gas, which do not react with each other under normal operating conditions, but under the drastic conditions of high temperature and pressure caused by cavitation, they can react to form NO. The formed NO is further oxidized to give NO_2 which combines with water molecule to form HNO_3 and HNO_2. Due to the formation of acids, there is a change in electrical conductivity of water which can be used to quantify the cavitational activity [24]. In this method, intensity of cavitational activity mainly depends on the amount of oxygen and nitrogen dissolved in liquid medium.

2.1.2.3. Fluorescence determination. When aqueous solution of non fluorescent Terephthalic acid (TA) is sonicated, reaction of generated hydroxyl radical ($OH^{\bullet}$) with TA gives highly fluorescent hydroxyterephthalic acid (HTA). Based on this principle, TA in alkaline aqueous solution can be used for investigation of the cavitational activity. The reaction is very specific and can be considered as a true measure of the cavitational activity.

The measurement of fluorescence intensity of TA solution after subjecting to cavitating conditions can be carried by using Fluorescence Spectrophotometer at 310 nm excitation and 426 nm emission wavelength. However, while performing the experiments, the irradiated TA solution should be always kept in dark and their fluorescence intensities should be measured within 2–4 h of sonication [24,26]. It is also reported that aldrich IrC_6^- can be used as a potent oxidant to enhance the yield and intensity of HTA [24]. Time required in this method is high as compared to other methods and experiments should always be performed in dark room.

2.1.2.4. Physical methods.

1. Sonochemiluminescence
   Sonochemiluminescence (SCL) gives visualization of the cavitationally active zone where sonochemical reaction can take place in the reactor. The intensity of luminescence is proportional to the intensity of cavitation (number of collapses). Luminol (3-aminophthalhydrazide) is widely used as the SCL reagent [31–33]. When aqueous solution of luminol is irradiated by ultrasound under alkaline conditions, luminol is oxidized by $OH^{\bullet}$ radicals, to give 3-amino phthalate resulting in blue light spectrum. This property of luminol can be used for the determination of cavitational activity in the sonochemical reactor. The SCL images can be captured by a digital camera. Hu et al. [31] have reported the use of chemiluminescence (CL) method in combination with the Flow Injection technology applied for in-line and real-time determination of amounts of hydrogen peroxide generated in aqueous solutions under the effect of ultrasound.
2. Aluminum foil erosion
   The phenomena of aluminum foil erosion can also be used for investigation of the cavitational activity in the reactor [34]. In this method, aluminum foil is kept parallel to the, direction of location of transducers (cavitational activity is measured in that reaction plane). The cavitational activity is measured

qualitatively in terms of the erosion pattern obtained on the aluminum foil. This requires use of high resolution digital camera to capture the erosion patterns and can be used only for low frequency operation where physical effects are significant. At low frequency, collapsing bubble size and wavelength of ultrasound is larger as compared to the high frequency operation, which results in generation of higher intensity micro jets and hence physical effects are significant.

The main drawback of this technique is that it only gives qualitative information about the cavitational activity distribution. Also the presence of aluminum foil in the medium might disturb the sound wave propagation and alter the obtained results.

3. Electrochemical method based on mass transfer

In this method, measurement of the solid-liquid mass transfer coefficient (to or from electrode) is done using an electrochemical reaction. Mao et al. [35] has electrochemically determined the formation of hydrogen peroxide and developed mechanism of oxygen electroreduction by enzymatic reaction. It has been reported that the use of redox agent $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ results in enhancement of the mass transfer rate and hence can be used for better sensitivity [9,36–38]. These systems exhibit a fast quasi-reversible electron transfer so that the electrode kinetics is considered as mass transfer controlling.

The main difficulty associated with this technique is that the sensitivity and reproducibility depends on the amount of hydrogen peroxide formed during the process, which is usually very small. Also hydrogen peroxide is unstable and hence this technique may not give true characteristics.

4. Polymer degradation

When a solution of long chain polymer dissolved in a solvent is sonicated, high shear stress is created in the vicinity of bubble and micro jets are formed, which results in chain breakage and reduction in viscosity/molecular weight of the polymer (high molecular weight polymer gets converted into lower molecular weight polymer monomer). The degree of breakage is dependent on the cavitational collapse intensity [39,40] and hence the cavitational activity can be found out by measuring the change in molecular weight of reaction mixtures strategically placed at different locations in the reactor.

5. Particle image velocimetry (PIV) technique:

Particle image velocimetry is a flow velocity measurement technique which is extensively used to study fluid dynamics. It is an optical visualization method consisting of determination of particle displacement as a function of time using a double-pulsed laser technique. In this method, liquid media is seeded by tracers. A laser light sheet illuminates a plane in the flow and the positions of particles in that plane are recorded using a digital camera. After fraction of a second, another laser pulse illuminates the same plane, creating a second particle image. From these two images, analysis algorithms obtain the particle displacements for the entire flow region and thus the local liquid circulation currents can be quantified. Earlier, PIV measurements were performed based on the assumption that the cavitation bubble can act as tracers. However, the obtained results were not reliable because bubbles of different sizes are distributed non-uniformly in the liquid medium. Thus, cavitation bubbles cannot be used as tracers for PIV measurements. To overcome this problem, the reactor media is seeded with fluorescent tracers [41–43]. Boldo et al. [44] reported the use of PIV measurement method for determination of liquid circulation velocity and vibration amplitude by time averaging holography method. Obtained results show that maximum liquid velocity is observed near to the irradiating surface. The extent of liquid circulation is used to explain the extent of uniformity in cavitational activity in the reactor.

2.2. Theoretical investigations

The objective of efficient scale up of sonochemical reactor is the reproducibility of cavitational activity and associated improvement in the product quality. The cavitational activity in a reactor is non homogeneous, dynamic in nature and depends on the design and location of the transducers. So, it is necessary to characterize cavitational activity in sonochemical reactor to optimize the design parameters. Determination of variation in the cavitational activity by experimental investigation is not always feasible due to the following reasons:

- Experimental techniques are usually quite expensive and time consuming.
- Cavitation medium gets disturbed due to the presence of external instrument such as thermocouple, hydrophone, aluminum foil, test tube, etc. and hence we may not get a realistic picture of the cavitational activity distribution
- Obtained results may not be reproduced due to the dynamic nature of cavitation phenomena.

Theoretical predication of cavitational activity in terms of pressure field gives an efficient alternative to experimental mapping techniques. Based on theoretical analysis, one can obtain the pressure field distribution in any new sonochemical reactor with different geometries and operating conditions, which can aid in optimization for maximum/uniform cavitational activity. The modeling studies can be extended to quantification of other useful parameters such as distribution of temperature, mass transfer coefficient, etc., which can be controlling parameters depending on the type of application. One of the earliest works in this area has been by the group of Keil [45–49], who investigated the variation in cavitational activity in different sonochemical reactors by solving the Helmholtz and Kirchhoff integral equation with homogenous and inhomogeneous bubble distribution. It has been shown that the cavitational activity is maximum very near to the transducer and decreases away from transducer, which is line with experimental measurements. It has been also reported that the influence of the bubble fraction on the distribution on pressure field can be neglected and damping effects are more dominant for the homogenous distribution of bubbles as compared to the inhomogeneous distribution. It should be also noted that there is some scope for improvement in the models developed by Keil and coworkers. The homogenous density distribution of the bubbles as assumed in the work [47,48] is difficult to be achieved even in a well stirred ultrasonic bath. In addition, bulk movement of the liquid in the bath due to stirring and acoustic streaming can disturb the pressure fields due to the scattering of ultrasound waves. In the simulation with inhomogeneous distribution of the bubbles [47–49], the assumption of homogenous bubble distribution in one plane (radial variation of bubble size and number has been neglected) is also not possible practically since the bubble volume fraction changes continuously with sound wave propagation due to continuous generation and collapse of the cavities and also the number of these cavities vary with time. Also the assumption of small-amplitude sinusoidal motion in the modified wave equation is questionable especially in the case of pressure waves with much higher amplitudes (>1 atm), which are again likely to be used at larger scales of operation. Nevertheless, this work surely cannot be underestimated and can be taken as a starting point for obtaining a clearer picture of the cavitation phenomena.

More recently, Saez et al. [50] have carried out numerical simulations to characterize the ultrasonic field propagation and to obtain the spatial distribution of the mechanical effects. The model is based on the assumption of linear wave propagation in a homogeneous media and the results are based on the solution of the

Table 2
Effect of frequency on sonochemical efficiency (SE) of KI decomposition and Fricke reaction [9].

Frequency (kHz)	SE of KI (mol/J) × 10^{10}	SE of Fricke solution (mol/J) × 10^{10}
20	0.6 ± 0.22	2.3 ± 0.1
40	0.6 ± 0.22	2.8 ± 0.1
45	0.6 ± 0.22	3.7 ± 0.1
96	4.1 ± 0.2	16.8 ± 1.0
130	5.6 ± 0.4	22.6 ± 0.9
200	8.3 ± 0.6	15.2 ± 0.9
400	7.8 ± 0.2	19.3 ± 1.2
500	7.1 ± 0.2	20.3 ± 1.2
1200	0.64 ± 0.3	2.6 ± 0.1

Helmoltz equation using a finite element method considering an optimized mesh size. Comparison of theoretical results with those obtained with different experimental mapping techniques (calorimetry, aluminium foil erosion and use of thermal probes) represents a good agreement with the obtained trends in terms of cavitational activity distribution. Klima et al. [51] have used similar approach for optimizing the geometry of the sonochemical reactor. It has been reported that use of appropriate selection of the reactor geometry, in terms of the reactor dimensions, liquid volume and the length of the immersion of ultrasonic horn in the reactor, can result in much better uniformity of the cavitational activity with intensification as compared to the conventional approach, possibly attributed to the multiple reflections of the incident sound waves from the reactor walls and liquid surface leading to resonance effects. The work truly indicates the approach to be used for utilizing the theoretical techniques for optimization of the reactors as discussed earlier. Horst et al. [52] have also reported similar utility of theoretical analysis of the sound wave propagation in the reactor for the optimization of the geometry of the reactor.

Yasui et al. [53] have used solution of wave equation based on finite element method for characterization of the acoustic field distribution. A unique feature of the work is that it also considers contribution of the vibrations occurring due to the reactor wall and has evaluated the effect of different types of the reactor walls or in other words the effect of material of construction of the sonochemical reactor. The work has also contributed to the understanding of the dependence of the attenuation coefficient due to the liquid medium on the contribution of the vibrations from the wall. It has been shown that as the attenuation coefficient increases, the influence of the acoustic emission from the vibrating wall becomes smaller and for very low values of the attenuation coefficient, the acoustic field in the reactor is very complex due to the strong acoustic emission from the wall.

3. Analysis of effects of operating parameters

In order to successfully carry a chemical reaction or any given application in a sonochemical reactor, number of parameters such as frequency of ultrasound, intensity of irradiation, bulk temperature of liquid and amount of gas content/additive, etc. which affect the cavitational yields need to be optimized. We now aim at analyzing the effect of these operating parameters on cavitational activity in the sonochemical reactor.

3.1. Frequency of ultrasound

Koda et al. [9] have investigated the effect of frequency in seven different types of reactors in the range 19.5 kHz to 1.2 MHz with power rating in the range of 35–200 W. Comparison was made in terms of sonochemical efficiency (mole/J) for KI and Fricke solution. The observed results have been given in Table 2. It can be seen that sonochemical efficiency increases till 200 kHz and then

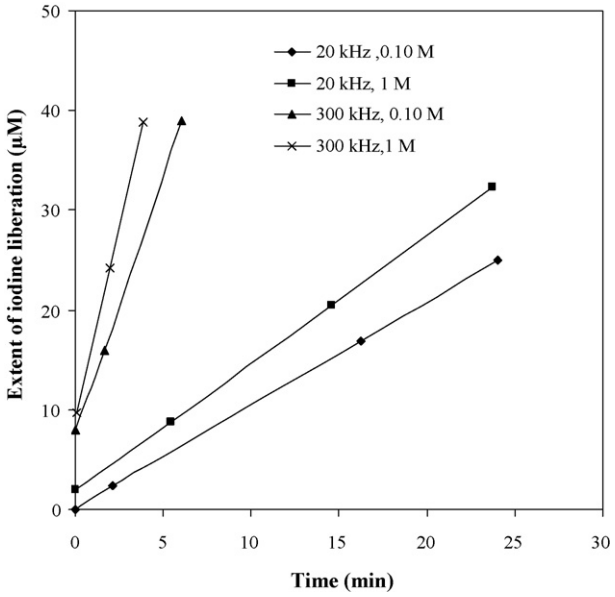


Fig. 2. Amount of I_3^- formation at 20 and 300 kHz frequency at 2.7 W power for different concentrations of potassium iodide [25].

decreases due to controlling attenuation of ultrasound at high frequency, leading to lower energy dissipation. Similar type of variation in sonochemical efficiency is observed for experiments with Fricke solution with maximum cavitational effects being observed at 130 kHz frequency.

Wayment and Casadonte [25] have described the design of a single-transducer variable-frequency (in the range 20–500 kHz) sonication system operating at constant acoustic power. They have observed the effect of frequency of ultrasound on oxidation of potassium iodide by varying concentration (0.1 and 1 M) and have reported that rate of decomposition is maximum at 300 kHz (for 1 M concentration) as shown in Fig. 2. Beckett and Hua [54] with studies on sonoluminescence and chemical reactions have reported an existence of optimum operating frequency as 358 kHz. Kang et al. [55] have reported lower hydrogen peroxide formation at higher frequencies of irradiation viz. 618 and 1078 kHz as compared to 358 kHz due to the controlling effect of the higher power dissipation per unit volume at 358 kHz frequency. Hung and Hoffmann [56] and Mark et al. [57] have also reported similar existence of optimum frequency of irradiation.

It can be seen from the above discussion, that usually increasing the frequency of irradiations for getting better results, especially for chemical processing applications, is not a good idea and there exists an optimum frequency of operation, magnitude of which usually depends on the specific system under question. Also, it is likely that continuous operation with high frequency irradiation leads to an erosion of the transducers surface. The power requirement for inception of cavitation events in a high frequency operation is also higher. Use of multiple frequency operation can be considered as an efficient alternative to the drawbacks associated with the single frequency operation especially when higher cavitational intensities are required for the application.

Tatake and Pandit [58] have reported the theoretical and experimental investigation of the effect of combination of two frequencies by using a combination of two reactors viz. ultrasonic horn and ultrasonic bath. It has been reported that cavitational activity is a function of the location of reaction vessel in the bath and cavitational activity is less at locations where nodes are formed (at distance of $n\lambda/2$ from the bottom of bath where $n = 2, 4, 6$, etc.). The combination gives better control over the cavitational activity with enhanced reaction rates due to higher resonance effect

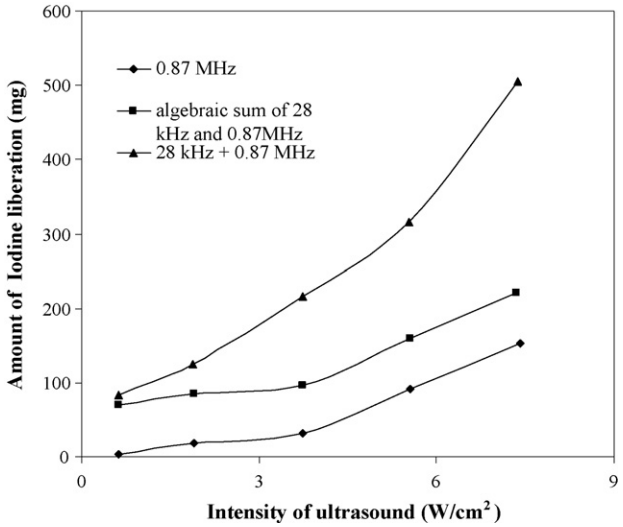


Fig. 3. Effect of frequency and intensity of irradiation on the extent of liberation of I_2 at 28 kHz, 0.87 MHz and combination of 28 kHz + 0.87 MHz frequency [24].

on bubble growth as compared to the single frequency operation. They have also investigated the effect of frequency on the maximum size of bubble reached during cavitation (with initial size of bubble as 2 μm), life time and collapse pressure. It has been reported that maximum size reached by the bubble for combination of frequencies is higher as compared to the single frequency operation, which results in enhanced cavitational activity and hence the sonochemical reaction yields. Servant et al. [59] have also reported that under the dual frequency operation, cavitation bubble volume fractions are higher as compared to that observed in mono-frequency sonochemical reactors. It has also been reported that the cavitation medium is intensely disturbed due to the combination of frequencies as more breakage of surface continuity in the liquid medium occurs resulting in overall higher cavitational activity due to generation of more cavities and stronger bubble-bubble, bubble-sound field interaction due to primary and secondary Bjerkens forces.

Feng et al. [24] have also reported a similar investigation of the effect of combination of low frequency (28 kHz) and high frequency (in the range of 0.87–1.06 MHz) with intensity of irradiation up to 8 W/cm^2 on KI decomposition, change in electroconductivity and fluorescence of TA. They observed that combination of frequencies gives synergistic results with yields greater than the algebraic sum of the obtained yields with single frequency operation, as shown in Fig. 3. There have been many other reports indicating that the combination of low frequency ultrasound can be used for intensification of cavitational effects as compared to the high frequency operation [60–62].

Prabhu et al. [63] investigated the dependency of bubble dynamics on the combination of frequency in the case of single, dual and triple frequency operation at a fixed 10 W/cm^2 intensity of irradiation, 100% fraction of gas and initial radius of cavity as 2 μm. The bubble dynamics parameters such as life time of cavity, ratio of initial to final radius and collapse pressure have been given in Table 3. The size and life time of cavity are maximum for triple frequency operation which indicates that cavitationally active volume in the reactor is higher for triple frequency operation as compared to the dual and single frequency operations. Gogate et al. [64] have also reported, with experimental investigations on degradation of formic acid as the model reaction, that the combination of three frequencies gives higher cavitational yields as compared to dual and single frequency operations.

Table 3
Effect of combination of frequency on cavity size and collapse pressure with 10 W/cm^2 intensity of irradiation and initial cavity size as 2 μm [63].

Frequency of combination	R_{max}/R_0	Life time of cavity(s)	Collapse pressure (atm)
Single	128.0	3.24×10^{-5}	47171.5
Dual	205.8	3.70×10^{-5}	45169.1
Triple	262.74	4.02×10^{-5}	44961.6

Overall, it can be summarized that, use of multiple frequency irradiations based on the use of multiple transducers gives much higher cavitational activity in the reactor and hence enhanced results. It is also recommended that a combination of low frequency irradiation (typically 20 kHz) with other frequencies in the range of 50–200 kHz should be used for obtaining maximum benefits from the cavitational reactors.

3.2. Intensity of irradiation

Intensity of irradiation is the amount of power dissipated in liquid medium per unit area of irradiating surface. As the intensity of irradiation increases, extent of power dissipation in bulk liquid increases for a given area of transducer.

Feng et al. [24] have investigated the effect of intensity of irradiation (W/cm^2) on the cavitational activity in terms of liberation of iodine, change in thermal conductivity and fluorescence intensity, in a sonochemical reactor operating at a combination of 0.87 MHz and 28 kHz. It has been observed that, as intensity of irradiation increases the cavitational activity also increases. The observed effects are attributed to the resonance effect and enhanced bubble-bubble interaction through primary and secondary Bjerknes forces. The obtained results for the extent of iodine liberation have been shown in Fig. 3.

Saez et al. [65] have performed experiments in a sonochemical reactor (of diameter 68 mm, height of 84 mm with frequency of 20 kHz and maximum power rating of 100 W) to investigate the effects of intensity of irradiation over the range of 0–8 W/cm^2 on the sonochemical yield. Results show that as intensity of irradiation increases, the yield of reaction increases up to threshold value and then decreases. The optimum intensity of irradiation has been found to be 2.8 and 3.5 W/cm^2 for iodine liberation and Fricke dosimerty respectively as depicted in Fig. 4. Xie et al. [66] and Sivakumar and Pandit [67] have also reported similar existence of optimum intensity of irradiation.

Prabhu et al. [63] have carried out studies using bubble dynamics analysis to determine the effect of intensity of irradiation (in the range of 1–50 W/cm^2) for triple frequency operation with

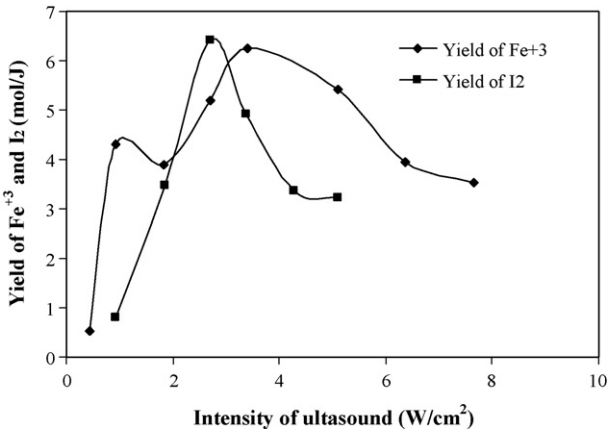


Fig. 4. Yield of Fe^{3+} and I_2 as a function of intensity of irradiation [65].

Table 4
Effect of intensity of irradiation on size, life time and collapse pressure of cavity for triple frequency operation (30–30–30 kHz) [63].

Intensity (W/cm^2)	R_{max}/R_0	Lifetime of cavity (s)	Collapse pressure (atm)
1	122.9	3.2×10^{-5}	41117.1
5	213.5	3.7×10^{-5}	61199.7
10	262.4	4.0×10^{-5}	44961.6
20	319.3	5.9×10^{-5}	59463.4
50	409.5	6.6×10^{-5}	55236.2

Table 5
Effect of presence of gases on the extent of iodine liberation in a sonochemical reactor [68].

Gas	Rate of reaction (μmol/min)
Ar	2.78
He	0.34
O_2	1.56
N_2	0.36
Air (N_2:O_2 ≈ 80:20)	1.0

individual frequency as 30 kHz each, on the maximum bubble size and collapse pressure. The results obtained have been reproduced in Table 4. It can be easily seen from the data that:

- As the intensity of irradiation increases, ratio of maximum radius to initial radius increases; thus at higher intensity of irradiation more cavitationally active volume is achieved with higher life time of cavity.
- Also with an increase in intensity of irradiation, collapse pressure increases slightly, leading to enhanced cavitational effects.

Overall, it can be said that for single frequency operation an optimum intensity of irradiation should be selected, whereas for multiple frequency operation, existence of optimum intensity has not been observed but this cannot be generalized.

3.3. Bulk temperature of liquid medium

Prabhu et al. [63] have analyzed the effect of temperature (in the range of 20–60 °C) by cavity dynamics model and observed 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). This can be attributed to the fact that as the temperature of the liquid is increased, its viscosity and/or surface tension decreases but more importantly vapour pressure increases substantially. The extent of increase in liquid vapour pressure (P_i) is much higher as compared to liquid temperature (T_i). This results in a decrease in final liquid temperature (T_f) as explained by following mathematical relationship:

$$\frac{T_f}{T_i} = \frac{P_f(\gamma - 1)}{P_i}$$

where T_f is final temperature, P_i is vapour pressure and γ is poly tropic coefficient of gas. Thus, it is expected that the cavitational activity will be reduced at higher operating temperature in the reactor. In other words, for an application where cavitational collapse is the primary cause of the activation, a low operating temperature is recommended. In other cases, where chemical reactions are also occurring, an optimum operating temperature might exist. This is attributed to the fact that there is always a possibility that the higher concentration of chemical species is present in the cavitating bubble due to higher vapor pressure at higher operating temperature and this generates much higher amounts of free radicals in the system leading to higher reaction rates.

3.4. Effect of presence of gases

The magnitude of temperature reached at the collapse is affected by the amount of gas dissolved in the liquid medium. Final temperature reached by the adiabatically collapsing bubble (mainly depends on polytropic coefficient of the gas (γ)) can be given by following mathematical relationship:

$$T_f = T_i \left(\frac{R_i}{R_f}\right)^{3(\gamma-1)}$$

where T_i is the initial temperature of liquid, T_f is final collapse temperature, γ is polytropic coefficient, R_i and R_f are the initial and final radius of the cavitating bubble respectively. The temperature of bubble during collapse not only depends on the polytropic coefficient of gas but also on the thermal conductivity and solubility of the gas in the liquid medium.

Segebarth et al. [68] have performed experiments in Janus sonochemical reactor, with an operating frequency of 20 kHz and maximum power rating of 100 W, to investigate the effect of oxygen, nitrogen and noble gases such as Argon (Ar) and Helium (He) on decomposition of KI. It has been reported that the rate of KI decomposition is maximum for Ar as evident from the relative rates of iodine liberated for different gases given in Table 5. The trends can be explained from the fact that monoatomic gases give higher collapse temperature than polyatomic gases. This is due to the fact that polyatomic gases have low polytropic coefficient. The variation in rate of iodine liberation as a function of the mole fraction of Argon (Ar) in a mixture of helium (He) and argon has also been investigated and it has been reported that the rate of reaction increases with an increase in the mole fraction of Ar.

Shimizu et al. [69] have investigated the effect of dissolved gases (Xe, Ar, O_2 and N_2) on the generation of OH radicals in the presence of TiO_2 catalyst. Experiments were performed in a sonochemical reactor of capacity 5.8 l with operating frequency of 36 kHz and power rating of 200 W. They observed that cavitational activity in terms of generation of DHBA increases with time as shown in Fig. 5. Maximum rate is observed for Xe followed by Ar, O_2 and N_2. From Fig. 5, it should be noted that, concentration of DHBA (μmole) in presence of Xe changes more rapidly as compared to Ar (both gases have same value of polytropic constant) which can be explained as follows:

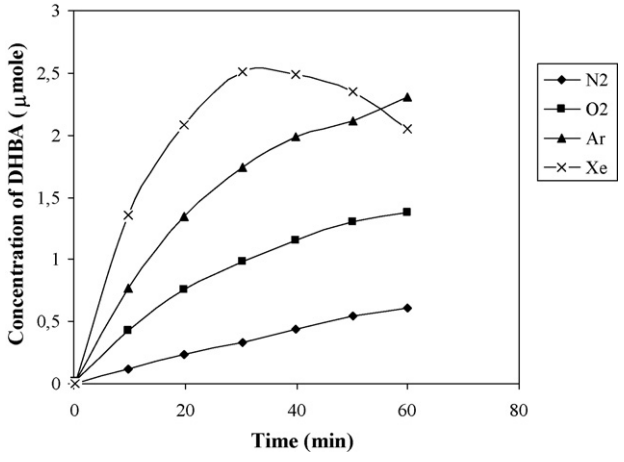


Fig. 5. Effect of dissolved gases on generation of DHBA in presence of TiO_2 [69].

- Thermal conductivity of Ar (0.01772 W/mK) is higher than Xe (0.00565 W/mK) and hence the loss of heat from bubble containing Ar is more rapid as compared to Xe. So the bubble temperature with Xe is always higher than bubble with Ar gas, resulting in higher cavitational intensity.
- Also, it should be noted that solubility of Xe in water is three times higher than Ar, which provides additional nucleation site for cavitation.

3.5. Presence of additives

The presence of solid particles mainly provides additional nuclei for the cavitation phenomena and hence the number of cavitation events occurring in the reactor is enhanced resulting in a subsequent enhancement in the cavitational activity. It must be noted that the presence of solids also have a negative effect on the cavitational activity as the solid particles result in scattering of the sound waves thereby decreasing the focused energy transferred into the system. The net effect of these two phenomena will be dependent on the system in question and hence optimization is a must before operating parameters are selected for actual operation. The earlier work of Gogate et al. [70] is recommended in this case to obtain an idea about the methodology to be used for the optimization of operating parameters. The typical additives which have been used for intensification of cavitational activity [70–78] include presence of salts such as NaCl, $NaNO_2$ and $NaNO_3$, presence of solid particles such as TiO_2, CuO and MnO_2 which can also act as a catalyst in some cases and presence of surfactants such as sodium dodecyl sulfate. The presence of additives (particles/salts in a typical concentration range of 1–10% by weight of the reactants; optimization is recommended in majority of the cases) in the sonochemical reactors results in intensification due to the following mechanisms:

- Formation of increased cavitation nuclei due to more number of discontinuities in liquid continuum to give larger number of collapse events resulting in increase in the number of free radicals.
- In a biphasic solid–liquid medium irradiated by power ultrasound, major mechanical effects are the reduction in particle size leading to an increased surface area and the formation of liquid jets at solid surfaces by the asymmetrical inrush of the fluid into the collapsing voids. These liquid jets not only provide surface cleaning but also induce pitting and surface activation effects and increase the rate of phase mixing, mass transfer and catalyst activation.
- Enhanced generation of free radicals due to some catalysts such as $FeSO_4$ or elemental iron.
- Better distribution of the organic pollutants increasing the concentration at reaction sites, e.g. due to the presence of NaCl.
- Alteration of physical properties (vapor pressure, surface tension) facilitating generation of cavities and also resulting in more violent collapse of the cavities.

3.6. Geometrical design of the reactor

The reactor design in terms of ratio of the diameter of the immersion transducer to reactor diameter, liquid height, position of the transducers and characteristics of the cell plays a important role in deciding the cavitational activity distribution and hence the efficacy of sonochemical reactors for the specific application. Based on a critical analysis of the existing literature, following important design related information can be recommended:

- With an increase in the diameter of immersion transducer relative to the reactor diameter, the cavitational activity increases till an optimum ratio, usually dependent on the application [78,79]. The ratio mainly affects the level of turbulent dissipation of energy and the intensity of the acoustic streaming and hence would be more crucial in the applications where physical effects are more important.
- The extent of immersion of the transducer in an ultrasonic horn or the extent of liquid height, which affects the extent of reflection of the incident sound waves from the liquid surface as well as the reactors walls, also shows an optimum value [33].
- The position of the transducers in reactors based on the multiple frequency arrangement should be done in such a way that maximum and uniform cavitational activity is obtained. Theoretical analysis of the cavitational activity distribution as discussed earlier aids in arriving at an optimum location of the transducers. Similar argument holds true for the geometry of the reactor.

4. Some remarks on the future prospects for reactor designs

Currently, ultrasonic horns are the most commonly used reactor designs. These are typically immersion type of transducers and very high intensities (pressures of the order of few thousands atmosphere) are observed very near to the horn [80]. The scale up prospects of horn type systems is very poor as it cannot effectively transmit the acoustic energy into large process volume. Also, they suffer from erosion and particle shedding at the delivery tip surface, they may also be subjected to cavitational blocking (acoustic decoupling), and the large transducer displacement increases stress on the material of construction, resulting in the possibility of failure. Thus, ultrasonic horn type systems are generally recommended for laboratory scale investigations. However, few novel designs are worth mentioning which can have an impact in the future applications. Horst et al. [52] have reported a novel modification in terms of using high intensity ultrasound from a concentrator horn. It has been shown that the concept of a conical funnel fits the demands for nearly perfect radiation effectiveness and a good reaction management. Dahlem et al. [81] have also reported a design based on radial vibrations as against conventional longitudinal vibrations for the immersion system. Very recently Dion [82] have described a new continuous reactor design based on the high power converging acoustic waves in a tube to produce a relatively large volume confined acoustic cavitation zone in flowing liquid reagents under pressure. It has been reported that the new cylindrical sonoreactor design does not contaminate the processed liquids with erosion products since the cavitation zone is maintained away from the wall of the tube. The processing capacity of the largest models may be up to several tons per hour, depending on the required cavitation energy per unit volume to produce the desired process enhancement, using an electric power input of about 50 kW.

The designs based on multiple transducers irradiating either same or different frequency are most feasible designs for large scale operation. To increase the active zones existing in the reactor, one can easily modify the position of the transducers so that the wave patterns generated by the individual transducers overlap, also resulting into uniform and increased cavitational activity. More recent developments have employed direct bonding of the transducer to the surface of the vessel. Improvements in the bonding method, and a move to transducers with lower individual outputs, have enabled the move to systems with large numbers of transducers to give an acoustic pattern that is uniform and noncoherent above the cavitational threshold throughout the working volume. Arrangements such as tubular reactors with two ends either irradiated with transducers or one end with transducer and other with a reflector [83], parallel plate reactors with each plate irradiated with either same or different frequencies [84] and transducers each on sides of hexagon [74] can be constructed. The use of multiple low-output transducers gives the additional advantage of avoiding the phenomenon of cavitational blocking (acoustic decoupling), which

arises where power densities close to the delivery point are very high. In addition these multi-transducer units very effectively concentrate ultrasonic intensity towards the central axis of the cylinder and away from the vessel walls, thus reducing problems of erosion and particle shedding.

5. Conclusions

Understanding of the cavitational activity, its distribution and dependence on the operating parameters is crucial in an efficient design and operation of sonochemical reactors, especially due to the dynamic nature of the cavitation phenomena. Based on the detailed analysis presented in the work, it can be said that theoretical analysis of the cavitational activity distribution with proper experimental validation can be used for arriving at optimum geometric design of the sonochemical reactors. The reactors based on multiple frequency operation seems to be a better alternative to single frequency reactors due to higher cavitational activity leading to much better overall cavitational yields. Presence of additives such as gases, catalysts and dissolved species can result in substantial intensification of the cavitational activity under optimized conditions. Overall, it can be said that considerable care is required for optimum selection of operating and geometric parameters for maximizing the benefits of the sonochemical reactors for the specific application under consideration as same effects may not be realized for different applications.

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