EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

<u>TECHNOLOGY:</u>
Ultrasound reactors for enhanced disintegration/phase dispersion/ mass transfer
<u>TECHNOLOGY CODE</u>: 3.2.7

<u>AUTHOR:</u> Uwe Neis, Technical University Hamburg-Harburg

Table of contents

1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Ultrasound represents a wide range of sound of frequencies beyond the human hearing between 20 kHz and 10 MHz. Ultrasound can be generated at a broad range of frequencies and acoustic intensities.

If high acoustic energy is applied to a liquid system it is possible to generate physical and chemical reactions which significantly can modify the character of dissolved and particulate substances present in the liquid. These reactions result from the generation and collapse of cavitation bubbles, which are produced under these acoustic conditions. At high acoustic intensities particularly in the low and mid frequency range the liquid is broken by sufficiently large negative pressure during rarefaction. Gas bubbles are generated, which will grow by taking in gas and vapour from the liquid. They alternate in size according to the acoustic wave action. They can finally collapse in the compression cycle ("implosion"). The phenomenon of sudden implosion of the bubbles is called cavitation. At implosion of the bubbles dramatic conditions in the gaseous phase exist: extreme temperatures (~5000 K) and high pressures (~500 bar). These dramatic conditions lead to pronounced sono-chemical reactions which are due to the creation of highly reactive radicals (H•, OH•) and thermal breakdown of substances (pyrolysis). In addition high shear stresses ("jet streams") are produced in the liquid. The vapour filled cavitation bubbles are surrounded by a liquid hydrophobic boundary layer. Therefore preferably volatile and hydrophobic substances are accumulated in the bubbles where they are subject to pyrolytic or radical reactions. Some of the radicals escape from the vapour, reach the liquid boundary layer and pass on into the bulk solution where reactions with hydrophilic substances take place. Recent studies indicate that sonochemical phenomena not only occur at low frequencies but also between 100 and 1000 kHz. The optimum frequency is substrate specific. Commonly accepted indicators for the selection of the optimum frequency are not available yet.
It is difficult to create cavitation beyond 1 MHz because the acoustic intensity which has to be applied in order to create cavitation increases with increasing frequency. In the range of high frequencies greater than 1 MHz mechanical phenomena are predominant. The acoustic wave impact on the liquid creates microcurrents altogether with stable swinging gas bubbles. They do not collapse.

1.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Ultrasound transducers are necessary to create the high frequency vibrations which are submitted into the liquid. They are one step in the overall energy conversion procedure from the energy source to the transducer and finally to the oscillating bubbles. In this energy cascade, the oscillating bubbles are the effective power amplifiers which collect sound energy and release this power in the very fast transient collapse.

Two mayor types of transducers are known for liquids: liquid driven and electromechanical devices. Liquid driven transducers are widely used in food industry for mixing and homogenization purposes. The principle is that of a liquid whistle. Electromechanical transducers are based on either **piezoelectric** or **magnetostrictive** principles. Both transducers need a high frequency generator for electrical supply. Magnetostrictive transducers are made of ferromagnetic material which on applying a magnetic field alters its geometrical dimension. Formed as a bar or rod from nowadays non-metallic ferrite ceramics, high driving forces are possible below 100 kHz. The major drawback for magnetostrictive transducers is their poor efficiency and rather broad frequency behavior. Piezoelectric materials change their dimension when charges are applied to opposite faces of the material. These types of transducers have a natural resonance frequency where the driving current produces highest efficiency. Piezoelectric transducers are often made of barium titanate, lead metaniobate and lead zirconate titanate ceramics and are supplied to most laboratory and industrial transducers. The high efficiency is responsible for the fixed frequency of common ultrasonic systems and the reason for the difficulty to examine the influence of frequency on sonochemical effects. Modern piezoelectric transducers have a sandwich structure with two electrically opposed piezoceramics between two metal blocks. The sandwich is clamped together and prevents mechanical damage by stress in the ceramic. It is usually half a wavelength long and generates amplitudes of up to 20µm.

One of the major drawbacks in industrial applications of ultrasound is the complex scale-up procedure. Readily available laboratory equipment like ultrasonic baths, high intensity disintegrator horns or cup horn reactors are used to measure sonochemical effects. All influence parameters like intensity, frequency, temperature or vessel geometry have to be the same for reproducible results. Critical ultrasonic parameters are for example the amplitude of the transducer, the ultrasonic intensity, the total power input, the specific power input per volume, the gas content, the local sound energy distribution and in the case of heterogeneous reactions the distribution of reactants. A successful scale-up must take these various demands into account.

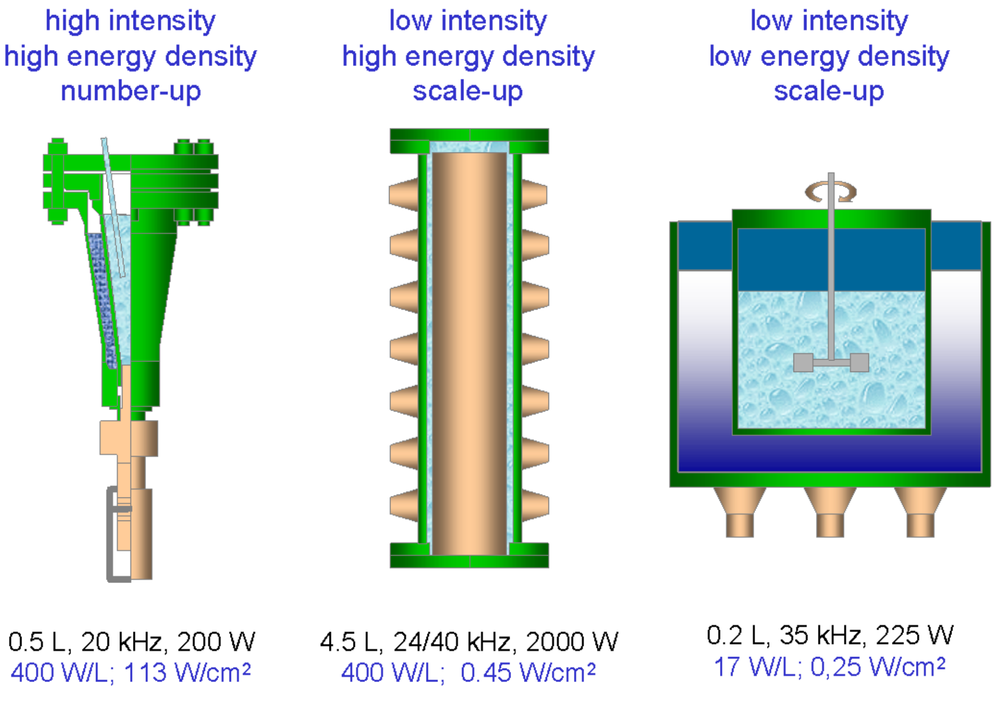
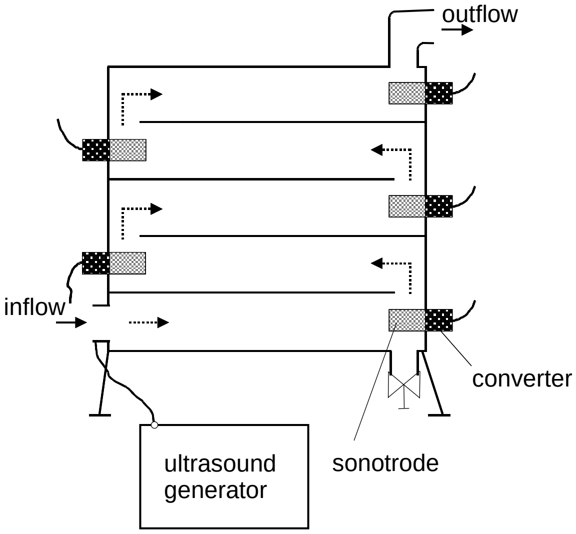


Figure 1: Comparison of three reactor types. Left: conical reactor with stepped horn; middle: SR1000 from BANDELIN electronic with two tube transducers. Right: ultrasonic bath with submersed reaction vessel (Horst and Hoffmann,1999).

Figure 2 (below): Full scale ultrasound reactor for sludge disintegration on German waste water treatment plant (Wolff et al., 2007). Left: Schematic of full scale Ultrawaves ultrasound reactor. Right: Uncovered sound insulated 5 kW reactor for sludge/biomass disintegration.



1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy gain (./. US energy consumption)	20-40% (10-30% net)	High-energy ultrasound (US) when applied for sonochemical reactions consumes energy. Beneficial is the acceleration/intensification of the reaction. For biomass/sludge treatment sonication can be beneficial insofar that an anaerobic digestion process used to degrade this material can be intensified, which yields more end product biogas on one hand and less end product digested organic solids, which have to be disposed off (e.g. incineration). Biogas as renewable energy carrier today has a high value. It can easily be converted to electrical energy. Cost benefit analyses show that considerable economic benefit can be derived from these ultrasound installations.
Less CO_2 emission	10-30%	See remarks above about energy gain
Cost savings (Anaerobic biomass/sludge Stabilization)	Up to 50%	Cost savings can result from: • faster processing (shorter reaction time, up to 50%, avoiding overload of existing digester) • faster processing (shorter reaction time allowing reduction of new digester volume, up to 50%) • less end product, hence less (organic) solids to dispose off, less disposal costs
Increased yield		See above
Increased safety		Not valid
Better product quality		Apart from ultrasound application for sludge disintegration prior to anaerobic treatment, there is recent evidence (full scale) that US impact on return biomass of biological waste water treatment systems (activated sludge) can prevent development of unwanted filamentous biomass,

		which is a serious operational problem on sewage treatment plants.

1.4 Stage of development

On a small-scale sonochemistry results today are excellent and costs are quite reasonable but there still is the question about the economics of scale-up. Nowadays academics, designers and manufacturers are actively engaged in planning for larger sonochemical processing. Full scale "green" applications however are already on the market and have shown economic benefit. Amongst those are (Mason, 2007):

- **Treatment of sewage sludge**
- Removal of biological contamination from water
- Soil remediation
- Destruction of foams
- Control of air-borne contamination

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

Low intensity applications can be tested in a commercial ultrasonic cleaning bath. Several transducers are mounted at the bottom of a bath and are driven with the same frequency. A complicated standing wave field is created and the sonochemical effects depend on the location of the samples in the bath and the filling height.

Probe systems are applicable in high intensity applications of up to some 100 W/cm^2 at frequencies below 100 kHz. A multiplication of the transducers amplitude by a booster and a horn make it possible to raise the original amplitude by a factor of around 10. The vibrating tip of the horn is dipped into the liquid and creates intense cavitation in its vicinity. Ultrasound is attenuated very fast and only some centimetres are sonochemically active. Such a probe generates a high amount of streaming which makes external stirring unnecessary. The intense cavitation causes erosion on the tip. Regular replacement of the horn is needed under hard continuous operational conditions.

Low intensity devices in technical scale are reactors with external or submersed plate transducers, which are easily fitted to existing tanks of several cubic meters and allow a fast scale-up. Tube transducers can be retrofitted to existing plants too. All low intensity devices transmit sound energy in rather great volumes with dimensions above the liquid wavelength. The typical transducer power input is roughly 50 W per transducer at a frequency of 20 kHz and a diameter of 6 cm.

Probe systems are used for high intensity devices in flow cells. Such a flow cell consists of several probes in series and can be retrofitted to an existing plant. Gap reactors force liquids through the most active zone of a probe transducer. The magnitude of the sonicated volumetric flow in one cell however is limited. Sonication of large volumetric flows necessitates a number of cells in parallel or series. The power input per transducer reaches 2000 W.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number

of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

Ultrasound enhanced process intensification is broadly applied on commercial scale in the field of anaerobic digestion of biomass/sludge on (municipal) waste water treatment plants (WWTP). In Germany about 20 WWTP are equipped with this technology, first installations exist in the Netherlands, Denmark, Japan and China. In recent tenders worldwide US disintegration is noted as desired technology.

Table 2. Industrial-scale applications of the Technology (excerpt)

Sector	**Municipality**	**Short characteristic of application**	**Plant size (popula-tion)**	**Year of applica tion**	**Reported effects**
Public (WWTP)	Bamberg, D	Anaerobic digestion of sludge: sonication of partial stream of waste activated sludge	330,000	2004	No new digester; EUR 80,000 annual savings due to more biogas/electrical energy and less solids to be disposed off
Public (WWTP)	Zeist, NL	Anaerobic digestion of sludge: sonication of partial stream of waste activated sludge	53,000	2005	No extra investment in new digester, stable operation of existing digesters secured
Public (WWTP)	Meldorf, D	Anaerobic digestion of sludge by sonication of waste activated sludge	70,000	2004	No foam in digester, normal operation secured
Public (WWTP)	Bünde, D	Improving nitrogen removal by sonication of 30% of thickened waste activated sludge	54,000	2006	Improved nitrogen removal, less waste activated sludge produced, return of investment: 1 year
Public (WWTP)	Seevetal, D	Fighting bulking sludge, process stabilization by sonication of 1% of return sludge	130,000	2006	No bulking sludge, stable operation of complete biological system

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

In the private sector in agriculture biomass disintegration projects on biogas pants have recently started. The objective is identical to sludge treatment on municipal WWTP: process intensification to produce more biogas and less digested organic solids. The biogas is used to produce on the spot electrical energy in combined heat and power stations.

Table 3. Demonstration projects related to the technology

Sector	**Who is carrying out the project**	**Short characteristic of application investigated, including product name/type**	**Aimed year of applicati on**	**Reported effects**
Private	Farmer A, in D	Disintegration of	now	Under investigation

		agricultural biomass prior to fermentation for intensified biogas production		
Private	Farmer B, in D	Disintegration of agricultural biomass prior to fermentation for intensified biogas production	now	Under investigation

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

In the 1990ies the majority of sonochemical research projects were linked to improved methods of synthesis. Then attention began to be given to cavitation theory, sonoluminescence, therapeutic ultrasound and environmental protection. It was clear from the early days of sonochemical research that sonication provided faster and cleaner syntheses and linked well to the emerging “green” chemistry and “green” engineering. Sonochemistry will certainly become a major contributor to green science (Mason, 2007). Sonochemistry involves:

- The use of less hazardous chemicals and environmental friendly solvents
- Developing reaction conditions to increase the selectivity for the product
- Minimizing the energy consumption for chemical transformations
- The use of alternative or renewable feedstocks e.g. biomaterials

There are currently several ultrasound systems commercially available; the industrial scale examples mainly relate to application in environmental protection and process technology.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to “boundary” issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

The future contribution of sonochemistry to green and sustainable science is dependant upon the possibility of scaling up excellent laboratory results for industrial use.

Table 4. Technology development issues

Issue	**Description**	**How and by whom should be addressed?**
Engineering & design concepts for commercial equipment	US reactors have been developed on the laboratory scale, so far, with a few exceptions (see above). New design concepts are needed of commercial scale continuous flow reactors, which would also address the issues of energy efficiency, low penetration depth of the cavitation field (integrated mixing devices?) and the way of oscillating. This may need the development of new geometries of horns etc. as well. Also, materials issues are of importance here in order to guarantee long lifetime/good resistance of the oscillating units under conditions of hard cavitation.	R&D projects carried out at universities, in collaboration with manufacturers of industrial US reactors

Modeling and scale-up methods	Research in the field of US reactors was almost entirely dominated by the organic chemists and attracted only very little attention of chemical or environmental engineers, so far. Robust and reliable mathematical models of the US reactors have to be developed, together with the scale up methodologies for those devices. However this is a very difficult task considering the complexity of the propagation of cavitation and the reactions caused in non-pure liquids, usually three phase systems.	R&D projects carried out at universities, in collaboration with manufacturers of industrial US reactors
Control systems for commercial scale US reactors	Proper control of the temperature of piezoceramic transducers of high-energy US systems must be carried out to avoid overheating to maintain the reliability of the operation.	Manufacturers and producers of industrial US reactors
Investigations on potential of new “green” US applications	The reluctance of potential end users of US equipment (operators etc.) and of the so-called “traditionalists” towards new/unknown technologies must be overcome by dynamic scientific curiosity to discover new “markets”, looking for possibilities to build up reference units and demonstration tests to deliver evidence for the usefulness and economy of the technology.	R&D projects carried out at universities, followed by demonstration tests and publicity

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Small cavitation field vs. required scale of production	The penetration depth of the high energy cavitation field in water medium is short (about 6 cm). This brings an important question concerning the maximum production capacity achievable in one US reactor. Thus US reactors by nature will be small units (“small footprint”). But because the sono-chemical reactions caused by cavitation are fast the necessary hydraulic retention time to be provided by such a US reactor can be kept very low (about 60 seconds) while considerable volumetric flows can be sonicated. For example the commercial US reactor produced by ULTRAWAVES Co. is designed for a volumetric biomass flow of 1.5 m^3/h. When it comes to treat larger quantities the number of reactors has to be multiplied accordingly, which of course finds limitations. Possible solutions to this problem could be for example tubular wave guide systems where the walls of tubes are acting as oscillating elements in combination with horn type oscillators.	This major challenge should be addressed in the R&D projects on engineering & design concepts for commercial scale US reactors
Applicability of ultrasound in terms of the type of media used in the process	US is applicable to almost all liquid media. Limitations to produce cavitation are given by high viscosity of the liquid or under high pressure in the reactor.	
Limitations related to the constructional materials of US sonotrodes	Sonotrodes in US flow reactors have to produce hard cavitation in the liquid, which, of course also acts on its surface. The challenge is to manufacture sono-trodes, which resist as best as possible to the attack of the cavitation forces, which on the other hand are needed to produce the sonochemical reactions.	This challenge should be taken on by material science in R&D projects

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/report)	Remarks
C. Horst and U. Hoffmann Design, operation and characterization of ultrasound reactors	In: Neis U., Tiehm A. (Ed.) (1999): Ultrasound in Environmental Technology. TUHH Reports on Sanitary Engineering, 25, 77-90, ISBN 3-930400-23-5.	
H.J. Wolff et al. Two years experience on a large German WWTP with acoustic disintegration of waste activated sludge for improved anaerobic digestion	Proc. 11th World Congress on Anaerobic Digestion, September 2007, Brisbane, Australia	
T.J. Mason Sonochemistry and the environment – Providing a “green” link between chemistry, physics and engineering	Ultrasonics-Sonochemistry, Special Issue, Vol. 14, Issue 4, 476-483, April 2007	
Different authors on different topics related to recent developments regarding sonochemical science and applications	Ultrasonics-Sonochemistry, Special Issue, Vol. 14, Issue 4, April 2007, Elsevier	Selected papers from the 10th bi-annual conference of the European Society of Sonochemistry (ESS), June 2006, Hamburg
T.J. Mason, J.P. Lorimer	Applied Sonochemistry, Wiley-VCH, 2002	The Uses of Power Ultrasound in Chemistry and Processing
T.J. Mason et al., Eds.	Advances in Sonochemistry, Vol. 1-6, Jai Press Inc. 1990-2001	Series of fundamental publications covering the wide range of sonochemical research/application since 1990
Oleg V. Abramov	High-Intensity Ultrasonics, Gordon & Breach Science Publ., 1998	Fundamental book on theory and industrial applications of ultrasound
T.J. Mason, S. Koda, D.J. Casadonte, Eds.	Ultrasonics-Sonochemistry, Elsevier	Leading journal

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under “remarks” provide, where applicable, the names/types of products targeted by the given patent.)

It would be unfair to select individual patents from the immense number of worldwide patents regarding high power ultrasound.

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Institute of Wastewater Management and Water Protection, Technical University Hamburg-Harburg (Prof. U. Neis)	Germany	10 years of research and development for "green" US applications
Ultrawaves GmbH	Germany	Developer, promoter and licensor of high power US equipment in environmental engineering, since 2001, 15 licensees worldwide
Sonochemistry Center, Coventry University (Prof. T.J. Mason)	UK	Leading sonochemical research center
Kurnakov Institute of General and Inorganic Chemistry, Moscow (Prof. O.V. Abramov)	Russia	Research, development and manufacturing of US equipment for industrial application
Friedrich Schiller University Jena (Prof. B. Ondruschka)	Germany	Broad range of research activities
VTT, Jyväskylä (A. Grönroos)	Finland	Research institute developing new US applications: improved dewatering of sludges, membrane cleaning
ESIGEC University de Savoie (Prof. C. Petrier)	France	Broad range of research activities since many years
Institute of Chemical Technology, University of Mumbai (Prof. Pandit, Gogate)	India	Fundamental research, modelling of US reactors

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	Country	Remarks

Sonotronic Nagel GmbH	Germany	Developer and manufacturer of high power US reactors designed for water, wastewater and biomass treatment
Sonico/Branson	UK/USA	Manufacturer of high power US reactors
Advanced Sonic Processing Systems	USA	Manufacturer of commercial US equipment

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

A wide variety of industrial users (textile, ceramics, …) might become interested in the potential of high power ultrasound for different purposes like oxidation of refractory organic substances, disinfection of process water… not to mention the well known application for synthesis.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

There is increasing global interest in research of physical and chemical reactions in high-energy ultrasonic microenvironment. Even more interesting is the fact that not only research in theory and experiment is well under way but that - on the other end of the scale - we learn about successful full scale technical applications of ultrasound like the improvement of deep oil well output. The reason behind this development lies in the particular nature of ultrasound: a non-quantum and virtually innocuous irradiation, yet capable of forming and breaking chemical bonds on a very short time scale; and based on this, a range of intellectual challenges and technical applications have followed. Research topics such as cavitation and sonoluminescence, sono-electrochemistry, environmental protection, disinfection, reactor design, food processing, improved preparation of nanomaterials and fine chemicals or medical application of ultrasound illustrate how the multifaceted nature of sonochemistry and sonoprocessing touches a broad range of scientific disciplines from physics to chemistry and biochemistry.