Proceedings of 20th International Congress on Acoustics, ICA 2010

23-27 August 2010, Sydney, Australia

Sonochemistry - a Proven Tool for Process Intensification

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PACS: 43.35.VZ, 43.35.EI

ABSTRACT

The global move towards developing environmentally friendlier preparations of chemical compounds and organic or inorganic materials should be accompanied by a saving of resources through the optimization of reaction conditions and/or the introduction of new processing technologies. Over the years sonochemistry has been shown to be a green technology that can provide provide both a minimisation of energy use and efficient reaction control for industry.. Examples will be chosen from a number of fields which illustrate the wide ranging applicability of this technology in the chemical and processing industries and some practical applications which use high-power ultrasound will be reviewed.

INTRODUCTION

It is interesting to trace the development of ultrasonic process optimisation in that it is driven from both industry and academia with the former looking for commercial advantage and the latter for innovative research [1-4]. Over the last few years a large number of chemists and engineers working in synthesis and materials processing have developed an interest in the many and varied applications of power ultrasound in industry. In the chemical industry these have been grouped together under the umbrella title of sonochemistry [1,2]. Unlike other "new" technologies, which require some special attribute of the system being activated in order to produce an effect *e.g.* the use of microwaves (dipolar species), electrochemistry (conducting medium) and photochemistry (the presence of a chromophore), ultrasound requires only the presence of a liquid to transmit its energy.

To a chemist, process intensification can be expressed as: faster reactions, better conversions, improved or new products and fewer by-products. Such improvements should, of course, be accompanied by a simplification of the production line and lower production costs.There are numerous examples of the ways in which the use of power ultrasound can achieve some if not all of these targets but the use of sound energy requires somewhat different considerations from those used in more traditional systems. Some of the factors which must be taken into account when designing an ultrasonic process include:

- the optimisation of the acoustic energy required
- the influence of reactor shape on the acoustic field generated
- whether the process must be batch, on line or in a loop circuit
- and factors such as the physical parameters of the reagents and liquid system used.

Ultrasound is most simply defined as sound with a frequency that is too high for the human ear to detect and this is generally considered to be above 20kHz beyond this the ultrasound frequency range can then be divided into two broad ranges. (a) power ultrasound (20 and 100kHz) which can be used for sonochemistry and processing and (b) diagnostic ultrasound (above 5MHz) which does not have enough power to produce cavitation and is used, for example, in foetal scanning**.**

However the range for sonochemical applications is becoming less well defined nowadays as more researchers are finding that frequencies above 100kHz can produce interesting effects up to around 1MHz. Perhaps the most obvious practical example of the expansion of the range is to be found in the field of ultrasonic cleaning. Traditional cleaning baths operate at the lower end of the ultrasound range, generally around 40kHz. However for the cleaning of electronic wafers the cavitation induced at this frequency is sufficiently powerful to damage them. At much higher frequencies (around 1MHz) the wafers can be cleaned efficiently and without significant surface damage. This process is often termed Megasonic cleaning and the acoustic power used is critical in order to avoid damage [5, 6]. In general it is clear that lower frequencies favour mechanical effects whilst higher frequencies induce generate more chemical effects via radical formation (7).

SONOCHEMISTRY AND ULTRASONIC PROCESSING

The potential of using acoustic cavitation to create changes in materials was identified in the USA in the late 1920's [8-10]. Over the succeeding years after a great deal of pioneering work in sonochemistry, two reviews on the applications of ultrasound in polymer and chemical processing were published in the 1940's [11, 12]. Yet there are very few references to ultrasound in chemistry from about 1955 to 1970 when a major renaissance in the subject began to occur which then accelerated. This revival of interest is undoubtedly due to the more general availability of commercial ultrasonic equipment. In the 1960's the ultrasonic cleaning bath began to make its appearance in metallurgy and chemical laboratories and in this period biology and biochemistry laboratories also began using ultrasonic cell disruptors on a regular basis. The next major reviews came some 40 years later [13,14] and now there are many publications and texts on a wide variety of applications [15,16]

Like any sound wave ultrasound wave passes through a liquid. as a series of compression and rarefaction cycles affecting the molecules of the liquid. When the negative pressure of the rarefaction cycle exceeds the attractive forces between the molecules of the liquid a void is formed. This void or cavity in the structure takes in a small amount of vapour from the solution so that on compression it does not totally collapse but instead continues to grow in size in successive cycles to form an acoustic cavitation bubble. There are many thousands of such bubbles in the liquid some of which are relatively stable but others expand further to an unstable size and undergo violent collapse to generate temperatures of about 5,000 K and pressures of the order of 2000 atmospheres It is these tiny hotspots that provide the energy for some remarkable chemical and mechanical effects. If the bubble collapses close to or on a solid surface the collapse is not symmetrical and results in a microjet of liquid being directed towards the surface of the material at speeds of up to 200 m/sec. Sonochemistry harnesses the cavitation energy and has developed a range of research and development areas including synthesis, electrochemistry, environmental protection food processing and materials technology.

Even from the early days of sonochemistry it was clear that acoustic cavitation would provide faster and cleaner syntheses and that this linked well with what was then an emerging interest in so-called “Green Chemistry”. Indeed the objectives that were set out for sonochemical synthesis and for green chemistry were very similar [17]. There is particular interest in the applications of ultrasound in electrochemistry to make such processes more environmental friendly and the benefits of sonoelectrochemistry have been reported for a number of processes including electrosynthesis, electroanalysis, bioelectrochemistry, synthesis of conducting polymers, electroplating, nanomaterial preparation and electrocatalysis [18].

In water treatment, the degradation of chemical pollutants is possible through the effects of acoustic cavitation [19]. Depending on the pollutants to be eliminated, the combination of Advanced Oxidation Processes such as ozonation with ultrasound or an integrated ultrasonic/biological treatment can significantly improve process efficiency and economy.

Applications of power ultrasound in the food processing are broad and amongst these are to be found ultrasonic improvements in cutting, dispersal/mixing/homogenization, brining/ pickling/marination, drying, extraction, sterilization/ pasteurization and degassing/defoaming [20]. Nowadays, when minimal processing is a driver for food preparation, power ultrasound can provide useful possibilities for the food technologist but perhaps more significantly it can provide concurrent combinations that include mixing with sterilization, controlled crystallisation with improved heat transfer and more.

There are many areas of materials science where ultrasound has been employed and amongst these are the preparation and modification of nanoparticles to yield new types of material [21] and the surface modification of materials used in electronics manufacturing without the need for strong chemicals [22].

An extremely important aspect for the adoption by industry of any of the applications of sonochemistry identified in the laboratory is that the laboratory scale experiments must be capable of being up-scaled. This is an aspect of sonochemistry that has been of interest for many years [23]. Ideally this requires an understanding of the appropriate design parameters for an ultrasound reactor and some of these are still under development. Several models are available from the very fundamental involving cavitation bubble dynamics and its chemical effects through radical formation, to more empirical ways of trying to reproduce the same acoustic pressure field on larger scale. Convenient measurement and modelling of the pressure and cavitation bubble fields are the central problem. Complete models are extremely complex due to the fact that high acoustic intensities generate cavitation and thus oscillating bubbles. Such bubbles will modify pressure wave propagation through the sonicated fluid and also cause damping. With a heterogeneous system, e.g. one involving suspended solid particles, the acoustic field is even more complex. Despite these difficulties a number of larger scale sonochemical reactors have been developed.

There are two types of ultrasonic processing for liquid systems either batch or flow. The former is appropriate where lower power treatment is required but for high power sonication it is necessary to use a flow system through an intense sonication zone. There are a number of examples of commercially available flow reactors. The PROSONITRON P500 system developed by PROSONIX (Figure 1) [24] uses piezoelectric transducers attached to the outside surface of a metal tube through which the process liquid flows. The system has the advantage that the tube itself resonates thus delivering sound energy towards a focus in the centre of the flow.

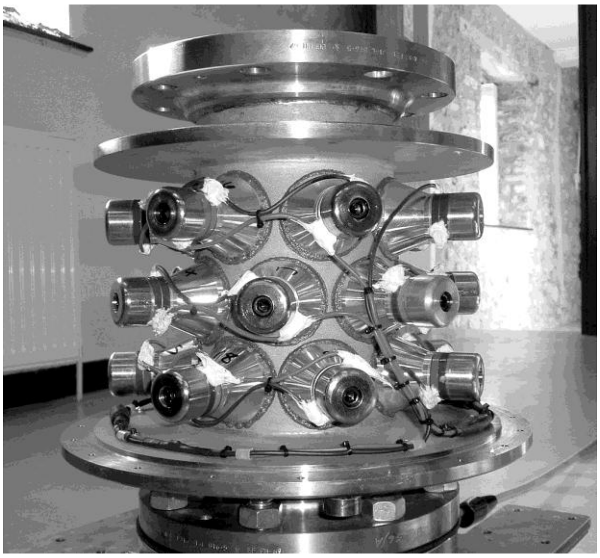

Figure 1 Prosonitron P500

A different approach is the Dual Frequency Reactor or DFR made by Advanced Sonic Processing Systems (Figure 2) [25]. It is produced in variety of sizes but the system configuration has two parallel vertical plates through which the fluid to be processed is pumped (from the bottom). It uses magnetostrictive transducers with each plate operating at different frequencies (20 and 16kHz) to produce high cavitational activity in the fluid flowing through.

Hielscher have produced what they claim to be currently the most powerful ultrasonic processor in the world the UIP16000 operating at 16000 watts (Figure 3) [26]. I**t is** designed to work in clusters of three or more units, for large volume processing, such as to homogenization, dispersion and deagglomeration at up to 50 m^3/h.

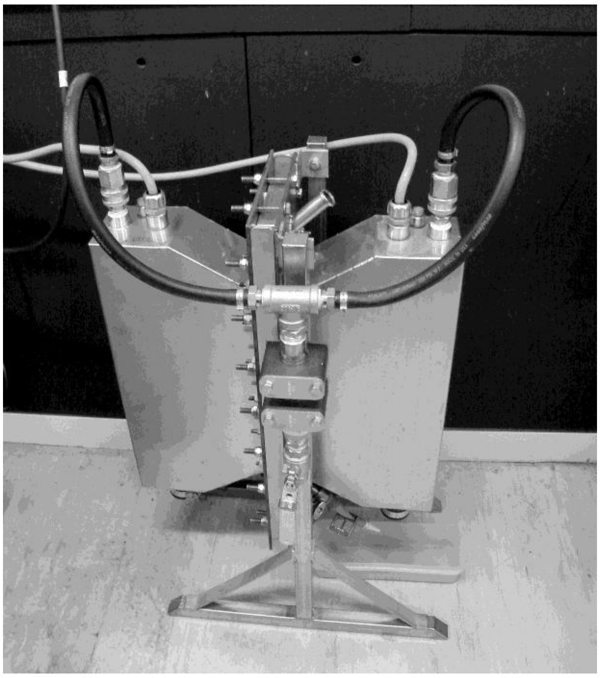

Figure 2 Advanced Sonic Processing Systems DFR

Figure 3 Hielscher UIP16000

RECENT EXAMPLES OF LARGER SCALE SONOCHEMISTRY.

Simultaneous generation and coating of fabric with nanoparticles

Laboratory studies have reported that the deposition of some metal nanoparticles onto fabrics to give them excellent anti-bacterial properties. The design of sonochemical devices for the scale up of such processes could provide bandages and hospital clothing for the future. An instrument has been developed that will simultaneously generate antibacterial nanoparticles and drive them into a fabric fed through a gap between two flat ultrasonically vibrating plates [27]. This work demonstrated for the first time the potential for the scale up of a sonochemical system for the production of biocidal cotton bandages coated with metal oxide nanoparticles. Cotton bandages containing 0.65 and 1.50 wt% CuO demonstrated activity for killing *E. coli* microorganisms.

Ultrasonic crystallisation

The application of power ultrasound to the crystallization of organic molecules has been the subject of research for many years but has now become a real option for industry [28]. In one applicationan an improvement in the characteristics of pharmaceuticals for drug inhalation has been developed. Traditional pharmaceutical manufacture uses technologies such as micronisation, a destructive and energy inefficient technique to turn large, regular crystals into irregular 1-5μm powder. A new type of application of ultrasound in crystallization is Solution Atomisation and Crystallization by Sonication (SAX^{TM}) it has been applied to the production of corticosteroids, including Budesonide a synthetic anti-inflammatory drug administered by inhalation [29].

Stimulation of oil well production

The oil industry is forever searching for more effective ways of getting crude oil from the bottom of wells. Sometimes the oil itself is very heavy and difficult to pump or the well begins to slow output as the well bottom becomes blocked. A traditional solution to the latter is to set off a small explosive device at the well bottom to break apart the substrata and release the blockage but this is a costly solution in terms of down-time and therefore loss of production. A solution to this is to use high power ultrasound at the oil well bottom through a device lowered down the shaft [30].

CONCLUSIONS

The future contribution of sonochemistry to green and sustainable science is dependent upon the possibility of scaling up excellent laboratory results for industrial use. This will always bring up the important question of how to deliver the ultrasound properly. It is the answer to this question upon which the future of industrial sonochemistry lies and maybe we are now coming nearer to that answer. The knowledge has always been out there somewhere but because it does not reside in one person or one academic discipline or even one industrial manufacturer it is not easy to determine. Fortunately with a greater cross-disciplinary interest in scale-up a number of larger installations are being developed.

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