Ultrasound in Chemical Processes

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Summary: The use of ultrasound to promote 'chemical' reactions or Sonochemistry is a field of chemistry which involves the process of acoustic cavitations *i.e.* the collapse of microscopic bubbles in liquid. There are two essential components for the application of sonochemistry, a liquid medium and a source of high-energy vibrations. The liquid medium is necessary because sonochemistry is driven by acoustic cavitations that can only occur in liquids. The source of the vibrational energy is the transducer. The chemical effects of ultrasound include the enhancement of reaction rates at ambient temperatures and striking advancements in stoichiometric and catalytic reactions. In some cases, ultrasonic irradiation can increase reactivities by nearly million fold. The ultrasound has large number of applications not only in emending old chemical processes but also in developing new synthetic strategies. Ultrasound enhances all chemical and physical processes *e.g.*, crystallization, vitamin synthesis, preparation of catalysts, dissolution of chemicals, organometalic reactions, electrochemical processes, etc. High-power ultrasonics is a new powerful technology that is not only safe and environmentally friendly in its application but is also efficient and economical. It can be applied to existing processes to eliminate the need for chemicals and/or heat application in a variety of industrial processes.

Introduction

To carry out chemical reactions, energy is required in various forms. As temperature approaches to absolute zero, chemistry stops. Differing from traditional energy sources such as light, heat or ionizing radiation, ultrasound is different in interacting with matter. It varies in duration, pressure and energy per molecule [1, 2] Fig. 1. No direct interaction of ultrasound takes place with molecular species. Sonochemistry originates principally from acoustic cavitation: the creation, expansion, and implosive collapse of bubbles in liquid. Concentrating the diffuse energy of sound serves as a mean of cavitation. It is the underlying phenomenon responsible for sonochemistry and sonoluminiscense. The collapsing of bubble, induced by cavitation, produces intense local heating, high pressures and very short lifetimes [3].

Sources of Ultrasound

There are two essential components for the application of sonochemistry, a liquid medium and a source of high-energy vibrations. The liquid medium is necessary because sonochemistry is driven by acoustic cavitations that can only occur in liquids. The source of the vibrational energy is the transducer, of which there are different types [4].

Liquid driven transducers are usually used for homogenization and efficient mixing. It has no moving parts, other than a pump; the system is considered rugged and durable. With no significant advances in the basic design, it has a range of applications and new uses continue to emerge.

Magnetostrictive transducers cause magnetostriction in some materials, *e.g.* nickel, which reduce in size when placed in a magnetic field and then return to normal dimensions when the field is removed. These are very powerful devices but have an operational upper frequency limit of 100 kHz with an electrical efficiency of less than 60%. One of the more stimulating advancement in magnetostrictive technology has been the introduction of Terfenol. This is an alloy of the rare earths terbium and dysprosium together with iron that is zone refined to produce a crystalline material. A transducer based on this material can generate more power than a conventional piezoelectric transducer; it is more compact and lighter than other magnetostrictives.

The most widely used are the piezoelectric transducers for the generation of ultrasound. Such transducers operate *via* the inverse piezoelectric effect *i.e.*, if a potential difference is applied across

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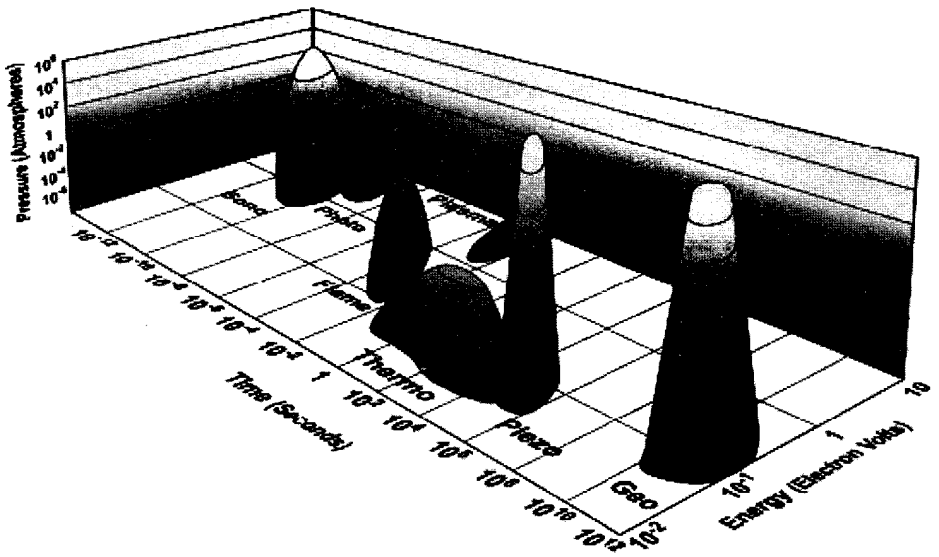


Fig. 1: The comparison of different energy sources in terms of pressure, energy per mole and duration for sonochemistry are shown [2].

such faces, the material will respond by either expanding or contracting depending on the polarity of the applied charges. The most frequently used types are composed of a ceramic containing a piezoelectric material, lead zirconate titanate. Such transducers are highly efficient (greater than 95 %) depending on dimensions. These can be used over the whole range of ultrasonic frequencies from 20 kHz to many MHz. The usual piezoelectric ceramic is PZT a lead zirconate titanate ceramic [1] Fig. 2.

For large scale processing at audible frequencies the magnetically driven vibrating bar is used. It has a large cylindrical steel bar which is the main source of vibrations. The bar is driven into a clover-leaf-type motion by firing three powerful magnets that are located at each end of the bar in sequence. The bar is supported by air springs to rotate at a resonance frequency. A liquid or slurry can then be pumped through the reaction cells attached to each end of the bar in order to perform operations such as mixing, grinding and the destruction of hazardous waste [5].

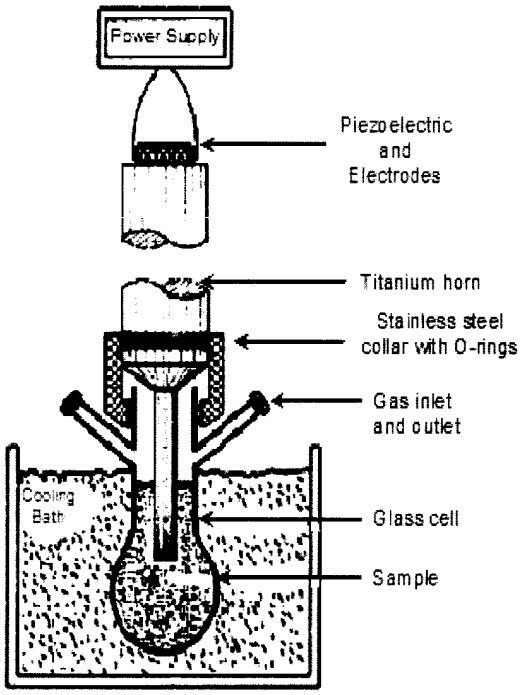


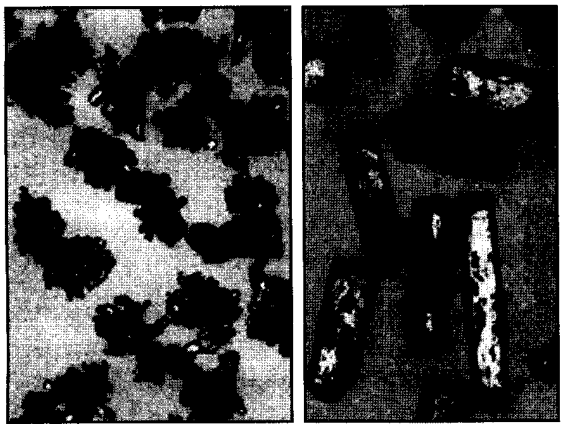
Fig. 2: The sonochemical apparatus with piezoelectric ceramic and a lead zirconate titanate ceramic [1].

Ultrasound in Application

Crystallization Processes

To initiate seeding and control subsequent crystal growth in a saturated or super cooled medium, ultrasound has proven to be extremely useful. The cavitation bubbles themselves act as nuclei for crystal

growth and due to the disruption of seeds nuclei already present within the medium increase the number of nuclei present in the medium. It is possible to produce crystals of a uniform and designated size through the correct choice of sonication conditions, which is of great importance in pharmaceutical preparations Fig. 3 [6].



(a) Normal crystallization (b) Ultrasonic crystallization

Fig. 3: The effect of ultrasound in the crystallization of sorbitol hexa-acetate [5].

Chemical Synthesis

The beneficial effects of sonochemical reactions are better yields, higher product clarity and rate accelerations [7, 8]. In some reactions, changes of stereo- and regio-selectivity have been noted and have a preferential acceleration of one mechanism where two or more possibilities exist [9-13]. Jean-Louis Luche made the first real attempt at categorising reactions in chemical synthesis [5, 10]. Briefly, on the basis of a large amount of published work, he proposed that sonochemical reactions could be classified into three types. In Type I, radical intermediates are formed in homogeneous medium. In Type II, ionic reactions are stimulated by mechanical effects in heterogeneous solutions. And in Type III, reactions occurring also in heterogeneous medium, sonication favours the radical formation. A number of systems are known which show each of these types. These have become known as 'Luche's rules' mainly on empirical basis. A number of the effects described above are potentially useful in polymer synthesis. The enhanced production of radicals could be utilized as a method of instigation in pure vinyl monomers. Several polymers, for example poly vinyl chloride (PVC) are produced in emulsion or suspension systems and the efficient mixing allowed by ultrasound could be of advantage. Heterogeneous reactions are mainly susceptible to sonication, the most noticeable example in polymer chemistry being the Ziegler-Natta catalysts by which polyolefins are produced. Beneficial concerns are presently stating that novel materials do not arise from new polymers but from chemical alterations of existing polymers so that sonochemical methods may prove to be of increasing importance. Among previous work in polymer chemistry has been on extensive study of the chain cleavage caused by sonication [14-16]. Radical initiation in vinyl monomer, emulsion or suspension polymerizations has also been studied. A small amount of work has also been published on other reactions such as ring-opening organometallic and electrochemical polymerizations [17-19].

Vitamin Synthesis

In control experiments it was shown that the dehydration of hydroxenin monoacetate (vit. A) in CCl_4 and an aliphatic alcohol does not occur in absence of ultrasound irradiation. The reaction was influenced by temperature in two different ways. The first being related to the sonochemical effect. It was reported that low temperatures causes lower vapor pressures of the solvents and more violent collapses of the cavitation bubbles. The observed results were higher sonochemical reaction rate. On the other hand an increase in the temperature will cause rise in the vapor pressure which facilitate cavitation. Thus, to produce cavitation less power is required [20]. The second effect is related to the dehydration reaction [21].

Preparation of Catalysts

In the preparation of catalysts for different reactions, *i.e.* dehydration reactions, ultrasound is used. Atom economy and the E-factor are the criteria for new synthetic methods. Atom economy is the number of atoms in the starting materials, which are present in the product [22]. The E-factor is the amount of waste in kg per kg product which can also be correlated with the toxicity of waste, which means for example the difference in toxicity between cyanides and water. This factor includes not only the atoms in products/starting materials but also the loss in solvent [23]. The applications of ultrasound and problems based on the reactor geometry in hydrogenation reactions of fatty acids, *e.g.* olive oil, were first described by G. Saracco [24]. Excellent

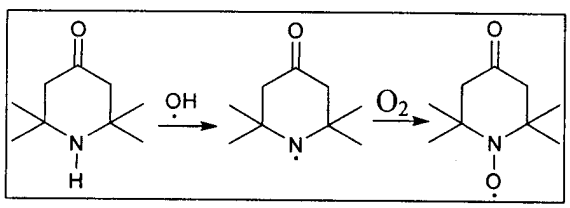
yields could be achieved at room temperatures. The reaction rate depends on the reactor geometry. For each frequency there is an optimal reaction rate. The reaction rate depends on the amount of catalyst used and the concentration of oil. An additional application of ultrasound in catalyst preparation was the enantioselective hydrogenation of β-ketoester in presence of sonicated Raney-nickel [25]. Advantages are shorter reaction time (decreased by 50–60%), and higher yields (increase by 6% up to 90% yield). The catalyst was prepared from Raney-nickel and tartaric acid under sonication [26].

Dissolution of Chemicals

Esterification process can be accelerated by ultrasonic irradiation. By micromixing and erosion produced by ultrasound, the dissolution rate of reactants is accelerated and the time taken to dissolve the reactants is greatly reduced. For example in the esterification of palmitic acid with ascorbic acid in the presence of concentrated sulfuric acid (taken as catalyst and solvent), cavitation effect produced by ultrasound increases the mass transfer and accelerates the reaction rate. The reaction time of esterification is reduced from 36 hours to 2 hours and better yield (90–93%) of ester L-ascorbyl 6-palmitate is obtained by using 95% concentrated sulfuric acid as the solvent and catalyst, contrast to the yield of 75–85% by using 99% concentrated sulfuric acid without ultrasound. The excess mole ratio of palmitic acid, the proper mount of solvent, the appropriate reaction temperature and the enough output power of sonication increases the reaction yield [27].

Organometalic Reactions

In presence of oxygen bubbling through the reaction mixture, stable nitroxides were produced as a result of hydroxyl radical abstraction of the hydrogen followed by the reaction of oxygen with nitrogen-centered radicals.



Sonication can greatly improve the rates and yields of organometallic reactions *via* enhancement of the electron transfer processes [28].

Sonoeletrochemical Processes

The use of high frequency ultrasound in electrochemical systems is of major interest for the optimization of electrosynthetic and electroanalytical procedures, especially when the strong mechanical effects of 20 kHz ultrasound are detrimental. The characterization of a 500 kHz ultrasound reactor for sonoelectrochemical experiments by Volta metric and potentiometric measurements revealed the presence of considerable thermal as well as mass transport. These effects depend upon geometric parameters and the material used for the construction of the working electrode. Micromixing and cavitation processes govern the mass transport to and from the electrode surface and are shown by atomic force microscopy (AFM) to cause erosion on the electrode surface [29].

In Fig. 4 a gold surface freshly polished (a) and after a period of 30 min sonication (b) in the high intensity region of the 500 kHz reactors are shown. The erosion process can be seen to effect slightly indicated by the loss of sharp edges of the scratch lines. However, the surface effects of the cavitation process are important as may be revealed by a film of Prussian blue deposited electrochemically onto the gold electrode surface. Prussian blue is [30] one of a large family of electro-active materials with zeolitic structure, which have been utilized in the form of films deposited on electrode surfaces for catalytic processes, *e.g.* the hydrogen peroxide [31] and hydrazine [32] detection.

For high frequency ultrasound, the mass transport model is suggested to be the best based on microjetting or micromixing. The relatively small dependence of the mass transport controlled limiting current on the diffusion coefficient suggests that at even higher ultrasound frequencies electrochemical processes could be independent of the diffusion coefficient, thereby relatively favouring processes involving very slowly diffusing species such as proteins. The implications of this kind of characteristics for analytical methodology have been noted in the literature. On the basis of the results described, it may be concluded that cavitation processes are very important in 500 kHz sonoelectrochemistry but the observed currents may not be a simple measure of cavitational activity. Thermal and degassing effects are important along with the reactor geometry and electrode materials. The effects of the unusual mass transport characteristics in the presence of 500 KHz ultrasound

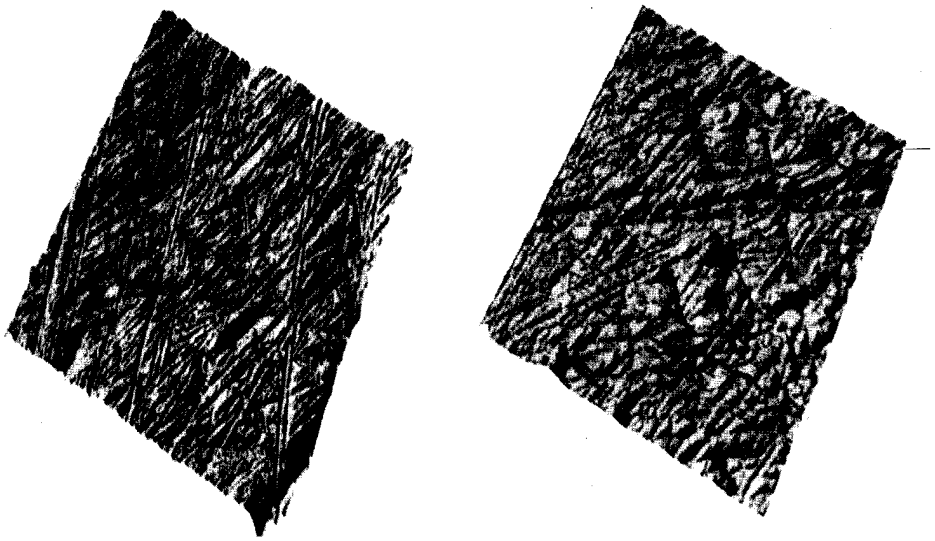


Fig. 4: AFM images of a polished gold electrode surface (a) before and (b) after 30 min treatment with 1.4 Wcm^{-2} 500 kHz ultrasound [29].

Table 1: Comparative results for different industrially important reactions in hydrodynamic[a] and acoustic[b] cavitation reactors [33].

S. No.	Reactants	Product[c]	Cavitational yield/hydrodynamic cavitation reactor (gm/J)	Cavitational yield/acoustic cavitation reactor (gm/J)
1.	Toulene	Benzoic acid	3.3×10^{-6}	5.6×10^{-7}
2.	*p*-Xylene	Terephthalic acid	2.1×10^{-6}	3×10^{-7}
3.	*o*-Xylene	Phthalic acid	1.9×10^{-6}	3×10^{-7}
4.	*m*-Xylene[d]	Isophthalic acid	1.9×10^{-6}	-
5.	Mesitylene	Trimesic acid	7×10^{-6}	1×10^{-7}
6.	*o*-Nitrotoluene	*o*-Nitrobenzoic acid	1.9×10^{-6}	1×10^{-7}
7.	*m*-Nitrotoluene	*m*-Nitrobenzoic zcid	1.3×10^{-6}	1×10^{-7}
8.	*p*-Nitrotoluene[e]	*p*-Nitrobenzoic acid	-	3×10^{-7}
9.	*o*-Chlorotoluene	*o*-Chlorobenzoic acid	1.1×10^{-6}	1×10^{-7}
10.	*p*-Chlorotoluene[f]	*p*-Chlorobenzoic acid	2×10^{-6}	-
11.	Sunflower oil	Bio-diesel(methyl ester of sunflower oil)	2.1×10^{-6}*	5.1×10^{-7}*

*In moles/J.

[a] Toluene (1 mol), (*o*-/*p*-/*m*)-xylene (0.5 mol), mesitylene (0.4 mol), (*o*-/*m*)-nitrotoluene (1 mol) and (*o*-/*p*)-chlorotoluene (1 mol), sunflower oil (1 mol) with excess of methanol, $KMnO_4$ for reactions 1–10 (2 mol), and for all above reactions, water (5 l), pressure 3 kg/cm^2, orifice plate no. 1 time = 5 h, except for oxidation of toluene where it is 3 h and trans-esterification where it is 30 min.

[b] Toluene (10 mmol), (*o*-/*p*)-xylene (5 mmol), mesitylene (4 mmol), (*o*-/*m*-/*p*)-nitrotoluene (10 mmol) and *o*-chlorotoluene (10 mmol), sunflower oil (1 mol) with excess of methanol, $KMnO_4$ for reactions 1–10 (20 mmol), and for all above reactions, water (50 ml) time = 5 h except for oxidation of toluene where it is 3 h and trans-esterification where it is 15 min.

[c] Identification of compounds was done by TLC and melting point.

[d] Not used in the acoustic cavitation.

[e] This compound is not used in hydrodynamic cavitation.

[f] Not used in the acoustic cavitation.

on heterogeneous and homogeneous chemical processes may be significant and have yet to be explored [29].

Table-1 shows the values of cavitational yields obtained for all the reactions in hydrodynamic and acoustic cavitation reactions (the specific operating conditions are in the footnote for the table). It can be clearly seen from the table that the cavitational yield values in the hydrodynamic cavitation reactors are of higher magnitude for all the reactions considered in the work and also the processing volume is about 100 times more as compared to the conventional sonochemical reactor. The results have conclusively proved the better efficacy of the hydrodynamic cavitation reactors as compared to the ultrasonic bath reactor considered in the work [33].

Conclusion

There is a need to employ such technologies, which are safe, cost-effective, environmentally benign and energy efficient. The use of ultrasound in

chemical processing leads towards the development of cleaner, cost-effective and energy efficient processes. The advantages of ultrasound in chemical reactions, shorter reaction time and higher yields, could be used in industrial application in pharmaceutical or fine chemical industry. Sonochemistry can be used for fast reactions or in the synthesis of expensive products. This innovative new technology, of low frequency, high-power ultrasound can be applied to a large number of industry processing applications including food safety related areas. The use of high-power ultrasonics in industry is rapidly expanding. There is a wide range of possible applications for high power ultrasound in all industries. Development of process technology (reactor design, process simulation) is necessary. Important is the establishment of a commercialised process. And as a 'clean' technology, the use of ultrasound is expected to rapidly increase in importance throughout the world. Until recently, the advancement in this field was known as sonochemistry and had been carried out only at laboratory level with little work being scaled up for use on a commercial basis. Over the last 10 years, many advances have been made in turning this laboratory-based technology into fully operational commercial processes.

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