Large-scale sonochemical reactors for process intensification: design and experimental validation

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Abstract: Acoustic cavitation results in substantial enhancement in the rates of various chemical reactions but the existing knowledge about the application of reactors based on acoustic cavitation is limited to very small capacities (of the order of few millilitres). In the present work, an overview of the application of acoustic cavitation for the intensification of chemical reactions has been presented briefly, discussing the causes for the observed enhancement and highlighting some of the typical examples. A novel reactor has been developed operating at a capacity of 7 dm³ and tested with two reactions, ie liberation of iodine from aqueous potassium iodide and degradation of formic acid. The energy efficiency of the reactor has been calculated and compared with the conventional sonochemical reactors. The effect of frequency of irradiation on the percentage conversion of the reactants has been studied. Due to quite low conversions in the case of formic acid degradation, further intensification was attempted using aeration, addition of hydrogen peroxide, and the presence of solid particles (TiO₂). Compared with conventional reactors the novel reactor gives excellent results and it can be said that the future of using acoustic cavitation for process intensification lies in the development of large-scale multiple frequency multiple transducer reactors. © 2003 Society of Chemical Industry

Keywords: acoustic cavitation; large-scale operation; sonochemical reactors; Weissler reaction; degradation of formic acid; process intensification

INTRODUCTION

Cavitation can be in general defined as the generation, subsequent growth and collapse of the cavities, releasing large magnitudes of energy over a very small area (resulting in very high energy densities of the order of $1-10^{18}$ kW m⁻³). Cavitation occurs at millions of locations in the reactor simultaneously and generates conditions of very high temperatures and pressures (few thousand atmospheres pressure and few hundreds K temperature) locally with overall ambient conditions. Thus chemical reactions requiring stringent conditions can be effectively carried out using cavitation at ambient conditions. Moreover, free radicals are generated in the process due to the dissociation of vapours trapped in the cavitating bubbles, which results in either intensification of the chemical reactions or may even result in the propagation of certain reactions. The effect of cavitation phenomena on chemical reactions in terms of process intensification or changing the reaction mechanism has been known over the years¹⁻⁴ and many review articles have also been published.5-8

Depending on the methods of generation, cavitation has been classified into four types, but the most important type and that generating the maximum intensity of cavitation is acoustic cavitation. In the case of acoustic cavitation, the pressure variations in the liquid are effected using high frequency sound waves, usually ultrasound (16 KHz–100 MHz). Cavities are generated during the rarefaction cycle, and then grow in the presence of continued pressure reduction and subsequently collapse in the next compression cycle. These steps have been schematically depicted in Fig 1.

CHEMICAL EFFECTS OF CAVITATION

In order to understand the way in which cavitational collapse can affect chemical transformations, one must consider the possible effects of this collapse in different systems.

Homogeneous liquid phase reactions

In the case of homogeneous liquid phase reactions, there are two major effects. First, the cavity that is formed is unlikely to enclose a vacuum (in the form of

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Figure 1. Mechanism of generation of acoustic cavitation.

void)-it will almost certainly contain vapour from the liquid medium or dissolved volatile reagents or gases. On collapse, these vapours will be subjected to extreme conditions of high temperatures and pressures, causing molecules to fragment and generate highly reactive radical species. These radicals may then react either within the collapsing bubble or after migration into the bulk liquid. For example, sonication of water gives rise to OH[•] and H[•] radicals and subsequently to hydrogen peroxide. Both OH[•] radicals and hydrogen peroxide are strong oxidizing agents. Secondly, the sudden collapse of the bubble also results in an inrush of the liquid to fill the void, producing shear forces in the surrounding bulk liquid which are capable of breaking the chemical bonds of any materials which are dissolved in the fluid or of disturbing the boundary layer, thus facilitating the transport resulting in process intensification.

Heterogeneous reactions

The sonochemical activation in heterogeneous systems is mainly a consequence of the mechanical effects of cavitation.

Solid-liquid heterogeneous reactions

In a heterogeneous solid-liquid system, the collapse of the cavitation bubble results in significant mechanical defects. Collapse near the surface produces an asymmetrical inrush of the fluid to fill the void, forming a liquid jet targeted at the surface. This effect is equivalent to high-pressure/high-velocity liquid jets and is the reason why ultrasound is used for cleaning solid surfaces. These jets activate the solid catalyst and increase the mass transfer to the surface by disruption of the interfacial boundary layers as well as dislodging the material occupying the inactive sites. Collapse on the surface, particularly of powders, produces enough energy to cause fragmentation (even for finely divided metals). Thus, in this situation, ultrasound can increase the surface area for a reaction and provide additional activation through efficient mixing and enhanced mass transport.

Immiscible liquid-liquid heterogeneous reactions

In heterogeneous liquid–liquid reactions, cavitational collapse at or near the interface will cause disruption and mixing, resulting in the formation of very fine emulsions. When very fine emulsions are formed, the surface area available for the reaction between the two phases is significantly increased, thus increasing the rates of reaction. This is very beneficial particularly in the case of phase-transfer catalysed reactions or biphasic systems.⁸

APPLICATIONS OF ACOUSTIC CAVITATION Chemical synthesis

The following paragraph describe some of the important applications of acoustic cavitation in chemical reactions or in synthesis.

Reduction in reaction time

Ultrasound can be used for substantially enhancing the rates of chemical reactions (eg Javed *et al*⁹ have shown that the Diels–Alder cyclization reaction gives a 77.9% yield in 35h by conventional means but application of ultrasound results in a yield of 97.3% in only 3.5 h).

Increase in the yield

The conventional way of the epoxidation of longchain unsaturated fatty esters results in a yield of 48% in 2h of reaction time whereas application of ultrasound (20 kHz frequency of irradiation) increases the yield to 92% and, importantly, in just 15 min of reaction time.¹⁰

Switching of the reaction pathway

In some cases the use of ultrasound switches the reaction pathway, thereby totally changing the product distribution, eg with conventional reaction, stirring benzyl bromide and toluene in the presence of KCN and Al_2O_3 results in benzylation (Friedel–Crafts reaction) whereas sonication of the same components under identical conditions yields benzyl cyanide. This is due to the fact that sonication impregnates cyanide ions on Al_2O_3 , thereby masking the acidic sites and hence prevents it proceeding by the Friedel–Crafts route.¹¹

The examples mentioned here are a very few from the vast number available in the literature and some useful reviews/books are available on this subject.^{5,8,12-14}

Water and effluent treatment

Water and effluent treatment is one of the most important applications of acoustic cavitation. Ultrasonic irradiation effectively destructs contaminants in water because of localized high concentrations of oxidizing species such as hydroxyl radicals and hydrogen peroxide in solution, high localized temperatures and pressures, and the formation of transient supercritical water. Optimization of aqueous phase organic compound degradation rates can be achieved by adjusting the energy density, the energy intensity, and the nature and properties of the saturating gas in solution. The hydrophobic compounds react with OH^{\bullet} and H^{\bullet} at the hydrophobic gas bubble/liquid interface, while the hydrophilic species react to a greater extent with the OH^{\bullet} radicals in the bulk aqueous phase.

The variety of chemicals that have been degraded using acoustic cavitation though in different equipment and on a wide range of operating scales are *p*-nitrophenol, Rhodamine B, 1,1,1-trichloroethane, parathion, pentachlorophenate, phenol, CFC 11 and CFC 113, *o*-dichlorobenzene, dichloromethane, potassium iodide, sodium cyanide, and carbon tetrachloride among many others. A comprehensive review of the use of ultrasound in the field of wastewater treatment has been given in an earlier work.¹⁵

Polymer chemistry

In the field of polymer chemistry, application of ultrasound has been used for degradation of polymer compounds (eg polystyrene in toluene) as well as for initiation of polymerization reactions due to the formation of radical species acting like initiators¹⁶ (eg polymerization of vinyl monomers, styrene, methyl methacrylate).

Sono-electrochemistry (ultrasound with electrolysis)

The application of an ultrasonic field to an electrosynthetic reaction is a relatively unexplored technique. Benefits resulting from the use of ultrasound include lowering cell voltages, enhanced current efficiencies, minimization of electrode fouling, obviation of process-enhancing additives and simplified electrolysis systems.

Textile industry

The efficacy of conventional dyeing techniques could be enhanced by ultrasound because of the ultrasonicinduced dispersion and break-up of dye aggregates, the expulsion of entrapped air from fibre capillaries and the acceleration of the rate of diffusion of the dye along with an increased penetration inside the fibre. Ultrasound also improves dye fixation and increases the colour yield without affecting the fastness properties (wash fastness and staining) of the dyed fabric.

In addition to the above mentioned applications, acoustic cavitation has also been found to be beneficial in solid-liquid extraction and crystallization operations as well as in the petroleum industry for refining fossil fuels, determination of the composition of coal extracts and extraction of coal tars.

CURRENT STATUS OF SONOCHEMICAL REACTORS

It must be stated here that though acoustic cavitationbased reactors offer numerous advantages over the conventional reactors, there is hardly any processing carried out on an industrial scale. The main problem in efficient scale-up of the reactors is that the existing information is available mainly on a laboratory-scale, which would give very large scale-up ratios and hence very high degrees of uncertainty. The scaleup is further hampered by the fact that information is required from diverse fields such as chemical engineering (gas-liquid hydrodynamics and other reactor operations), material science (for construction of transducers efficiently operating at conditions of high frequency and high power dissipation) and acoustics (for better understanding of the sound field existing in the reactor). Previous experimental^{17,18} as well as modelling studies^{19,20} have indicated that operation at higher frequencies gives better results but, at the same time, frequency cannot be increased beyond a certain limit and there exists an optimum value beyond which the sonochemical effects are retarded.^{21,22} Continuous operation with high frequencies at larger scales of operation (and hence at higher power dissipation levels), leads to an erosion of the transducer surface, which makes it practically unfeasible to operate sonochemical reactors under these conditions. Moreover, the power required for the onset of cavitation increases with an increase in the frequency of irradiation and hence the process may become uneconomical at much higher frequencies of irradiation. One more problem associated with the design of large-scale reactors is the directional sensitivity of the reactors, ie the active cavitational volume is restricted locally very near the transducer surface.²³ Thus the immediate need is to design and successfully operate a largescale sonochemical reactor generating severe and uniform conditions of cavitation and at the same time operating at relatively lower frequencies.

DESIGN OF NOVEL REACTOR

Rationale for the design based on the theoretical studies on effects of ultrasound

Tatake and Pandit²⁴ have investigated the effect of multiple frequencies on the bubble dynamics and the maximum size of the cavity reached in the cavitation phenomena and indicated that the use of multiple frequencies results in violent collapse of the cavities as compared with the single frequency operation. Thus, for the large-scale reactors it is better to use multiple operating frequencies.

Gogate and Pandit¹⁹ have performed bubble dynamics simulations using the realistic equation considering the compressibility of the liquid and reported that a decrease in the intensity by dissipating the same power input through wider areas also results in an increase in the intensity of cavitation. Use of wider irradiating surfaces also results in an added advantage of better mixing characteristics in the reactor as predicted by Vichare *et al.*²⁵

Dahnke and Keil^{26–28} have investigated the pressure fields existing in the reactor with the help of numerical simulations using homogeneous and nonhomogeneous distribution of the cavitating bubbles and indicated that a large variation exists in the cavitational activity. The intensity of cavitation is maximum very near to the transducer surface and diminishes away from the transducer in both the axial and radial directions. Use of multiple sound sources and optimization of the power input to the systems helps in achieving uniform cavitating conditions. Taking a lead from this theoretical analysis, it was decided to use multiple transducers irradiating with different frequencies, with wider dissipating areas and variable power dissipations, in the novel reactor.

Rationale for the design based on the experimental studies on effects of ultrasound

In earlier work,²³ it was confirmed that the ultrasonic horn, which operates on the principle of irradiation through a single transducer, gives maximum variation in the cavitational activity in the reactor and there is a very small zone where maximum cavitational intensity is present. Further, it was also observed that in the case of an ultrasonic bath (three transducers situated at the bottom of the reactor), the cavitational intensity is comparatively more uniform as compared with the ultrasonic horn and the active cavitational volume is also substantially increased. Thus, it is better to use multiple transducers for achieving near-uniform distribution of the cavitational activity and hence in the present design, three transducers have been used on each side of the hexagon (thus a total of 18 transducers have been used in the reactor).

Gonze *et al*²⁹ have performed a mapping exercise in different reactors and have concluded that the cavitational activity is uniform in the case of parallel plate reactors where the active cavitation zones of two neighbouring transducers overlap and also standing waves are formed if a reflector/transducer is placed opposite to the transducer. The design in the novel reactor is adjusted in such a way that standing waves are indeed formed and result in significant enhancement in the cavitational intensity.

In earlier work,³⁰ a dual frequency flow cell (rectangular construction with opposite faces having series of transducers operating at 25 and 40 kHz with a capacity of 1.5 dm^3) was used successfully for the degradation of *p*-nitrophenol. The use of multiple transducers in the design helped to increase the active cavitational volume, thereby resulting in enhanced effects as compared with the single transducer reactor, ie ultrasonic horn. Thoma *et al*³¹ have also reported similar results using a near-field acoustic processor.

Actual design of the novel reactor

Considering all the points mentioned above, a triple frequency hexagonal flow cell was designed with each side of the hexagon hosting multiple transducers (three on each side). The hexagonal triple frequency flow cell



Figure 2. Schematic representation of triple frequency hexagonal flow cell, consisting of a hexagonal Reactor with 10 cm sides. The central quartz tube is kept as provision for simultaneous irradiation with UV light which forms further work.

has a total capacity of 7.5 dm³ and can be operated in batch as well as continuous mode Schematic representation of the hexagonal flow cell is given in Fig 2. Transducers (three in number in each set per side) having an equal power rating of 150 W per side have been mounted (thus the total power dissipation is 900 W when all the transducers with combination of 20 + 30 + 50 kHz frequencies are functional). The two opposite faces of the flow cell have the same irradiating frequency. The operating frequency of the transducers is 20, 30 and 50 kHz and can be operated in different combinations (seven in total) either individually or in combined mode. It should also be noted that there is provision for simultaneous irradiation with UV light as photocatalytic oxidation has been reported to act in synergism with cavitation³² and the results for combined irradiation are much better compared with the individual operation. The synergism of the combined operation was not tested in this work but forms a part of the current investigation being carried out in this department.

EXPERIMENTAL

Two different reactions, viz Weissler reaction, which is commonly used for studying the efficacy of sonochemical reactors, and degradation of formic acid (removal of lower molecular weight acids is usually the rate-controlling step in deciding the degradation of pollutants which again is one of the most important applications of cavitation) were studied to check the efficacy of the designed novel reactor. The total irradiation time was divided into equal fragments of 15 min each for achieving cooling of the transducer surface and the reaction mixture, ie the reactor was kept on for 15 min followed by a gap of 15 min. In the gap of 15 min, the solution was circulated through an external heat exchanger for cooling of the reaction mixture (cooling was achieved using chilled water at $5-10^{\circ}$ C)

Weissler reaction

The Weissler reaction is the reaction of the decomposition of KI, liberating free iodine. It should be noted at this stage that the Weissler reaction is only induced due to the cavitation and not by shear temperature and pressures.^{33,34} This is due the fact that free OH[•] radicals are formed in the solution only under cavitating conditions. These free radicals are responsible for the liberation of iodine from potassium iodide. Iodine also reacts with some amount of the remaining KI to form I₃-ions, which form a blue colored complex when starch is added to the solution. The extent of iodine liberated during the reaction is estimated with the help of a UV/VIS spectrophotometer by measuring its absorbance at 355 nm. The rate and amount of the iodine liberation depends on the formation and supply of OH[•] radicals, which are dependent on the efficacy of the cavitating equipments. Thus decomposition of KI (Weissler reaction) can be effectively used for comparing various types of equipment. In the present work 7 dm³ of 1% (w/v) KI solution was irradiated with seven different combinations of frequencies for 30 min.

Degradation of formic acid

Experiments with formic acid were performed with 7 dm³ of an aqueous solution of formic acid (100 ppm initial concentration), with total irradiation time being 90 min. Some experiments were repeated with continuous aeration using a sintered multi-point sparger, at a rate of $1.02 \text{ cm}^3 \text{ s}^{-1}$; in the presence of H₂O₂ (concentration of $0.5 \text{ cm}^3 \text{ dm}^{-3}$) and in the presence of solid particles of TiO₂ (anatase grade with concentration of 300 ppm) to study the extent of enhancement observed due to an increase in the intensity of cavitation as discussed in detail later.

The amount of the formic acid remaining in the solution was determined using titration with the standard alkali (NaOH). The concentration of the standard alkali (NaOH) was so adjusted that the readings of titration were in the range of $20-25 \text{ cm}^3$ with the smallest reading of the burette used being 0.1 cm³. Moreover the titration was repeated two or three times to get accurate readings and reduce errors to <0.1%.

Energy efficiency calculations

A calorimetric method is used to determine the energy efficiency of the equipment under study. Energy efficiency gives an indication of the quantity of energy effectively dissipated in the system, a fraction of which is utilized for the generation of cavities and should be as high as possible for the particular equipment. Large-scale sonochemical reactors for process intensification

The details of the concept of energy efficiency can be obtained from earlier work.³⁵

RESULTS AND DISCUSSION

The results and discussion section has been divided into three sections, viz energy efficiency of the novel reactor, results with the model reaction (Weissler reaction) and results with reaction of industrial importance (degradation of formic acid which is important more specifically for wastewater treatment applications).

Energy efficiency

Energy efficiency (electrical to mechanical energy transfer) of the hexagonal flow cell was found to be in the range of 75-78% depending on operating frequencies, but the variation can be safely taken as within the limit of the experimental errors. Thus, operating frequency does not greatly influence the transfer of energy into the medium. Comparison with earlier work³⁵ indicates that the energy efficiency of the equipment is much better than that of the conventional reactors. The ultrasonic horn, which is the most commonly used equipment for various applications, resulted in an energy transfer efficiency of less than 10% whereas the efficiency for the ultrasonic bath was observed to be 35%, and the dual frequency flow cell, another novel reactor designed by our group, results in similar energy efficiency. Thus the triple frequency hexagonal flow cell reactor seems to be extremely efficient in transferring the supplied electrical energy to energy used for generation of cavities, which can be attributed to the higher transducer surface area. It should also be noted that increasing the transducer's surface area results in lower intensity of irradiation and should also lead to more intense cavitation.¹⁹

Results with model reaction

The results obtained for the model reaction are shown in Fig 3. It can be seen that the extent of iodine liberation was found to increase with an increase in the frequency of operation using a single frequency as well



Figure 3. Results for the model reaction: effect of operating frequency. Iodine liberation is for 1% (w/v) KI solution and at the end of 15 min reaction time.

as for operation using a combination of frequencies, ie 20 + 30 + 50 kHz > 30 + 50 kHz > 20 + 50 kHz >20 + 30 kHz. The observed variation can be explained on the basis of the variation in the cavity collapse pressures and temperatures with the frequency of irradiation. In earlier work,19 we have shown that at a constant intensity and for a fixed initial radius of the nuclei, the magnitude of pressure pulse generated at the end of collapse of a single cavity increases with an increase in the frequency of irradiation. Moreover as the event of the collapse is adiabatic, increased collapse pressures naturally increase the maximum temperatures reached in the cavity. Thus in accordance with the hot-spot theory (to which some of the chemical reactions are attributed), the rate of chemical reaction increases with an increase in the magnitude of the temperature. Vichare *et al*²⁰ have also shown that the energy released at the end of cavitation event increases with an increase in the frequency of irradiation, and a cavitational efficiency (ratio of effective energy utilized for cavitation to the total energy supplied) analysis indicates an increase in the cavitational efficiency with an increase in the frequency of irradiation. Thus the cavitation phenomenon is rapid (lifetime of bubble decreases with an increase in the frequency) and more violent, releasing a higher concentration of OH[•] radicals which have a strong oxidizing potential, thereby increasing the extent of iodine release. A similar explanation also holds good for multiple frequencies.

Similar experimental results can be seen in the literature. Francony and Petrier¹⁸ have shown that degradation of carbon tetrachloride is faster at higher frequencies. Kruus *et al*³⁶ have also shown that the decomposition of chlorobenzene proceeds much faster at higher frequencies. Sivakumar *et al*³⁰ have also reported similar results for the effect of frequency of irradiation.

It is interesting to compare the amount of iodine liberated as obtained in the present case with that obtained with conventional reactors, eg ultrasonic horn. In earlier work,³⁵ experiments were done using 50 cm^3 of 1% (w/v) KI solution with an ultrasonic horn operating at 20 kHz frequency and supplied electric power at 240 W. The amount of iodine liberated was estimated to be 0.204 mg dm^{-3} . In the present case, for 20 kHz operation, the amount of iodine liberated is $0.03091 \text{ mg dm}^{-3}$ which is an order of magnitude less than the ultrasonic horn but when operation is switched to multiple frequency operation (20 + 30 + 50 kHz), iodine liberation increases to $0.205 \,\mathrm{mg} \,\mathrm{dm}^{-3}$, which is comparable to that obtained with the ultrasonic horn. Thus similar results are obtained for multiple frequencies as compared to conventional reactors, but most importantly the reaction volume is about 140 times more than the ultrasonic horn and this itself is the most important achievement of the current work. It is also important to note that the volume that is being used here is also 10-15 times more than that being treated in ultrasonic bath-type reactors (transducers at the bottom of the reactor). With the efficacy of the novel reactor being conclusively established for the model reaction, some additional experiments using an industrially relevant reaction, were thought to be desirable, ie degradation of formic acid as discussed earlier.

Results with degradation of formic acid

Effect of frequency of irradiation

Figure 4 shows the variation of the percentage degradation with time for different combinations used in the triple frequency flow cell (seven in total; 20, 30 and 50 kHz operating individually, combinations of two frequencies, viz 20 + 30 kHz, 20 + 50 kHz, 30 + 50 kHz and all frequencies operating, ie 20 + 30 + 50 kHz). It can be seen that as the frequency of irradiation increases, the rate of degradation also increases which is exactly identical to the trends obtained for the model reaction. The percentage degradation, however, was quite less, which can be attributed to the fact that degradation of formic acid is slow and requires much more intense cavitation. Thus the aim should be to increase the intensity of cavitation.

Effect of introduction of air

The presence of air provides additional nuclei for the generation of cavitation, resulting in an enhanced number of cavitation events which increase the overall pressure/temperature pulse generated in the system and hence the cavitational intensity. The presence of air also increases the percentage of the dissolved gases in the collapsing cavities, resulting in the release of a higher number of free radicals. The results are shown in Fig 4 and the extent of degradation was found to increase by about 30% at the end of 1 h but the extent of enhancement decreases at longer time periods (at the end of 90 min, the enhancement was a mere 10%). This can be attributed to a strong degassing



Figure 4. Results of degradation of formic acid (100 ppm initial concentration) and effect of aeration (1.02 cm³ s⁻¹ through sintered multipoint sparger).

effect of cavitation, which decreases the amount of gas remaining in the solution. Senthilkumar *et al*³⁴ have obtained similar results though for a different type of cavitation. To counter the effect of degassing due to ultrasonic action, some adjustment in the air flowrate can always be made as the time of irradiation increases. Another novel system in terms of separate aeration and ultrasonic irradiation in two different reactors can also be considered, with continuous re-circulation between the reactors. More work is being done in this direction. It should also be noted that the extent of enhancement in the reaction rates and contribution of degassing also depends on the operating conditions, the type of the reaction as well as the geometry of the reactor. Sivakumar *et al*³⁰ have shown that the presence of air results in an increase in the rate constant (by about 15%) for degradation of *p*-nitrophenol in a dual frequency flow cell with a capacity of 1.5 dm^3 .

Effect of addition of solids

The presence of solid particles affects the cavitation phenomena in two different and opposing ways. On one hand, where it increases the intensity of cavitation, again by providing additional nuclei for the generation of cavities as well as by surface cavitation, it also acts as a barrier for the propagation of sound waves, thereby decreasing the overall average intensity transmitted into the system. The negative contribution of scattering of sound waves might decrease at larger scales of operation and hence degradation of formic acid was studied in the presence of TiO₂ particles, with an aim of increasing the extent of degradation. The results are shown in Fig 5 and it can be indeed observed that the percentage degradation increased by about 55% at the end of 90 min of irradiation for a loading of 300 ppm of TiO₂. Shirgaonkar and Pandit³² have also reported that the presence of TiO₂ increases the extent of degradation of 2,4,6-trichlorophenol for the operation with 22 kHz frequency and power input range of $0.4-0.12 \text{ W cm}^{-3}$. Some preliminary experiments have indicated that the extent of enhancement observed in the rates of phenol degradation using the ultrasonic horn are marginal for a solid loading of 100 ppm and even less for an increased loading of 500 ppm. Thus, the effect of sound scattering is significant in the case of an ultrasonic horn and quite less in the largescale operation using the novel reactor studied in the present work.

Effect of addition of hydrogen peroxide

It is a known fact that the generation of free radicals controls the overall reaction rates, as the majority of the chemical reactions are driven by a free radical mechanism³³⁻³⁵ and the aim should also be to maximize the rate of generation of free radicals along with the intensity of cavitation. Thus, with the aim of increasing the extent of degradation further, an additional source of free radicals in the form of hydrogen peroxide was supplied. It is well known



Figure 5. Effect of addition of solid catalyst (300 ppm) on percentage degradation of formic acid (100 ppm initial concentration) in the absence and presence of catalyst.

that hydrogen peroxide in the presence of ultrasonic irradiation undergoes a dissociation reaction, forming free hydroxyl radicals, which are strong oxidizing agents. As hydrogen peroxide is itself a strong oxidizing agent, the effect of hydrogen peroxide alone on the degradation of formic acid was investigated and it was found to be quite marginal (percentage removal of just 1.65% in 90 min of treatment time for initial concentration of formic acid at 100 ppm and hydrogen peroxide [industrial grade, 30% by volume] loading at $0.5 \text{ cm}^3 \text{ dm}^{-3}$). Thus it can be said that hydrogen peroxide alone is ineffective in the treatment of formic acid.

The results for experimentation with a combination of ultrasonic irradiation (20 + 30 + 50 kHz) operating simultaneously, power input of 900 W and 300 ppm TiO₂ loading) and hydrogen peroxide (loading of $0.5 \,\mathrm{mg}\,\mathrm{cm}^{-3}$) are shown in Fig 6. The degradation for the combination is almost double that of ultrasonic irradiation alone. Thus it is now confirmed that in the presence of ultrasonic irradiation, hydrogen peroxide does dissociate, forming highly reactive hydroxyl radicals and resulting in an expected enhancement in the overall rate of degradation. Teo $et al^{37}$ have also reported that the initial rate of degradation of an aqueous solution of 0.4 mM p-chlorophenol increases substantially (by about three times for concentration of hydrogen peroxide of 15 mmol dm⁻³ as compared with that in the absence of hydrogen peroxide) but



Figure 6. Results for the degradation of formic acid using combination of ultrasonic irradiation and hydrogen peroxide.

observed that the addition of hydrogen peroxide results in enhancement of the destruction process only till optimum concentration of hydrogen peroxide $(40 \text{ mmol dm}^{-3} \text{ for initial concentration of pollutant as } 0.4 \text{ mmol dm}^{-3}).$

Synergism between addition of solid particles and hydrogen peroxide

It can be also seen from Fig 6 that the extent of degradation for the combination of ultrasound and hydrogen peroxide is marginally higher for the catalyst loading of 500 ppm as compared with 300 ppm, which can be attributed to the enhanced contribution of surface cavitation at the surface of solid particles, as discussed earlier. Thus it is confirmed that both the presence of solid particles as well as addition of hydrogen peroxide results in an increase in the extent of degradation of formic acid in a synergistic manner. It should also be noted that though the effect of solid particles will be valid for all the chemical reactions, the enhancement observed due to hydrogen peroxide alone would be obtained only for those chemical reactions which are controlled by the attack of free radicals.

CONCLUSIONS

Acoustic cavitation generates conditions of high temperature and pressure along with the release of reactive radicals, which enables many the chemical transformations to proceed under much less severe conditions as well as with significant intensification, but the application is hampered by problems associated with scale-up of sonochemical reactors. The novel reactor operating on the principle of irradiation using multiple frequency and multiple transducers gives excellent results for both the model reaction as well as the industriallyrelevant reaction considered in the present work. The reaction rates are further intensified by aeration and addition of solid particles and hydrogen peroxide in the large-scale operation. More work is also required to study the variation of the extent of enhancement over a wider range of these intensifying parameters. It should also be noted here that, as a first step, dilute solutions have been used and further experiments are currently being carried out with more concentrated solutions.

At this stage of development of sonochemistry, it seems that there are considerable technical and economic limitations, and practically no processing on an industrial scale is being carried out. Undoubtedly, the combined efforts of chemists, physicists, chemical engineers and equipment manufacturers will be required for the Chemical Process Industry (CPI) to harness acoustic cavitation as a viable option for process intensification. Finally it can also be said that the future for application of sonochemical reactors lies in development of multiple frequency/multiple transducer reactors and the present work should serve as a useful starting point for this activity.

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