Direct Sonication System Suitable for Medium-Scale Sonochemical Reactors

Olivier Dahlem, Vincent Demaiffe, and Véronique Halloin
Dept. of Chemical Engineering, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

Jacques Reisse
Dept. of Organic Chemistry, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

A radially vibrating horn is studied as a possible system for scaling up sonochemical reactors. The anisotropic behavior of this horn was demonstrated, as were strong correlations among the acoustic field, the acoustic streaming, and the sonochemical reactivity. A comparison with the classic laboratory horn exhibits the benefits of the larger emitting surface of the radially vibrating horn for homogeneous reactions, but not for polymer degradation reactions or for heterogeneous liquid–liquid reactions. The experimental techniques used proved to be very useful in characterizing the sonochemical reactors.

Introduction

Sonochemistry can be defined as chemistry induced by intense pressure waves in a liquid medium. Sonochemistry is observed only in cavitating liquids; each collapsing bubble can be described as a microreactor. The interest in sonochemistry is due to the spectacular reaction-rate increases frequently observed when chemical reactions are performed in the presence of ultrasound. Even though the chemical effects of ultrasound have been known for a long time (Richards and Loomis, 1927), intensive study in this area only began at the beginning of the 1980s.

Chemical effects

When a pressure wave with an intensity higher than what is called the acoustic cavitation threshold passes through a liquid, the microbubbles stabilized inside the microcrevices in the solid microdust particles that were initially present in the liquid expand (Harvey et al., 1944; Apfel, 1970) and oscillate with an increasing amplitude before imploding violently. During this collapse, molecular fragmentation occurs, producing the highly reactive radical species that are responsible for the chemical effects of ultrasound.

The reasons for this specific reactivity are not yet fully understood, even if theoretical and experimental arguments strongly favor the so-called hot-spot theory (Rayleigh, 1917; Noltingk and Neppiras, 1950; Neppiras and Noltingk, 1951), which suggests that the collapse is so rapid that the compression of the gas and vapor inside the bubble can be considered adiabatic. Consequently, the temperature and pressure can reach values as high as 4,200 K and 1,000 atm, respectively, just before bubble fragmentation occurs.

These conditions are so extreme that H· and HO· free radicals are produced when water is submitted to ultrasonic irradiation. Hydrogen and hydrogen peroxide are then produced thanks to the recombination of these H· and HO· radicals after the homolytic splitting of the oxygen–hydrogen bond in the water molecule (Makino et al., 1982). A free radical chemistry is therefore possible using ultrasound, but it must be noted that, as the current production of radicals by ultrasound is not very efficient in terms of quantities of radicals produced per unit of electrical energy consumed, industrial utilization of the chemical effects of ultrasound is still restricted. Typical rates obtained at the laboratory scale (10–100 mL) of primary sonochemical reactions, that is, reactions that occur in the intrabubble gas phase, are of the order of 10^{-5}–10^{-4} mol/min.

Mechanical effects

Taking advantage of the mechanical effects associated with the cavitation phenomenon is a very promising road for het-

Correspondence concerning this article should be addressed to V. Halloin.

erogeneous liquid–liquid and liquid–solid reactions (Lindley and Mason, 1987; Abdulla, 1988; Pandit and Moholkar, 1996), but also for various physical treatments such as emulsification (Walstra, 1983), cleaning (Hunicke, 1990), biological cell disruption (Hugues and Nyborg, 1962), or depolymerization (Szent-Györgyl, 1933; Price et al., 1994). For a review, see for example Suslick (1988).

Three different phenomena are responsible for the mechanical effects:

Shock Wave. A shock wave as large as 300 MPa is produced in the surrounding liquid during the bubble collapse (Vogel and Lauterborn, 1988). This shock wave is, according to Doktycz and Suslick (1990), responsible for the effects of ultrasound on particles in suspension. For example, the activity of Ni as a hydrogenation catalyst increases by $> 10^5$ when the Ni powder is submitted to ultrasonic irradiation because of remarkable changes in particle aggregation, surface morphology, and the thickness of the surface oxide coating (Suslick and Casadonte, 1987).

Liquid Jet. During the collapse of a bubble near an interface, a liquid jet is formed, whose velocity is around 100 m/s (Kornfeld and Suvorov, 1944; Benjamin and Ellis, 1966; Vogel et al., 1989). In the case of heterogeneous liquid–solid reactions, this high-speed liquid jet erodes the solid surface, the mechanism of erosion being equivalent to liquid impact erosion (Preece and Brunton, 1980), which justifies using ultrasound for cleaning. This effect can also activate solid catalysts, as well as increase mass and heat transfer to the surface by disruption of the interfacial boundary layers (Sukanta Banerjee et al., 1995; Ratoarinoro et al., 1995).

Acoustic Streaming. Absorption of the ultrasonic wave during its propagation in the cavitating liquid is responsible for an energy gradient that induces a macroscopic liquid flow called acoustic streaming (Nyborg, 1965). In the case of cavitating water, this absorption consists of both the attenuation by the liquid itself and the absorption of the sound wave by heterogeneities such as cavitating bubbles. Whatever the absorption phenomenon responsible, acoustic streaming is induced (Nyborg, 1953).

Scale-Up Problems

The results observed in sonochemistry were, until now, mostly obtained in the laboratory, with little application in production. This has to a large extent been due to a lack of scale-up strategies, which has essentially resulted from an insufficient understanding of the basic physical phenomena, and therefore an insufficient control of the parameters affecting cavitation. It has also been due to the politics of secrecy within the few industries that have solved the scale-up problems for their own specific applications.

However, a few high-power sonochemical reactors have been produced, such as, for example, the ARC system (ARC Sonics Inc., P.O. Box 24, Suite 722, 601 West Broadway, Vancouver, British Columbia, Canada V5Z 4C2), which consists of a cylindrical steel beam, supported at its nodal points, with resonant oscillation caused by a series of electromagnets, to which the reaction chambers (351 each) are attached. This unit operates at 104 Hz (low-frequency audible sound) with a 75-kW power supply, and is proposed mainly as a sonochemical reactor, with cavitation introduced into it.

Parameters

Even if, until now, it has been impossible when designing a sonochemical reactor to ensure the control of all the parameters likely to have an effect on the sonochemical yield, an incomplete list of these parameters can be compiled: the frequency and the intensity of the pressure wave; the physical properties of the solvent, that is, the cavitating medium (viscosity, surface tension, vapor pressure); the temperature; the hydrostatic pressure; the presence and the nature of the dissolved gas; and the way in which ultrasonic energy is distributed within the system, which depends on the size and shape of the reactor as well as on the design of the ultrasonic transducer (Reisse et al., 1992). Implementing a large-scale sonochemical process is a rather complicated task, not only because of the number of parameters involved, but also because of the strong relationships existing between all these parameters.

Sonochemical efficiency and reactor equipment

When it comes to the scaling up of a specific sonochemical process, in practice the problem is twofold: estimating the acoustic energy required to perform the application; and designing a high-power ultrasonic transducer in a convenient vessel in such a way that an appropriate distribution and intensity of ultrasonic energy inside the large volume of reactants will reliably generate conditions resulting in the highest yield and selectivity of the desired products. An extensive description of the various types of sonochemical equipment currently available on the market can be found in Mason and Lorimer (1991) and Pandit and Moholkar (1996). One of the most common techniques uses the so-called immersion horn system, which seems to allow the best coupling between the transducers (generally piezoelectric ceramics) and the liquid medium.

The present study focuses on identifying and investigating several typical scale-up problems in connection with reactors equipped with this type of direct sonication system.

Experimental Devices

In this article, the characteristics and performances of a commercial radially vibrating horn (Telsonic SG1000), identified as a possible design for large-scale applications, are studied and compared to those of a currently used laboratory horn. These horns and the reactors in which they are vertically immersed from the top are shown in Figures 1 and 2, while major characteristics of both devices are listed in Table 1.

Both horns are made of titanium and both use piezoelectrical elements to transform electrical energy into mechanical energy. The difference in the vibration mode is due to the differences in design, the Telsonic horn being constructed in order to produce radial vibrations, while the laboratory horn is designed to produce essentially longitudinal vibrations.

Both reactors are equipped with external temperature-controlled envelopes, and both are made of transparent material (glass) to facilitate optical measurements. They were both operated under batch conditions. The second reactor was made large enough to endure the typical scale-up problems.

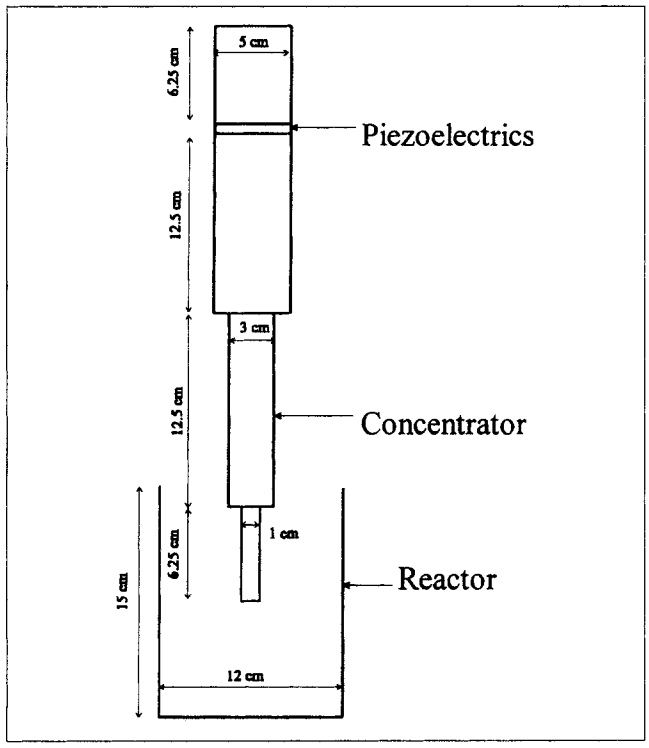

Figure 1. Laboratory horn and its associated reactor.

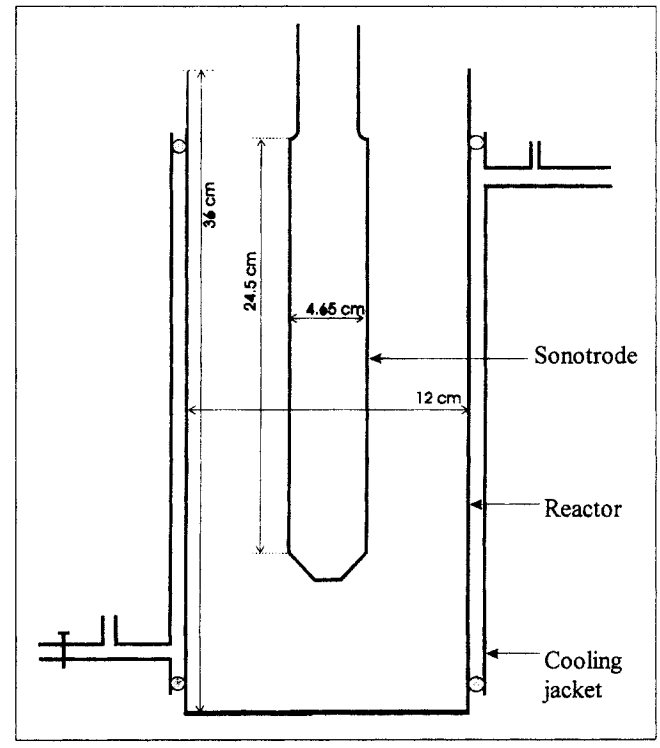

Figure 2. Telsonic horn and its associated reactor.

Experimental Techniques

Two major goals were considered in the present article: first, a thorough study of the characteristics of the Telsonic radial horn, and second, a comparison between the widely used laboratory horn and the radial one. Attention was focused on the following factors: acoustic field, acoustic streaming, sonochemical yield, and the mechanical effects of ultrasounds for homogeneous liquid-phase and heterogeneous liquid–liquid reactions. The measurement techniques discussed in the following subsections were used to reach these goals.

Hydrophone

It is essential to study the acoustic spectrum (i.e., the Fourier transform of the signal recorded by the hydrophone) in order to confirm that the operating acoustic energy level is sufficient to induce cavitation in the reactor. Nonlinear bubble oscillation is associated with the presence in the spectrum of an intense subharmonic at half the driving frequency as well as with the detection of an important white noise (Leighton, 1994). A hydrophone probe (Brüel & Kjaer 8104) connected to a fast Fourier transform (FFT) spectrum analyzer was used to map the acoustic field. Moreover, the hydrophone can also be used to study the spatial distribution of the acoustic field in order to reveal the possible existence of noncavitating and therefore nonreactive zones within the reactor. In our operating conditions, the hydrophone is enclosed inside a glass tube, thus reducing the local energy and preventing its destruction by cavitation. This operation implies that the hydrophone needs recalibrating.

Particle image velocimetry

To acquire information on acoustic streaming, the particle image velocimetry (PIV) technique (Merzkirch, 1987) was used. This technique consists of taking a photograph of the trajectories of small tracer particles (including, in our case, the cavitation bubbles) in suspension in a thin illuminated plane of fluid. The two components of the velocity vector in the illuminated plane are given by the traces left on the photographs during the exposure time. This technique has already been used to study acoustic streaming under the acoustic cavitation threshold (Liebermann, 1949; Murata et al., 1997).

Weissler reaction

The Weissler reaction (Weissler et al., 1950) was used to study the sonochemical reactivity in the homogeneous liquid phase. This so-called reaction refers to the oxidation of iodide into iodine in the presence of carbon tetrachloride. In this case, the Cl· radicals or chlorine molecules resulting from the recombination of two such radicals act as the oxidizing agent, while the oxidation due to HO· and hydrogen perox-

Table 1. Characteristics of Experimental Devices

	Laboratory Device	Telsonic Device
Electrical power (W)	300	1000
Principal vibration mode	Longitudinal	Radial
Emitting surface (cm^2)	0.8	365
Frequency (kHz)	20	20
Reactor volume (L)	0.3	3.5

ide can be neglected. The accelerating effect comes from the lower bond energy and the higher vapor pressure of CCl_4 compared to H_2O, leading to a higher concentration of oxidizing species. In our experiments, the reaction was performed during 10 minutes in a solution containing 80% 0.1-M KI solution and 20% CCl_4 saturated water. The final concentration in iodine was measured using a light absorption technique at 352 nm. The Weissler reaction was carried out within the whole volume of the reactor and within a closed glass tube set at various locations in the reactor, in order to measure local reactivity and to separate the chemical effects of ultrasound from their stirring effects (Contamine et al., 1994).

Degradation of polymers

Since the mechanical stresses induced by a cavitating bubble on a polymer solution submitted to ultrasound can induce breakage in the vicinity of the bubble, a study of the mechanical effects of ultrasound in homogeneous liquid-phase can be made by measuring the degradation rate of polymers in solution. We chose to study the initial degradation kinetic of dextran in water (Szent-Györgyl, 1933), the progress of the reaction being determined by using a Couette viscosimeter to measure the viscosity of the solution. In our experimental conditions, we used a solution of 15 g/L of dextran of molecular weight $5\times10^6-40\times10^6$ (Sigma). In our case, because of the length of the macromolecule, and because we were working at low ultrasonic frequency (20 kHz), it was supposed that the chemical effects of ultrasound, that is, radical-like attack of the polymer, are negligible (Portenlänger and Heusinger, 1997).

Hydrolysis of carboxylic acid esters

For information on the effects of ultrasound in liquid–liquid heterogeneous reactions, the basic hydrolysis of methyl benzoate was studied (Moon et al., 1979). In this case, the ultrasounds are known to be responsible for an acceleration of the reaction rate because of the very fine emulsions produced (Suslick, 1988). This can be attributed to the turbulence prompted by the acoustic streaming and the cavitation itself, which generates a large spectrum of turbulence eddies of different sizes. The size of the stable droplets is thus linked to the smallest eddies, which is called the Kolmogorov scale (Walstra, 1983).

In our experimental conditions, a 20% (v/v) solution of methyl benzoate in toluene was added to a 100-g/L aqueous solution of NaOH in, respectively, 10/90 proportions. The reaction rate was measured using gas chromatography to track the methyl benzoate disparities in the organic phase. Naphthalene was used as an internal reference.

Characterization of the Telsonic Radial Horn

All the results presented below were obtained using the Telsonic radial horn immersed in the 3.5-L reactor operated under batch conditions.

Acoustic streaming

Acoustic streaming causes the mixing effects of ultrasounds and is therefore important in the design of sonochemical reactors. An efficient mixing is indeed necessary, because, until now, there has been no tranducer design that ensures a homogeneous distribution of the cavitation field within the reactor.

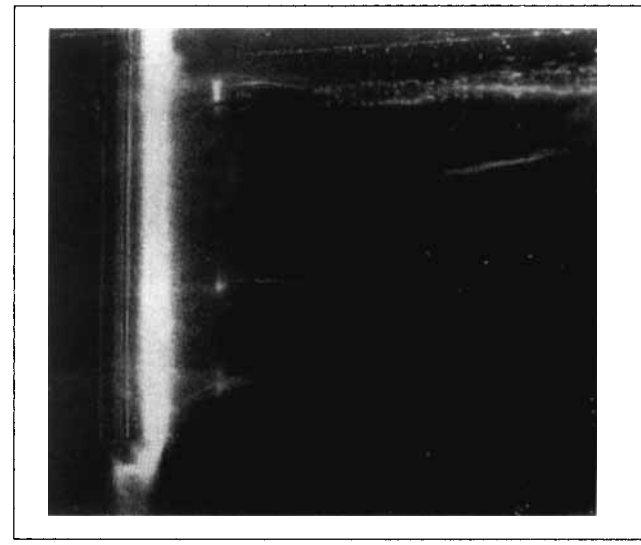

Figure 3. Acoustic streaming and the bubble fields induced by the Telsonic horn.

The velocity field associated with the acoustic streaming was studied using the PIV technique in the batch reactor. A typical photograph taken in the vertical plane for 1-kW electrical power and a 20-kHz working frequency is presented on Figure 3. Three streams of bubbles can be observed perpendicular to the radial surface and regularly distributed along the height of the cylindrical horn. Since the active length of the sonotrode is equal to the sound wavelength in titanium at 20 kHz, and since the distance between the three emitting zones corresponds to the half-wavelength of sound in titanium at that working frequency, this phenomenon is ascribed to the presence in the horn of a standing wave that acts as a resonator. The resulting motion of the fluid is also radial, away from the sonotrode at the levels of the bubble streams and toward the sonotrode between them. Under these specific experimental conditions, the average velocity of this acoustic streaming was measured to be around 5 cm/s.

A stream of bubbles is also located just below the horn. The velocity of the fluid there reaches 30 cm/s and is about one order of magnitude higher than along the horn. Figure 3 shows clearly that the horn does not act as a pure radial emitter. Indeed, a rather large amount of energy is transmitted to the fluid at the bottom of the horn, while the rest of the energy is distributed inhomogeneously at three specific positions along the horn.

Acoustic field

An axial profile of the pressure intensity was measured 2 cm from the horn by using a hydrophone probe enclosed in an immersed glass tube to detect at each vertical position the white noise and the harmonic at half the driving frequency, both of which are known to be characteristic of nonlinear bubble oscillation. The profile of the white noise is similar to

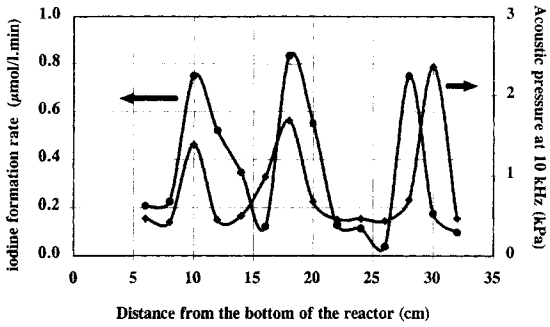

Figure 4. Profiles along the Telsonic horn.

The first curve (■) represents the iodine formation rate following the Weissler reaction; the second curve (●) represents the pressure amplitude at half the driving frequency.

the one at half the driving frequency presented in Figure 4. They both exhibit three maxima equally distant by a half-wavelength at the working frequency (20 kHz) in titanium.

Chemical effects of ultrasound

Similarly, in order to separate the chemical effects of ultrasound from the mechanical ones responsible for mixing during homogeneous liquid-phase reactions, an axial profile of local sonochemical reactivity was measured equidistantly from the horn by performing the Weissler reaction in a glass tube used as a microreactor.

Again, three maxima are observed (Figure 4), at axial positions corresponding to those of the bubble streams and of the maxima in pressure intensity. Moreover, the reaction rate below the horn, where a fourth stream of bubbles was previously observed, was found to be 50% higher than the highest rate measured along the horn.

Conclusions

According to the different types of measurements performed, the so-called Telsonic radial horn was seen to be far from a perfect radial transducer, as a rather large amount of energy is transmitted longitudinally into the solution, while only three maxima of energy corresponding to the presence of bubble streams are visible along the horn, equally distant of a half-wavelength in titanium at the working frequency (20 kHz). The location of the bubble streams corresponds to the location of the maxima in acoustic pressure and in sonochemical reactivity, which displays the strong coupling that exists between mass transfer and energy transfer in sonochemistry.

Comparison Between a Typical Laboratory Horn and the Telsonic Radial Horn

Most of the published results on sonochemistry are related to experiments performed using a stepped laboratory horn. In order to compare the efficiency of such a standard device to that of the radial horn, and to display in each case the problems associated with scale-up, it was decided to first compare the acoustic streaming in both configurations, and second use these three test reactions, ensuring in each case that the same rate of electrical power was delivered by the generator upon the reactor volume. The Weissler reaction and the degradation reaction of a polymer in solution were used as test reactions to study, respectively, the chemical effects and the mechanical effects of ultrasound in homogeneous sonochemistry, while the basic hydrolysis of an ester was chosen as the test reaction to study the mechanical effects of ultrasound in heterogeneous liquid–liquid reactions, that is, the emulsification effect.

Acoustic streaming

The average acoustic-streaming velocity induced when the radial horn was used was determined to be about one order of magnitude lower than when working with a classic laboratory horn (Figure 5), for the usual range of power of each device. The higher velocity reached in this last case (about 50 cm/s) comes from the concentration of all the energy on a much smaller emitting surface, thus generating these high acoustic intensities. Therefore, since most of the published results on sonochemistry are related to experiments performed using this type of laboratory horn, we can assume that from a chemical engineering point of view, all these results are obtained in perfectly mixed reactors. If the radial horn is to be used for larger-scale applications, we should first check the degree of mixing produced in the reactor by acoustic streaming.

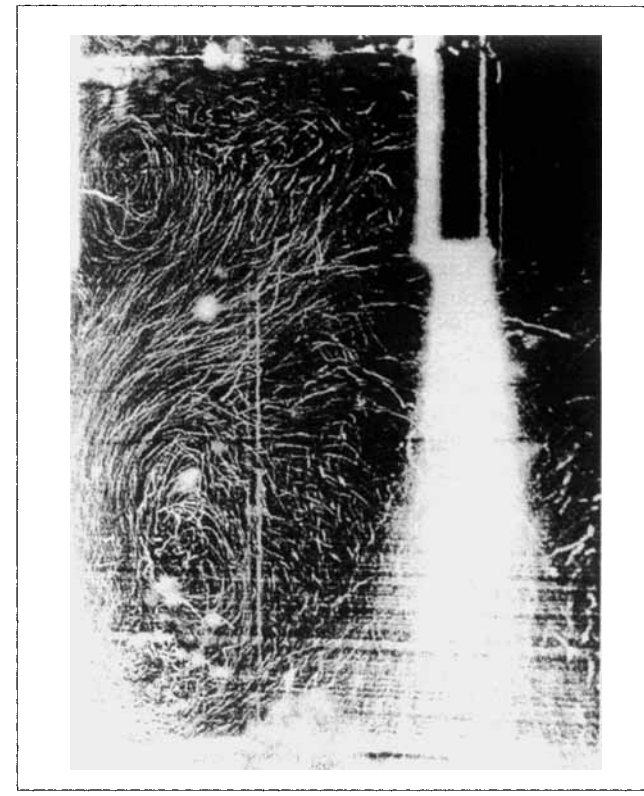

Figure 5. Acoustic streaming induced by the laboratory horn.

The tip of the horn is visible on the top right part of the photograph. The white zone visible under the tip is the cavitation zone. The velocity pattern, consisting of two contrarotating vortices, is visible using the PIV technique.

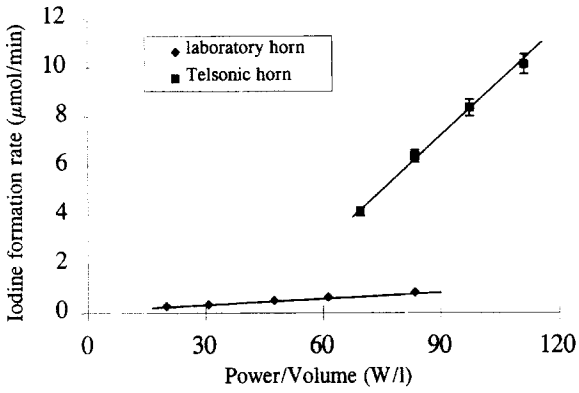

Figure 6. Iodine formation rate following the Weissler reaction as a function of the electric power delivered by the generator per volume unit.

Weissler reaction

As can be seen in Figure 6, where conversions obtained after 10 min are plotted as a function of the electric power of the ultrasonic source per unit of reacting volume, the effect of the Weissler reaction is completely different in each of the two devices. The radial horn proved to be more efficient in performing free-radical sonochemical reactions and to be more sensitive to an increase in the emitting power. These positive effects result from a better distribution of the acoustic energy that is due to the larger emitting surface. Indeed, considering the case of the stepped horn characterized by a much smaller emitting surface, and therefore a much higher delivered intensity in W/cm^2, the increasing power caused an increasing quantity of bubbles very close to the emitting surface. The screening effect of the bubble field therefore becomes more important (Berlan and Mason, 1992), and the phenomenon of bubble coalescence intensifies, generating large bubbles that cannot violently cavitate anymore and are therefore useless for homogeneous sonochemical reactions (Henglein and Gutierrez, 1990).

Degradation of polymers

The initial kinetics of degradation of dextran solutions are plotted as a function of the electrical power upon the reactor

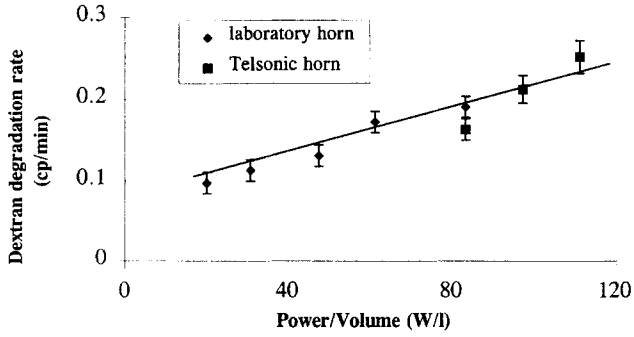

Figure 7. Dextran degradation rate as a function of the electric power delivered by the generator per volume unit.

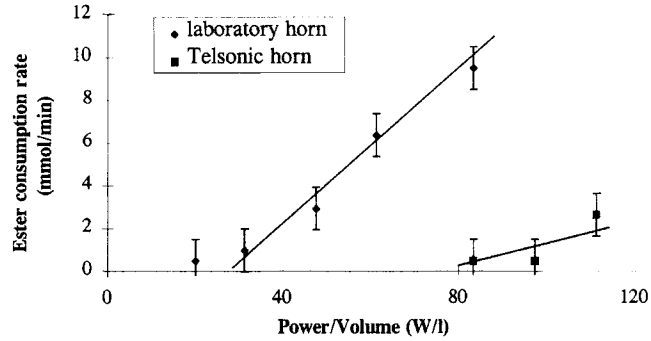

Figure 8. Ester consumption rate as a function of the electric power delivered by the generator per volume unit.

volume in each device (Figure 7). The conclusions are opposite to the ones drawn after performing the Weissler reaction, as there is no evidence in the present case of any difference between the two devices. An increase in the emitting surface does therefore not seem worthwhile, as in the case of free radical reactions, for the two following possible reasons. First, since the acoustic streaming induced by the stepped-horn is important, it could be partly responsible for the mechanical degradation of the polymer. The second and more probable reason is that the chemical effects are considerably affected by the coalescence of bubbles, while the mechanical ones remain unchanged (Heinglen and Gutierrez, 1990). This is due to the fact that, while too large a bubble cannot cavitate violently anymore, and therefore cannot produce free radicals efficiently, its oscillations remain sufficient to induce hydrodynamic stresses capable of breaking macromolecules.

Hydrolysis of carboxylic acid

Figure 8 gives the reaction rates of the hydrolysis reaction as a function of the power per volume unit. In this case, the reaction rate is much higher when the laboratory horn is used. This can be explained by the fact that the acoustic streaming induced by the Telsonic horn is essentially parallel to the interface between the two phases. There is therefore no mass transport of the organic superior phase to the cavitation zones. Moreover, the velocities of the streaming induced by the laboratory horn are large enough to generate turbulence, which helps produce emulsions (Walstra, 1983).

Conclusions

Designing sonochemical reactors for large-scale applications is a difficult task, but a wide range of techniques are available to study this problem. Those presented here are very useful in the study and correlation of the acoustic field, the acoustic streaming, and the local sonochemical reactivity. The radially vibrating horn that we chose for a first scale-up attempt exhibits strong anisotropic behavior. Its active surface is therefore much smaller than one would expect (about 25 cm^2 instead of 365 cm^2).

However, the rate of a homogeneous reaction test related to the electrical power consumed per unit of volume treated is higher using the Telsonic radially vibrating horn than with a classic laboratory one. The lower acoustic intensity when

the Telsonic horn is used is probably responsible for this difference. On the other hand, the mechanical polymer degradation reaction is not improved by the better ultrasonic energy distribution. Finally, the mechanical effects of ultrasound involved in the case of liquid–liquid reactions seems to be more efficient when the laboratory horn is used. This very surprising result, even if not directly transferable to other systems or reactions, is a clear-cut demonstration of the need for designing a sonochemical reactor dedicated to a specified reaction. We strongly believe that significant progress can only be made through the development of coupled acoustic and hydrodynamic models of sonochemical reactors.

Acknowledgments

We thank the Fonds National pour la Recherche Scientifique of Belgium for financial support. One of us (O.D.) thanks the Van Buuren Foundation, the F.I.R.S.T. Program between the Région Wallonne and Lilly Development Centre (Belgium); another of us (J.R.) thanks the COST-Chemistry (D6 and D10) Programme, all for their financial support.

Literature Cited

Abdulla, R. F., "Ultrasound in Organic Synthesis," *Aldrichim. Acta*, **21**, 31 (1988).

Apfel, R. E., "The Role of Impurities in Cavitation-Threshlod Determination," *J. Acoust. Soc. Amer.*, **48**, 1179 (1970).

Benjamin, T. B., and A. T. Ellis, "Cavitation: The Collapse of Cavitating Bubbles and the Pressures Thereby Produced against Boundaries," *Philos. Trans. R. Soc. London Ser. A*, **260**, 221 (1966).

Berlan, J., and T. J. Mason, "Sonochemistry: From Research Laboratories to Industrial Plants," *Ultrasonics*, **30**, 203 (1992).

Contamine, F., A. Faid, A.-M. Wilhelm, J. Berlan, and H. Delmas, "Chemical Reactions under Ultrasound: Discrimination of Chemical and Physical Effects," *Chem. Eng. Sci.*, **49**, 5865 (1994).

Doktycz, S. J., and K. S. Suslick, "Interparticle Collisions Driven by Ultrasound," *Science*, **247**, 1067 (1990).

Harvey, E. N., D. K. Barnes, W. D. McLeroy, A. H. Whiteley, D. C. Pease, and K. W. Cooper, "Bubble Formation in Animals," *J. Cell. Comp. Physiol.*, **24**, 1 (1944).

Henglein, A., and M. Gutierrez, "Chemical Effects of Continuous and Pulsed Ultrasound: A Comparative Study of Polymer Degradation and Iodide Oxidation," *J. Phys. Chem.*, **94**, 5169 (1990).

Hugues, D. E., and W. L. Nyborg, "Cell Disruption by Ultrasound," *Science*, **138**, 108 (1962).

Hunicke, R. L., "Industrial Applications of High-Power Ultrasound for Chemical Reactions," *Ultrasonics*, **28**, 291 (1990).

Kornfeld, M., and L. Suvorov, "On the Destructive Action of Cavitation," *J. Appl. Phys.*, **15**, 495 (1944).

Leighton, T. G., *The Acoustic Bubble*, Academic Press, London (1994).

Liebermann, L. N., "The Second Viscosity of Liquids," *Phys. Rev.*, **75**, 1415 (1949).

Lindley, J., and T. J. Mason, "Sonochemistry: II. Synthetic Applications," *Chem. Soc. Rev.*, **16**, 275 (1987).

Makino, K., M. M. Mossoba, and P. Riesz, "Chemical Effects of Ultrasound in Aqueous Solutions. Evidence for ·OH and ·H by Spin Trapping," *J. Amer. Chem. Soc.*, **104**, 3537 (1982).

Mason, T. J., and J. P. Lorimer, *Practical Sonochemistry*, Ellis Horwood, Chichester, UK (1991).

Merzkirch, W., *Flow Visualization*, 2nd ed., Academic Press, London (1987).

Moon, S., L. Duchin, and J. V. Cooney, "Application of Ultrasound to Organic Reactions: Ultrasonic Catalysis on Hydrolysis of Carboxylic Acid Esters," *Tetrahedron Lett.*, **41**, 9317 (1979).

Murata, Y., S. Kimura, S. Takei, K. Minagawa, J. Takimoto, and K. Koyama, "Generation of an Enhanced Acoustic Streaming in a Bounded Space," *J. Acoust. Soc. Amer.*, **102**, 2536 (1997).

Neppiras, E. A., and B. E. Noltingk, "Cavitation Produced by Ultrasonics: Theoretical Conditions for the Onset of Cavitation," *Proc. Phys. Soc.*, **B64**, 1032 (1951).

Noltingk, B. E., and E. A. Neppiras, "Cavitation Produced by Ultrasonics," *Proc. Phys. Soc.*, **B63**, 674 (1950).

Nyborg, W. L., "Acoustic Streaming Due to Attenuated Plane Waves," *J. Acoust. Soc. Amer.*, **25**(1), 68 (1953).

Nyborg, W. L., "Acoustic Streaming," *Physical Acoustics — Principles and Methods*, W. P. Mason, ed., Academic Press, New York/London (1965).

Pandit, A. B., and V. S. Moholkar, "Harness Cavitation to Improve Processing," *Chem. Eng. Prog.*, 57 (1996).

Portenlänger, G., and H. Heusinger, "The Influence of Frequency on the Mechanical and Radical Effects for the Ultrasonic Degradation of Dextranes," *Ultrasonics Sonochem.*, **4**, 127 (1997).

Preece, C. M., and J. H. Brunton, "A Comparison of Liquid Impact Erosion and Cavitation Erosion," *Wear*, **60**, 269 (1980).

Price, G. J., P. J. West, and P. F. Smith, "Control of Polymer Structure Using Power Ultrasound," *Ultrason. Sonochem.*, **1**, S51 (1994).

Ratoarinoro, F. Contamine, A. M. Wilhelm, J. Berlan, and H. Delmas, "Activation of a Solid-Liquid Chemical Reaction by Ultrasound," *Chem. Eng. Sci.*, **50**, 554 (1995).

Rayleigh, O. M., "On the Pressure Developed in a Liquid during the Collapse of a Spherical Cavity," *Philos. Mag., Ser. 6*, **34**, 94 (1917).

Reisse, J., D.-H. Yang, M. Maeck, J. Vandercammen, and E. Vander Donckt, "Sonochemistry: A Systematic Study of the Maleate-Fumarate Isomerization in the Presence of Alkyl Bromides," *Ultrasonics*, **30**, 397 (1992).

Richards, W. T., and A. L. Loomis, "The Chemical Effects of High Frequency Sound Waves. I. A Preliminary Survey," *J. Amer. Chem. Soc.*, **49**, 3086 (1927).

Sukanta Banerjee, R. Kumar, and K. S. Gandhi, "Analysis of Ultrasonically Enhanced Hydrogen Evolution for Zn-$NiCl_2$ System," *Chem. Eng. Sci.*, **50**, 2409 (1995).

Suslick, K. S., and D. J. Casadonte, "Heterogeneous Sonocatalysis with Nickel Powder," *J. Amer. Chem. Soc.*, **109**, 3459 (1987).

Suslick, K. S., *Ultrasound, Its Chemical, Physical and Biological Effects*, VCH, New York (1988).

Szent-Györgyl, A., "Chemical and Biological Effects of Ultra-Sonic Radiation," *Nature*, **131**, 278 (1933).

Vogel, A., and W. Lauterborn, "Acoustic Transient Generation by Laser-Produced Cavitation Bubbles Near Solid Boundaries," *J. Acoust. Soc. Amer.*, **84**, 719 (1988).

Vogel, A., W. Lauterborn, and R. Timm, "Optical and Acoustical Investigations of the Dynamics of Laser-Produced Cavitation Bubbles near a Solid Boundary," *J. Fluid Mech.*, **206**, 299 (1989).

Walstra, P., "Principles of Emulsion Formation," *Chem. Eng. Sci.*, **48**, 333 (1983).

Weissler, A., H. W. Cooper, and S. Snyder, "Chemical Effect of Ultrasonic Waves: Oxidation of Potassium Iodide Solution by Carbon Tetrachloride," *J. Amer. Chem. Soc.*, **72**, 1769 (1950).

Manuscript received Apr. 16, 1998, and revision received Sept. 11, 1998.