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Sonochemistry: current uses and future prospects in the chemical and processing industries

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Over the last few years, a large number of chemists and engineers working in synthesis and processing have developed an interest in sonochemistry: the applications of power ultrasound in chemistry. Scientific papers reporting the remarkable results obtained using sonochemistry are plentiful and yet the subject still does not seem to be accepted generally within the chemical community. There are two factors that contribute to this. One is a general resistance to the idea that sound energy can be used as a driving force for chemical transformations. The second relates to what appears to be a lack of equipment for scale-up. Many commercially important projects that involve sonochemistry are not within the strict confines of chemistry itself and can be found in processing technologies. In this article several current applications of power ultrasound in both chemistry and processing will be explored with a view to assessing the future for sonochemistry itself.

Keywords: chemical technology; decontamination of water; electrochemistry; large-scale equipment; materials processing; power ultrasound generation

1. Introduction

The first commercial application of ultrasound dates back to 1917 with the echosounding technique developed by Langevin for the estimation of the depth of water. From this has developed a whole range of sophisticated techniques for non-destructive testing and medical imaging, all essentially based on the pulse–echo technique. Such diagnostic uses of ultrasound have low powers and very high frequencies (in the MHz range) and do not affect the physical or chemical character of the medium that is probed. If, on the other hand, a lower frequency (generally in the 20–40 kHz range) and a higher power is applied to a fluid, then it is possible to produce significant physical and chemical changes in the medium through the generation and subsequent collapse of cavitation bubbles. It is acoustic cavitation produced by power ultrasound that is the basis of sonochemistry and a number of processing techniques.

The history of this use of power ultrasound is shorter than that for diagnostic ultrasound and can be traced to the years preceding World War II when power ultrasound was being developed for a range of processing, including emulsification and surface cleaning. By the 1960s, the industrial uses of power ultrasound were well accepted (Brown & Goodman 1965; Frederick 1965) and have since continued (Abramov 1998).

Paralleling these developments in processing were a growing number of chemists interested in the chemical effects of power ultrasound, which became known as sono-

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chemistry. It was not until 1986, however, that the first ever international symposium on a subject identified as sonochemistry was held at Warwick University in the UK as part of the Autumn Meeting of the Royal Society of Chemistry. This meeting signified the beginning of serious interest in the uses of cavitation in chemistry as a study in itself (Mason 1987). Since then, the subject has developed to generate an ever-expanding number of applications (Suslick 1988; Mason 1990; Povey & Mason 1998) and a growing interest in the underlying driving force: acoustic cavitation (Leighton 1994). There is an argument that the term sonochemistry should refer only to those reactions that are chemically influenced by cavitation, but it is often difficult to separate the chemical from the physical consequences of cavitation and so both aspects will be considered in this contribution.

While it is clear that sonochemistry is an expanding subject that is attracting interest from a range of scientific disciplines, there does appear to be a degree of constraint to its total acceptance, and hence advancement, within the chemical community. The constraint arises for the following reasons.

- 1. For the 'traditional' chemist, the use of sound as an energy source is a very strange idea. It is well outside of the scope of the normal training of a chemist.
- 2. Some of the benefits of sonochemistry are to be found in chemical processing, e.g. mixing, crystallization, heat and mass transfer. Unfortunately, the cross-fertilization of ideas between engineering and 'pure' science is somewhat lacking.
- 3. Among chemists there is a lack of knowledge of the equipment available for producing acoustic cavitation in liquids other than laboratory cleaning baths and probe systems. Alternative equipment does exist and its use provides the key to scale-up and the ultimate adoption of sonochemistry in industry.
- 4. Finally, it must also be recognized that a large number of chemists will have very little knowledge (or interest) in the mathematics and physics of cavitation. Within these disciplines lies the key to a better understanding of the ways in which acoustic cavitation could be optimized for use in chemical situations.

The constraints listed above mainly apply to the exploitation of power ultrasound by chemists. In today's industry, particularly in processing, there are fewer problems over the use of power ultrasound, indeed it is here that some of the major developments are happening. The adoption of ultrasound by chemists in industry will be an important step in the final acceptance of sonochemistry and this is why the important link between it and the uses of power ultrasound in processing should be considered. The link is close enough that some of the exciting laboratory results in sonochemistry could well use the techniques and equipment of the process engineer to progress the subject to a larger scale. This article will therefore give a chemist's overview of the possible uses of cavitation in both the processing and chemical industries.

2. Methods for the generation of power ultrasound

Whatever application of sonochemistry is to be studied or developed, there are two essential components, a liquid medium and a source of high-energy vibrations. The liquid medium is necessary because sonochemistry is driven by acoustic cavitation

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that can only occur in liquids. The source of the vibrational energy is the transducer, of which there are three main types: the liquid whistle and two electromechanical devices based on the magnetostrictive and the piezoelectric effects (Mason & Luche 1996). All three types have been in use for many years but there have been some recent developments in electromechanical transducers that have improved their performance. A fourth type of transducer, the magnetically driven vibrating bar, has been introduced, which generates very-high-power vibrations but in the audible range. This has some potential for heavy-duty processing and so has been included in the brief overview below.

(a) Liquid-driven transducers

Liquid whistles are particularly useful in applications where homogenization and efficient mixing are important. Process material is forced, under pressure generated by a powerful pump, through an orifice from which it emerges as a jet, into a mixing chamber. The jet impacts upon a thin steel blade that is caused to vibrate and, thereby, produce mixing of the process material flowing over it. Additional mixing is produced through the Venturi effect as the liquid rapidly expands into a larger volume on exiting the orifice. With no moving parts, other than a pump, the system is rugged and durable. There have been no significant advances in the basic design of this type of device in recent years although the range of applications is broad and new uses continue to emerge.

(b) Magnetostrictive transducers

These devices use an effect found in some materials, e.g. nickel, which reduce in size when placed in a magnetic field (magnetostriction) 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%. However, now that a range of industrial applications for sonochemistry is under consideration, particularly those requiring heavy-duty continuous usage, the magnetostrictive transducer is coming back into consideration.

Improvements in the operating efficiency of this type of transducer have been based on finding a more efficient magnetostrictive core. The original nickel-based alloys have been replaced by more electrically efficient cobalt-iron alloys and, more recently with aluminium-iron containing a small amount of chromium. One of the more exciting developments 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. It does have the same problem as other magnetostrictives in that it has an upper limit of frequency response: in this case 70 kHz.

(c) Piezoelectric transducers

These are the most widely used devices for the generation of ultrasound. Such transducers operate via the inverse piezoelectric effect, i.e. if a potential difference

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is applied across 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 (commonly referred to as 'pzt', where the 'p' represents plumbum). The most common form is a disk with a central hole. In a power transducer, two of these piezoelectric disks are clamped between metal blocks, a 'sandwich', to provide a durable unit with doubled mechanical effect. Such transducers are highly efficient (greater than 95%) and, depending on dimensions, can be used over the whole range of ultrasonic frequencies from 20 kHz to many MHz.

Current developments using such transducers exploit their versatility in terms of size and frequency range. Piezoelectric systems drive large and powerful ultrasonic welders and cleaning baths but are also finding use in a new field of medicine called therapeutic ultrasound (Crum & Hynynen 1996). One medical application is for the destruction of blood clots, where a miniaturized ultrasonic device (1 MHz) is attached to the end of a catheter so that it can be inserted into the blood vessel. The device is brought close to the clot, at which point a fibrolytic enzyme is released. When the transducer is activated, the acoustic energy accelerates the enzymatic dissolution of the clot.

(d) The magnetically driven vibrating bar

This provides a significantly different system for large scale processing at audible frequencies. The source of vibrations for this is a large cylindrical steel bar. 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 so that the ends and the centre are then caused to rotate at a resonance frequency depending on the size of the bar (figure 1). One such unit, developed by Arc Sonics in Canada, operates at a power of 75 kW, drives a bar that is 4.1 m long and 34 cm in diameter at its resonance frequency of 100 Hz. The bar itself weighs 3 t and produces a vibrational amplitude of 6 mm at each end, considerably larger than the amplitudes available through sonochemical processing and, hence, better for the dispersal of materials in liquids. Material in the form of 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.

3. A general overview of some current industrial uses of power ultrasound

It has been recognized for many years that power ultrasound has great potential for use in a wide variety of processes in the chemical and allied industries. Some of these have been known for many years and continue to flourish as major commercial applications, e.g. plastic welding and cleaning. Others, like ultrasonic drilling, while showing great potential, have not been widely exploited to date. The potential for the industrial use of power ultrasound is enormous and yet industry seems somewhat reluctant to adopt it. A selection of current uses of power ultrasound is presented in table 1. The first two of these are not driven by acoustic cavitation but the remaining fields generally use cavitation to some extent.

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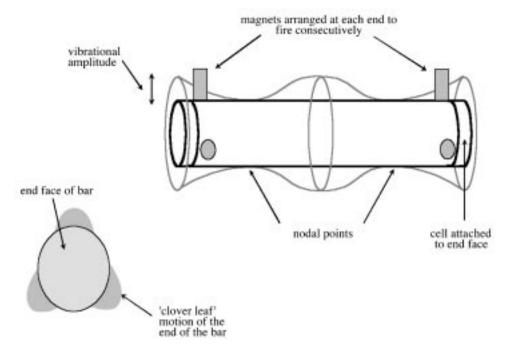


Figure 1. Mode of operation of a vibrating-bar transducer.

field	application
welding	fabrication of thermoplastic articles and welding of metals via specific heating at the junction between the pieces of material
cutting	accurate cutting of all forms of material from brittle ceramics to food products
atomization	water sprays for dust suppression and humidifiers, low velocity spray coating, spray drying nozzles
cleaning and decontamination	cleaning of engineering items, small electronic items and jewellery using aqueous based solvents; cleaning and disinfection of medical instruments and food processing equipment
processing	dispersion of pigments and powders in liquid media and emulsification; extraction, impregnation, crystallization and filtration

(a) Cleaning and decontamination

Ultrasonic cleaning is now such a well-established general technology that laboratories without access to an ultrasonic cleaning bath are in a minority. Although the





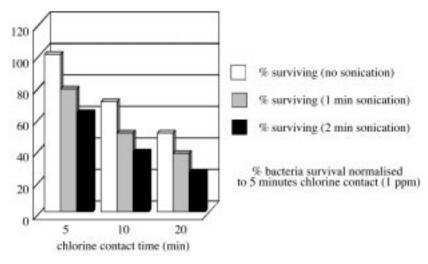


Figure 2. The effect of short bursts of ultrasound (20 kHz) and chlorine on the decontamination of river water.

laboratory ultrasonic cleaning bath is familiar, the industrial applications of such cleaning are perhaps less well known. Ultrasonic cleaning can be either delicately applied for the cleaning of microcomponents under clean-room conditions or used for very large items such as engine blocks in factories. It is particularly effective in the removal of biological contamination because the cleaning action is through jets induced by cavitational collapse on and near surfaces. These jets are easily capable of dislodging bacteria that may be adhering to the surfaces. The particular advantage of ultrasonic cleaning in this context is that it can reach crevices that are not easily reached by conventional cleaning methods. For this reason, such cleaning is used for a range of items from large crates used for food packaging and transportation, to delicate surgical implements such as endoscopes.

Power ultrasound is currently under investigation for use in the biological decontamination of water (Phull *et al.* 1997). Conventional methods of disinfection involve the use of a bactericide, which, for the large-scale water industry, may be chlorine, chlorine dioxide or ozone. Current trends are towards the reduction in quantity of the biocide used in sterilization, however, some bacteria are capable of building up resistant strains that may require more concentrated biocide. Power ultrasound affords the opportunity of increasing the efficiency of a biocide such as chlorine (figure 2). The improvement in the biocidal effect of chlorine is thought to be the result of two major effects. Firstly, a mechanical break-down of bacterial clumps or the material in which the bacteria adhere. This will remove the protection afforded to live bacteria in the centre of the clumps and directly expose them to the biocide. Secondly, ultrasound can increase the permeability of the cell walls of the bacteria to the biocide and thus increase its rate of uptake.

When sufficient acoustic power is applied, it is, of course, possible to kill the bacteria through the direct disruption of cell membranes but this would be too expensive in terms of energy for industrial-scale usage.

A further possibility for environmental use of sonochemistry is in the treatment of sewage sludge. Anaerobic fermentation is the most commonly applied process for

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frequency (kHz) 20200500800 H_2O_2 formation 0.72.11.45.0phenol degradation 0.54.91.91.0CCl₄ degradation 33 37 5019

Table 2. Comparison between H_2O_2 production and the rates of phenol and carbon tetrachloride disappearance at different frequencies ($\mu M \min^{-1}$)

stabilization of sewage sludge and provides mass reduction, methane production, and improved dewatering properties. A disadvantage of the fermentation technique is that it is slow, with conventional residence times in anaerobic digesters of about 20 days. Ultrasound has been used to accelerate the anaerobic digestion of sewage sludge (Tiehm *et al.* 1997). Ultrasonic treatment at a frequency of 31 kHz and high acoustic intensities at half technical scale shortened the residence time to eight days with a biogas production 2.2 times that of a control fermenter. Once optimized, it is likely that this type of process will also be adopted on an industrial scale.

Ultrasonic irradiation has also been employed for chemical remediation of water. The mode of sonochemical degradation of organic compounds in aqueous solution depends upon their physical and chemical properties. This is because there are two ways in which the cavitation bubble can function. In the case of volatile chemicals that enter the bubble, destruction occurs through the extreme conditions generated on collapse. In the case of chemicals remaining in the aqueous phase the bubble acts as a source of radicals (H[•], HO[•] and HOO[•]), which enter the bulk solution and react with pollutants. This is neatly illustrated in a comparative study of the decomposition of phenol (to carboxylic acids) and carbon tetrachloride (to CO_2 and Cl^{-}) in water saturated with oxygen at different frequencies (see table 2; Petrier & Francony (1997)). The results clearly show a difference in the behaviour of the chemical contaminants (original concentration 10^{-3} M) with the phenol degradation mirroring the peroxide formation, indicating this reaction proceeding at the bubble interface or outside of the bubble. The volatile CCl_4 , however, is decomposed within the bubble, and increasing frequency slightly accelerates the process. An intriguing calculation for these reactions shows that the efficiency for each of these processes over one ultrasonic cycle decreases as frequency increases.

The occurrence of an optimum frequency at 200 kHz was explained through a twostep reaction pathway. In the first step, water sonolysis produces radicals within the bubble. In step two, the radicals must migrate to the bubble interface or into the bulk aqueous medium to form peroxide or react with the phenolic substrate. The authors suggest that the lower frequencies are the most efficient for the decomposition of molecules inside the bubble but a proportion of the radicals recombine inside the bubble at high temperature to form water, thereby reducing the overall yield of H_2O_2 (equations (3.1) and (3.2))

$$2\mathrm{HO}^{\bullet} \longrightarrow \mathrm{H}_2\mathrm{O} + \tfrac{1}{2}\mathrm{O}_2, \tag{3.1}$$

$$\mathrm{HO}^{\bullet} + \mathrm{HOO}^{\bullet} \longrightarrow \mathrm{H}_{2}\mathrm{O} + \mathrm{O}_{2}. \tag{3.2}$$

As the frequency increases, the pulsation and collapse of the bubble occurs more rapidly and more radicals escape from the bubble. However, as the frequency in-

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creases, the cavitation intensity decreases and this reduces the yield of radicals and consequently the number that reach the interface and bulk solution.

Studies involving sonochemical decontamination of water, and the mechanisms through which it can operate, continue to be an important subject for laboratory research. However, the sonochemical degradation of organic compounds requires long treatment times and/or high powers. For this reason, it seems unlikely that treatment with power ultrasound alone will prove to be economically viable for the chemical decontamination of water supplies.

(b) Processing

(i) Mixing and emulsification

There are a large number of industrial processes that employ cavitation as an energy source for the generation of fine emulsions and dispersions. One of the earliest devices that was developed for this purpose was the so-called liquid whistle and this continues to be used widely. Typical examples of the uses of such whistles include the preparation of emulsion bases for soups, sauces or gravies that consist of a premix of water, milk powder, edible oil and fat together with flour or starch as thickening agent. After passing through the homogenizer, a fine particle-size emulsion is generated with a smooth texture. Another example is the production of ketchup as a smooth product with increased thickness and improved taste compared with conventional mixers as a result of the complete dispersion of any clumps of tomato pulp. In the textile industry, poor quality dying of fabrics usually can be attributed to the mechanical mixing used. Agglomerates of non-dispersed dye can produce a speckled appearance and uneven mixing may change the shade. By passing the mixture through an ultrasonic homogenizer before use these problems can be overcome.

(ii) Extraction and impregnation

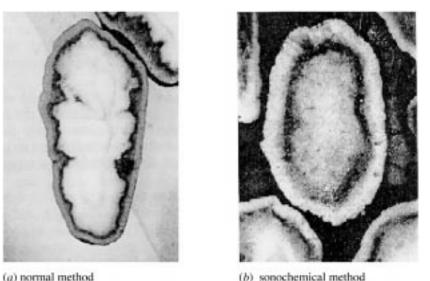
When cavitation bubble collapse occurs near a porous material, the jet that is generated is able to force liquid to penetrate the surface. This effect can be used to enhance any process that involves either extraction or impregnation of a liquid in a solid.

The classical techniques for the solvent extraction of chemical compounds from vegetable material are based upon the correct choice of solvent and conditions, e.g. heating or agitation. A range of commercially important pharmaceuticals, flavours and colourants are now derived from vegetable sources. It has been shown that the solvent extraction of organic compounds contained within the body of plants and seeds is significantly improved by the use of power ultrasound (Vinatoru *et al.* 1997).

The benefits of sonochemically forced impregnation of porous materials can be found in a wide variety of technologies. One of these is in the preparation of catalysts of the type often termed 'egg shell' where a catalytically active material is supported on the outside of an inert support material. Thus a catalyst comprising 1% (w/w) ruthenium on the surface of 4 mm grain size alumina can be made by adsorbing RuCl₃ from aqueous solution onto the alumina, followed by reducing the Ru³⁺ to Ru metal using hydrazine. The resulting catalyst prepared under sonochemical conditions is very different from that prepared conventionally in that there is a greater penetration of the metal into the support with no metal close to the surface (figure 3). Similar

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Figure 3. Preparation of sonochemically impregnated catalysts.

results have been obtained by the same group using catalytic palladium supported on carbon (Bianchi *et al.* 1997).

The same process of sonochemically forced impregnation can be used to enhance the dying of leather. A normal vat-dying process involves steeping the leather in an aqueous solution of the dye. For sheepskin dyed with Airedale Black at 60 °C for 40 min, note the small dye penetration through the top smooth surface under silent conditions (figure 4). In the presence of 20 kHz ultrasound (approximately 5 W cm^{-2}), the dye impregnation is substantially increased (Xie *et al.* 1997). Ultrasonically enhanced dying offers the commercially attractive possibilities of attaining a more rapid turnover and savings on the quantities of dye used. Since most of the processes in leather technology involve liquid treatments and surface penetration there are a number of tanning processes which may be helped by sonication.

(iii) *Filtration*

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The requirement to remove suspensions of solids from liquids is common to many industries. This separation can be either for the production of solids-free liquid or to isolate the solid from its mother liquors. Conventionally, membranes of various sorts have been employed for these processes, ranging from the simple filter pad through semi-permeable osmotic-type membranes to those that are used on a sizeexclusion principle for the purification of polymeric materials. Unfortunately the conventional methodologies often lead to 'clogged' filters and, as a consequence, there will always be the need to either replace filters or stop the operation and clean them on a regular basis. The application of ultrasound enables the filtration system to operate more efficiently and for much longer periods without maintenance, through two specific effects. Sonication will cause an agglomeration of the fine particles and will supply sufficient vibrational energy to the system to keep the particles partly suspended and therefore leave more free 'channels' for solvent elution. Studies of

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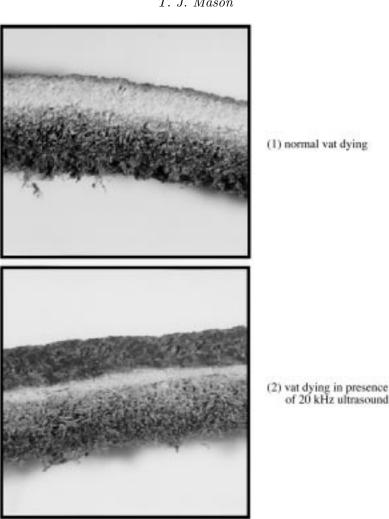


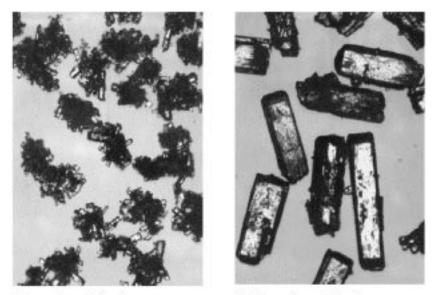
Figure 4. Sonically enhanced dying of leather.

acoustic filtration and separation processes continue to be an important area of applied acoustics research (Tarleton & Wakeman 1998).

(c) Chemical synthesis and technology

(i) Crystallization and precipitation

In conventional crystallization techniques (e.g. in penicillin production), a solution containing materials to be crystallized is super-saturated either by cooling or by evaporation and is then seeded. The problem with seeding is that it may be initiated non-uniformly and this can result in crystal growth proceeding at different rates at different nuclei sites. The resulting crystals may then show a very broad and uneven crystal-size distribution. It is also of considerable practical importance to be able to control the onset of crystallization in a large-scale production process. Often it



(a) normal crystallization

(b) ultrasonic crystallization

Figure 5. The effect of ultrasound in the crystallization of sorbitol hexa-acetate.

occurs in an uncontrolled manner simply due to a slight change in external factors such as a temperature or pressure fluctuation.

Ultrasound has proved to be extremely useful in crystallization processes since it can initiate seeding and control subsequent crystal growth in a saturated or supercooled medium. This is thought to be due to cavitation bubbles themselves acting as nuclei for crystal growth and to the disruption of seeds/nuclei already present within the medium thus increasing the number of nuclei present in the medium. Through the correct choice of sonication conditions it is possible to produce crystals of a uniform and designated size, which is of great importance in pharmaceutical preparations (Price 1997).

Power ultrasound also has an additional property that is particularly beneficial in crystallization operations, namely that the cleaning action of the cavitation effectively stops the encrustation of crystals on cooling elements in the crystallization vat and thereby ensures continuous efficient heat transfer.

(ii) Chemical synthesis

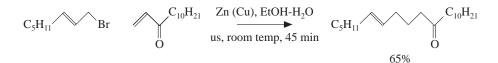
When laboratory research in sonochemistry began, it seemed to be mainly a method of initiating intransigent reactions, especially those that depended upon the activation of metallic or solid reagents. Now a vast range of reactions capable of sonochemical improvement has been identified. Within these are many that are improved to an extent that make them more environmentally friendly through features such as:

(a) improved yields, contributing to a reduction in waste emission;

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(1) the use of less toxic reagents and solvents: aqueous solvent in organometallic synthesis



(2) developing new and selective reagents: attaching functional groups to fluorocarbons

$$CF_3 - (CF_2)_5 - I$$
 $H \xrightarrow{O} 1. Al-SnCl_2$, us, room temp, 15 min
 $NMe_2 \xrightarrow{2. H_3O^+} CF_3 - (CF_2)_5 \xrightarrow{O} H$

Figure 6. Examples of benign synthesis through sonochemistry.

- (b) the generation of reactive intermediates and novel molecules under new conditions with improved selectivity that are sometimes impossible to obtain using more traditional methods;
- (c) the use of less toxic chemicals or solvents; and
- (d) the use of less forcing conditions, i.e. lower temperatures and pressures.

This makes sonochemistry an excellent possibility as a synthetic technology for the future (Mason & Luche 1996). Many new syntheses have been developed that incorporate ultrasound in key steps to afford new methodologies (Mason 1997). There are a variety of patented applications of sonochemistry that reflect the interest of industry (Mason & Cordemans 1996).

Examples of syntheses that illustrate the importance of sonochemistry are given (see figure 6; Mason & Luche (1996)). The use of aqueous solvents for some organometallic syntheses is remarkable in that it presents the possibilities of avoiding the expense and tedious procedures involved in drying and using high-purity solvents. The second provides an example of new and selective routes made available through sonochemistry.

4. Future prospects

Predictions of future trends in sonochemistry must be made in the light of the caveats listed at the beginning of this article. Changes are, however, occurring, albeit slowly, and advances in ultrasonic processing are certainly helping to advance sonochemistry itself. There are a variety of fields that will see great advances in sonochemistry in the future but many of these will be on a small scale in academic laboratories of chemistry or physics departments. It is in larger-scale projects that sonochemistry will make its major impact because this will arouse the interest of industry and establish the topic in mainstream chemistry.

The topics likely to be among those for exploitation will certainly include sonochemical processing but there will be a stronger theoretical back-up to the work. In the past, using power ultrasound in a process was accepted if it proved to be simply a better method than the existing technology. This is a good rationale but often the sonochemical process was not optimized. One would expect to see a much greater input from chemical engineering and computer modelling in the design of the next generation of sonochemical reactors (Migeot 1998). With these new reactors will come the scale-up of sonochemistry itself and the drive for this will almost certainly be a move towards benign synthesis (see § 3 c (ii)). There are, however, two major areas of research that are already under close industrial scrutiny and will certainly expand in the immediate future. They involve applications of sonochemistry in electrochemistry and environmental protection.

Electrochemistry normally involves a heterogeneous system consisting of a solid electrode and a liquid electrolyte. During sonication, the collapse of a cavitation bubble at or near to the electrode surface generates a liquid jet, targeted at the surface. It is primarily as a result of this jet that almost any electrochemical process can be improved by the application of power ultrasound (Mason *et al.* 1990). Electrochemical reactions are often complex but can be thought of as essentially the transfer of ions to and/or from the electrode surface. When an electrode is immersed in an aqueous solution, a thin diffusion layer forms at the interface and, since electrochemistry must involve ions crossing this layer, any disturbance of it will influence that process. The jet effect produced by cavitational collapse will reduce the thickness of this diffusion layer and assist diffusion to and from the electrode surface that is often the rate-controlling step. A number of beneficial sonoelectrochemical effects follow from this, including: enhanced mass transport; altered adsorption phenomena and surface effects; diminishing of electrode fouling; manipulation of reaction mechanisms; production of altered product distributions; increased yields and current efficiencies; improved synthetic routes, increased limiting current in analytical applications, and lessened cell power requirements. Sonoelectrochemical methodology can, therefore, offer considerable benefit for a range of different applications including electroplating, synthesis, analysis, environmental science, biotechnology, catalysis, sensor science and polymer synthesis (Walton & Phull 1996; Compton et al. 1997).

Environmental sonochemistry is a major growth area. However, the amount of energy required to remove chemical contaminants from water is large so it is not likely that sonochemistry will find an immediate industrial use in that particular field. Research into the sonolysis of aqueous solutions of chemicals will, however, continue to be in the mainstream of academic research since it is a valuable probe for the chemical effects of cavitation. A few groups have investigated the uses of ultrasound for microbiological decontamination (see $\S 3 a$). Although bacteria are difficult to kill with ultrasound in the absence of a bactericide, larger biological contaminants such as plankton and algae can be destroyed using low-power ultrasound without the need for additional chemicals. This does provide a real possibility for future development with several technologies approaching realization.

Zooplankton often accidentally pass through the purification cycle of a watertreatment plant, leading to re-germination and a clogging of filters located in the water distribution system. In order to inactivate plankton, a sound intensity of approximately 1 W cm^{-2} and a high air content in the water is especially effec-

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tive (Mues 1998). The economic viability of a system for plankton treatment has been tested using a flow through system with a capacity of $300 \text{ m}^3 \text{ h}^{-1}$. The actual volume of treatment in the system was 2 m^3 with an active acoustic area of 2 m^2 . Under these conditions a power of 0.05 kWh m^{-3} proved sufficient to inactivate a number of different types of plankton.

Algae may also be killed relatively easily on exposure to ultrasound. A reactor was constructed to treat water at a rate of $2 \text{ m}^3 \text{ h}^{-1}$ using an acoustic power of 450 W. At a temperature of 25 °C a deep-green, highly concentrated solution of the algae containing some 4×10^6 algal cells per cubic centimetre was passed through the reactor, which reduced the recovery threshold of the microorganism by some 60%. This indicates that the treatment, operating at algae concentrations that are far higher than might be encountered normally, offers the potential not only to kill the microorganism but also to severely restrict its reproductive ability. This ultrasonic anti-algae methodology has been combined with an electromagnetic antiscaling treatment to provide water remediation for large systems such as cooling towers (Cordemans & Hannecart 1998). The process tackles two major problems of cooling circuits, namely the build-up of scale and of algae. These are solved with a minimal energy requirement, without the need to use soft water and without the addition of chemicals.

(iii) Conclusions

Sonochemistry is an expanding field of study that continues to thrive on outstanding laboratory results that have even more significance with the availability of the types of scale-up systems used in processing. Compared with the past, there is now far greater contact and cooperation between the scientific disciplines interested in the effects of cavitation. The future of sonochemistry is therefore rosy, both from the point of view of a greater interest in the fundamental principles of its action and in the development of international programmes in applied research and technology.

References

- Abramov, O. V. 1998 High-intensity ultrasound: theory and industrial applications. London: Gordon & Breach.
- Bianchi, C. L., Gotti, E., Toscano, L. & Ragaini, V. 1997 Ultrasonics Sonochemistry 4, 317.
- Brown, B. & Goodman, J. E. 1965 High intensity ultrasonics. London: Iliffe.
- Compton, R. G., Eklund, J. C. & Marken, F. 1997 Electroanalysis 9, 509.
- Cordemans, E. & Hannecart, B. 1998 World Patent no. WO 98/01394.
- Crum, L. & Hynynen, K. 1996 Sound therapy. In Physics World, 28 (August), 28–33.
- Frederick, J. R. 1965 Ultrasonic engineering. London: Wiley.
- Leighton, T. G. 1994 The acoustic bubble. London: Academic.
- Mason, T. J. (ed.) 1987 Ultrasonics 25. (Special issue, January.)
- Mason, T. J. (ed.) 1990 Sonochemistry: the uses of ultrasound in chemistry. London: Royal Society of Chemistry.
- Mason, T. J. 1997 Chem. Soc. Rev. 26, 443.
- Mason, T. J. & Cordemans, E. D. 1996 Ultrasonic intensification of chemical processing and related operations. *Trans. Inst. Chem. Engng* 74, 511.

Mason, T. J. & Luche, J.-L. 1996 Ultrasound as a new tool for synthetic chemists. In *Chemistry* under extreme or non-classical conditions (ed. R. van Eldik & C. D. Hubbard), pp. 317–381. New York: Wiley.

Mason, T. J., Lorimer, J. P. & Walton, D. J. 1990 Ultrasonics 28, 333.

- Migeot, J.-L. Y. 1998 Proc. of the 16th Int. Congr. on Acoustics with the 135th Meeting of the Acoustical Society of America (ed. P. K. Kuhl & L. A. Crum), vol. 3, pp. 1539–1540. Acoustical Society of America.
- Mues, A. 1998 Allied Signal ELAC Nautic. In Proc. of 6th Meeting of European Society of Sonochemistry, vol. 53. Available from Professor R. Miethchen, Department of Chemistry, University of Rostock, Germany.
- Petrier, C. & Francony, A. 1997 Ultrasonics Sonochemistry 4, 295.
- Phull, S. S., Newman, A. P., Lorimer, J. P., Pollet, B. & Mason, T. J. 1997 Ultrasonics Sonochemistry 4, 157.
- Povey, M. & Mason, T. J. (eds) 1998 Ultrasound in food processing. London: Blackie.
- Price, C. 1997 Pharmaceutical Technology Europe (October issue), pp. 78-86.
- Suslick, K. S. (ed.) 1988 Ultrasound, its chemical, physical and biological effects. Weinheim: VCH.
- Tarleton, E. S. & Wakeman, R. J. 1998 Ultrasonically assisted separation processes in ultrasound in food processing (ed. M. J. W. Povey & T. J. Mason), pp. 193–218. London: Blackie.
- Tiehm, A., Nickel, K. & Neis, U. 1997 Wat. Sci. Tech. 36, 121.
- Vinatoru, M., Toma, M., Radu, O., Filip, P. I., Lazurca, D. & Mason, T. J. 1997 Ultrasonics Sonochemistry 4, 135.
- Walton, D. J. & Phull, S. S. 1996 Sonoelectrochemistry. In Advances in sonochemistry (ed. T. J. Mason), vol. 4, pp. 205–284. London: JAI.
- Xie, J.-P., Ding, J.-F., Mason, T. J. & Attenburrow, G. E. 1997 Proc. of the XXIV IULTCS Congr. London, p. 584. International Union of Leather Technologists and Chemists Societies.

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