UNIUNEA EUROPEANĂ

Instrumente Structurale 2014-2020

Proiect cofinanţat din Fondul European de Dezvoltare Regională prin Programul Operaţional Competitivitate 2014-2020
Axa prioritară 1 Cercetare, dezvoltare tehnologică și inovare (CDI) în sprijinul competitivităţii economice și dezvoltării afacerilor
Acţiunea 1.1.4. Atragerea de personal cu competențe avansate din străinătate pentru consolidarea capacității de CD
Titlul proiectului: **“Tehnici neconvenționale cu Ultrasunete/Microunde utilizate pentru activarea proceselor chimice şi nonchimice ”**
Număr de înregistrare electronică: P_37_471
Nr contract: 47/05.09.2016
Beneficiar: Universitatea POLITEHNICA din Bucureşti

In cadrul activității ***“1. Efectul US si MW asupra reacțiilor enzimatice, dezvoltarii celulelor şi formării catalizatorilor”*** , subactivitățile “*1.1.Studii referitoare la efectul US şi MW asupra reacţiilor enzimatice şi a celulelor vii”* și „*1.2.Sinteza nanocatalizatorilor şi utilizarea lor în reacţii asistate de US şi MW”* , seminarul de lucru:

“*An introduction to the uses of power ultrasound in chemistry*”.

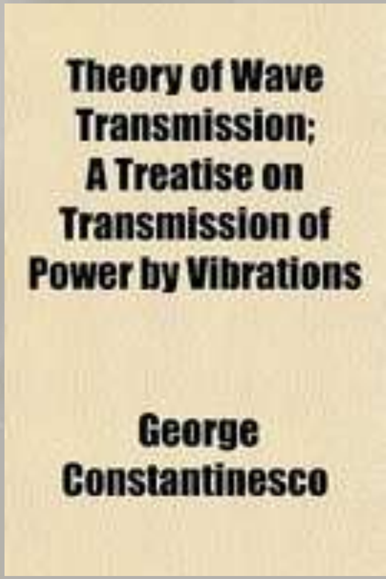
Mircea Vinatoru

11.01.2017

"In one way it could be said fairly, that Sonics is daughter of musical Harmony, because it is in that way it came into being"

. . . Constantinescu, G., Theory of Sonics: A Treatise on Transmission of Power by Vibrations, The Admiralty, London.

1918



A bit of history

The first steps in sonochemistry were taken in the early part of the 20th Century and in 1927 a paper was published entitled "The chemical effects of high frequency sound waves. A preliminary survey" by Richards and Loomis.

W.T. Richards and A.L. Loomis, J. Am. Chem. Soc. 49 (1927) 3086.

*The term **sonochemistry** is used to describe the effects of ultrasound on both chemical reactions and processing.*

*The name is derived from the prefix **sono** indicating sound paralleling the longer established techniques that use light (photochemistry) and electricity (electrochemistry) to achieve chemical activation.*

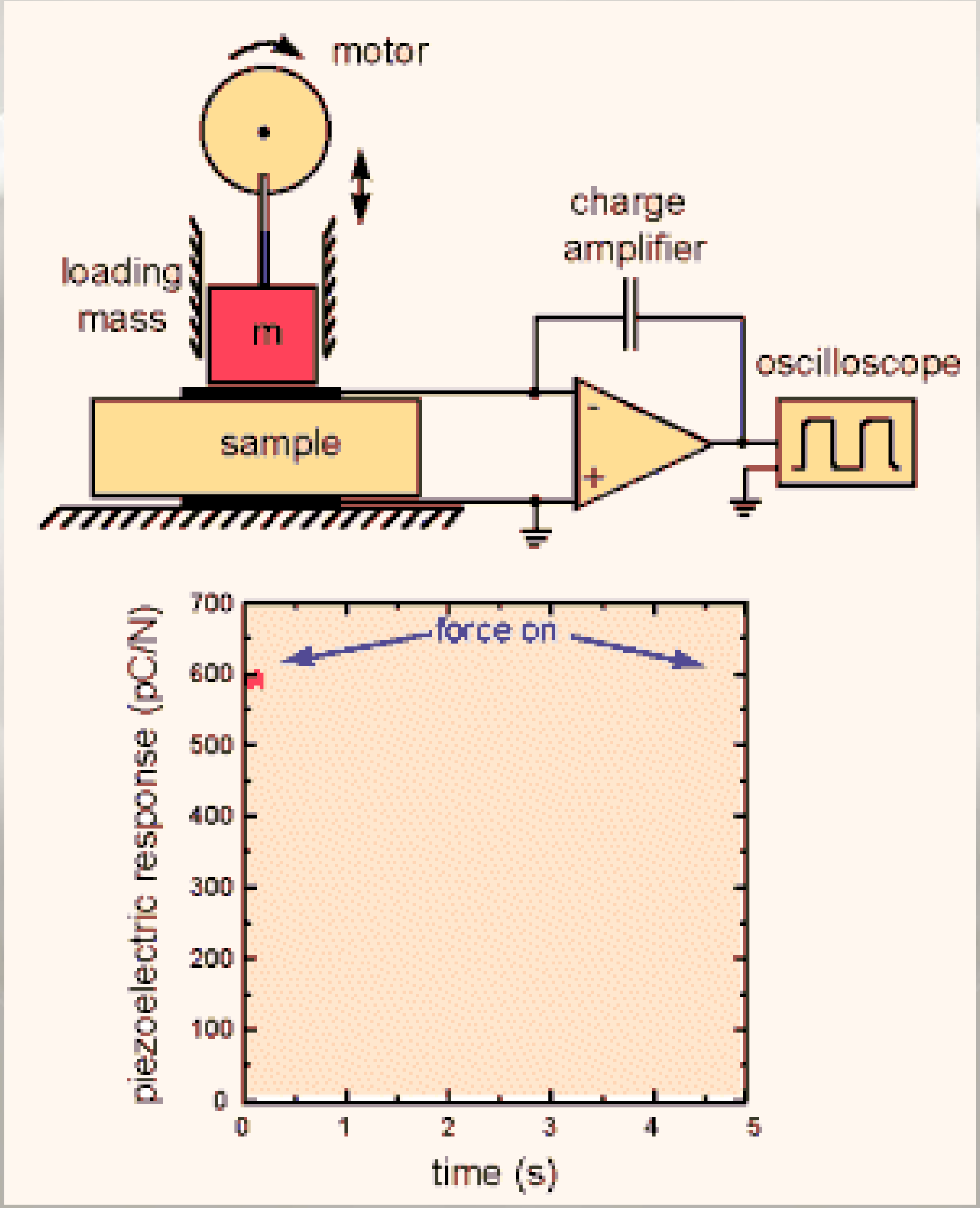
How Ultrasounds could be Generated?

- Using piezoelectric effect.
- Using magnetostriction effect.

PIEZOELECTRICITY

Piezoelectricity is a coupling between material's mechanical and electrical behaviors (electrostriction).
In other words, when a piezoelectric material is squeezed, an electric charge collects on its surface.
Conversely, when a piezoelectric material is subjected to a voltage, it mechanically deforms.

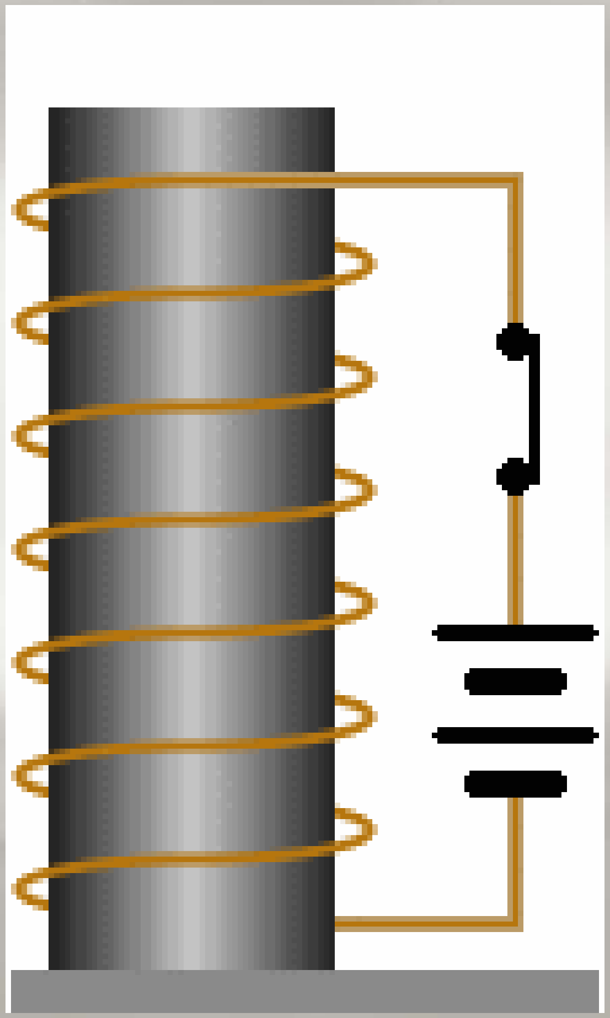
Generating ultrasounds using Piezoelectric Effect

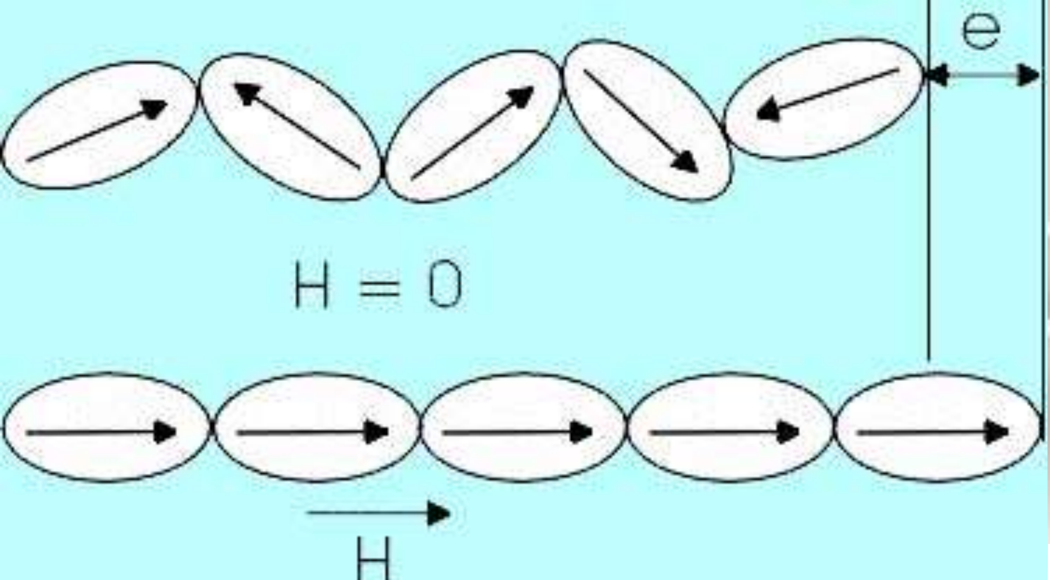


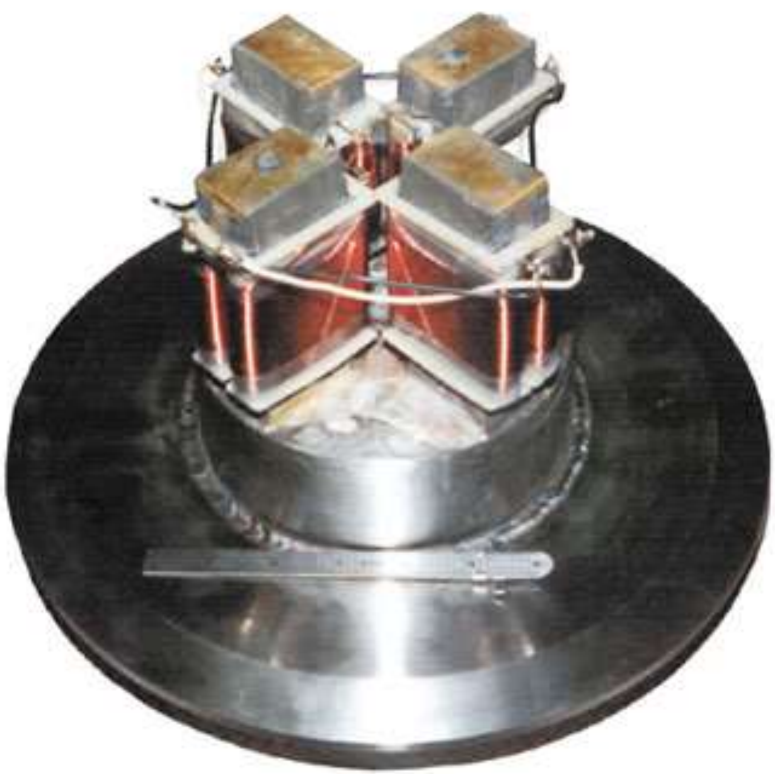
MAGNETOSTRICTION

Magnetostriction means slight changes in the geometrical dimensions of a metal, metal alloy or composite materials, resulting from changes in the magnetic fields acting on these components.

Generating Ultrasounds using Magnetostriction Effect




e
H = 0
H

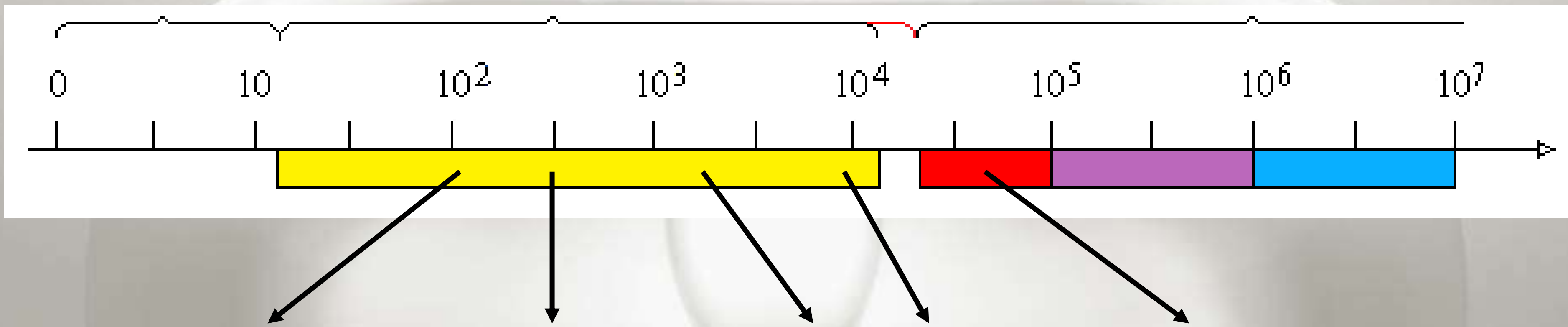


Reactor working in Food Technology Centre, Prince Edward Island, CANADA since 2005.

Design: M. Vinatoru; Manufacturer: Advanced Sonic Processing System

Sounds (Sonics) spectra

Infrasounds *Sounds* *Ultrasounds*



Bumble bee
150 Hz

Middle C (Mi)
~262 Hz

Mosquito
1500 Hz

Grasshopper
7 kHz

Upper-ranging bats
70 kHz

Human hearing
16 Hz – 16 kHz

Power ultrasounds
20 kHz – 100 kHz

Cleaning
Plastic welding
Sonochemistry
UAE

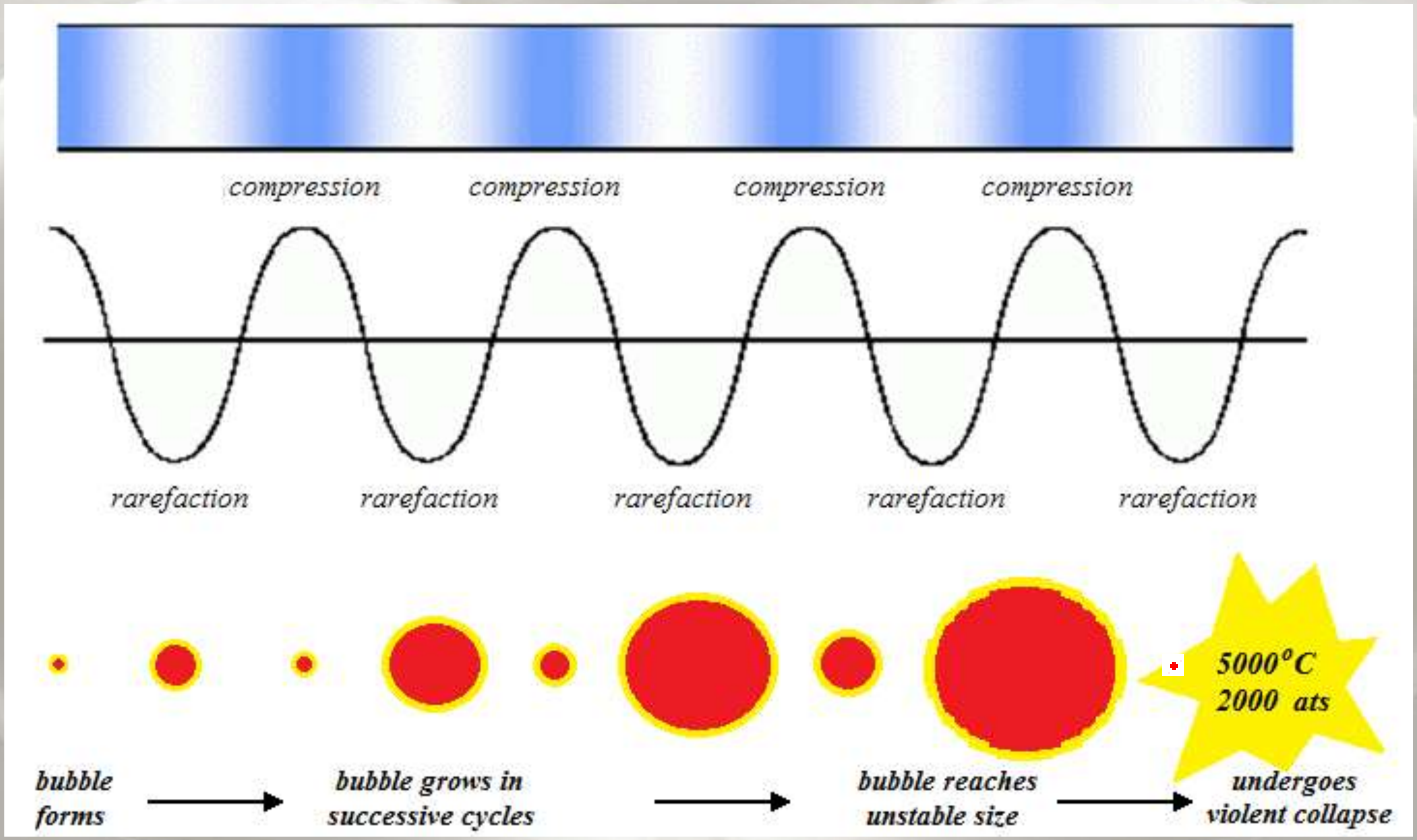
Extended range
100 kHz – 1 MHz

Sonochemistry
UAE

High frequency
1 MHz – 10 MHz

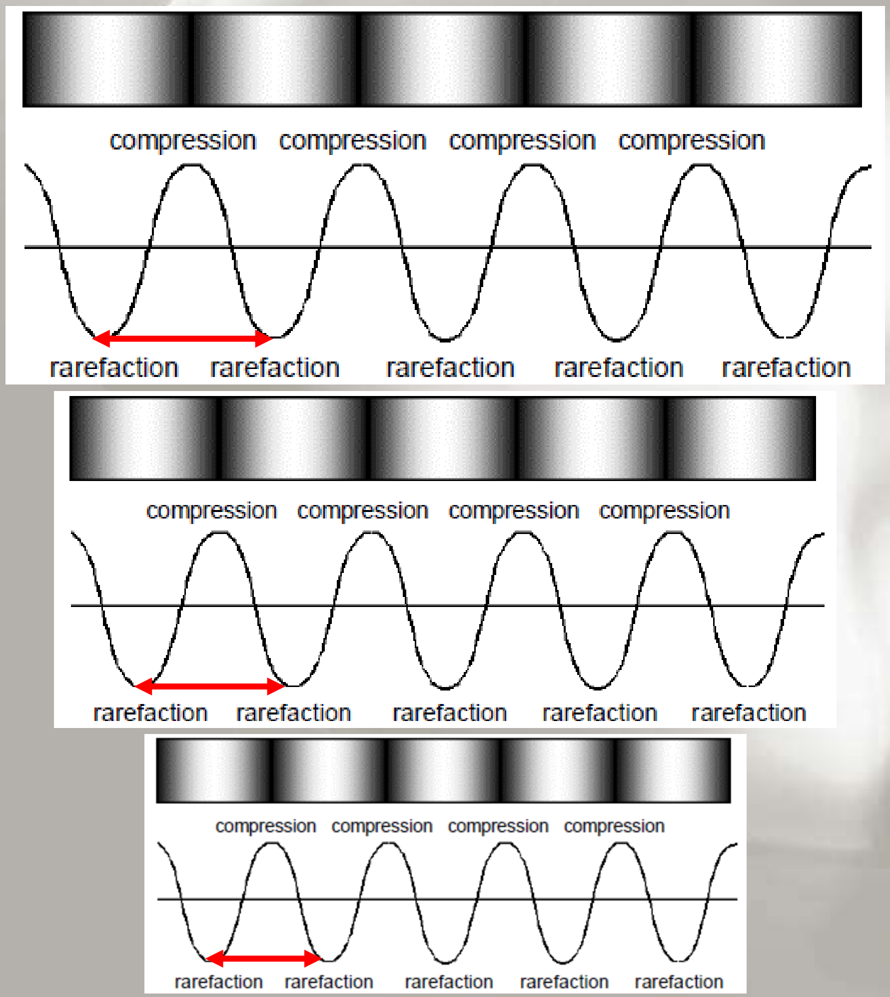
Medical diagnostic
Medical treatment
Chemical analysis
Some sonochemistry

Ultrasounds in Liquid Media



Acoustic factors:

Frequency



As the frequency of irradiation is increased so the rarefaction and compression phase shortens and this will have three consequences:

First consequence:

It will be necessary to increase the amplitude (power) of irradiation to maintain an equivalent amount of cavitation in the system.

In other words more power is required at a higher frequency if the same cavitational effects are to be maintained.

Ten times more power is required to make water cavitate at 400kHz, than at 10kHz. This is the main reason why the frequencies generally chosen for high power ultrasonic applications (e.g. emulsifying, cleaning) are between 20 and 40kHz.

Second consequence:

When the ultrasonic frequency is increased into the MHz region it becomes more and more difficult to produce cavitation in liquids. The simplest explanation for this, in qualitative terms, is that at very high frequency the rarefaction (and compression) cycle is extremely short.

The production of a cavity in the liquid requires a finite time to permit the molecules to be pulled apart so that when the rarefaction cycle approaches and becomes shorter than this time cavitation becomes difficult and then impossible to achieve.

It should also be recognised that transducers that operate at these high frequencies are not mechanically capable of generating very high ultrasonic power.

Third consequence:

At low frequency, where a long acoustic cycle exists, large bubbles are created.

At high frequency, the acoustic cycle is short and therefore the bubbles are smaller.

The consequence of smaller bubbles is a less violent cavitation collapse. Furthermore, the physical and chemical effects inside and outside the collapsing cavitation bubble also depend on frequency .

Acoustic factors:

Intensity

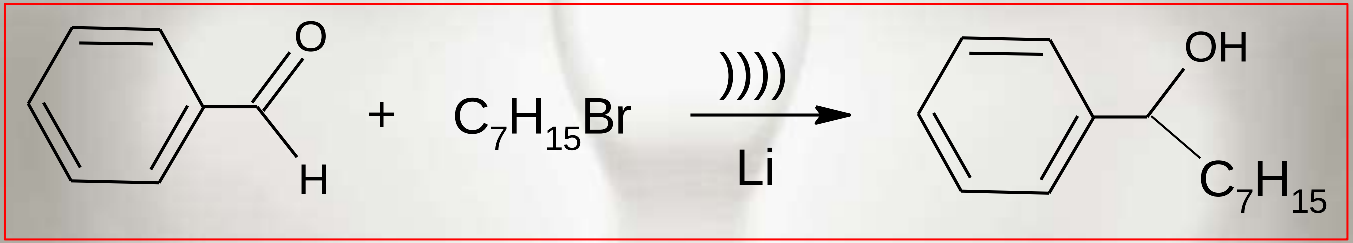
The acoustic intensity must exceed a threshold value in order to induce cavitation.

At low frequencies the intensities required are small (in air-saturated water the value is about 0.5 W/cm^2 at 20kHz).
A considerably higher intensity is necessary to obtain cavitation at higher frequencies.

However, in many chemical and non chemical processes instead of ultrasonic intensity the ultrasonic power density is used as much significant parameter for scale up of processes.

Example of ultrasonic parameter influence on a chemical reaction

Luche and co-workers have extensively studied the Barbier reaction. They have shown that the reaction rate strongly depends on both the temperature and input power (intensity).



*[Jayne C. De Souza-Barboza](), [Christian Petrier](), [Jean Louis Luche](), Ultrasound in organic synthesis. 13. Some fundamental aspects of the sonochemical Barbier reaction, J. Org. Chem., **1988**, 53 (6), pp 1212–1218.*

Power variation was achieved by varying the applied potential at the piezoelectric transducer. For both temperature and power, there is a clearly defined optimum value. A number of conclusions can be drawn from this work:

A minimum intensity for sonication is required to reach the cavitation threshold.

The viscosity of a liquid medium is increased when the reaction temperature decreases.

At higher viscosities cavitation is more difficult to induce (i.e. it requires higher powers) but this is to the benefit of sonochemistry in that more violent collapse of the bubble occurs.

When the reaction temperature is increased, the liquid viscosity decreases and the vapour pressure of the liquid increases. Under these circumstances cavitation is achieved at lower powers but the collapse will be less violent and overall the sonochemical effect will be reduced.

As the intensity at the vibrating surface increases beyond an optimum value the cavitation bubble density at the resonating face, "surface cavitation", restricts efficient transmission (coupling) of the ultrasonic energy to the bulk solution.

Acoustic factors: *Pulse*

Bubble formation and activity may be altered by pulsed ultrasound depending on the pulse width (a small number of cycles), shape of waveform and the interval between the pulses.

The effect of pulsed ultrasound depends especially on the ratio between pulse width and repetition interval (a more detailed discussion of this can be found in: A. Henglein, Ultrasonics Sonochem., 2 (1995) S115).

The pulsed ultrasound means that the on time will involve many thousands of cycles.

The influence of solvent

There are several solvent parameters which may influence cavitation: viscosity, surface tension, vapour pressure, thermal conductivity, compressibility, sound velocity and dissolved material.

For a more detailed discussion refer to the literature:

K.S. Suslick, "Ultrasound, Its Chemical, Physical and Biological Effects", VCH, Weinheim, 1988, T.G. Leighton, "The Acoustic Bubble", Academic Press, London, 1994, F.R. Young, "Cavitation", Mc Graw-Hill, London, 1989.

Solvent viscosity

The formation of voids or vapour filled microbubbles (cavities) in a liquid requires that the negative pressure in the rarefaction region must overcome the natural cohesive forces acting within the liquid. It follows therefore that cavitation should be more difficult to produce in viscous liquids where such forces are large.

The influence of solvent

Solvent surface tension

It might be expected that employing solvents with low surface tensions would lead to a reduction in the cavitation threshold. This is not a simple relationship but certainly where aqueous solutions are involved the addition of a surfactant facilitates cavitation.

Solvent vapour pressure

It is more difficult to induce cavitation in a solvent of low vapour pressure because the cavitation bubbles will contain less vapour from the solvent. A more volatile solvent will certainly support cavitation at a lower acoustic energy and produce vapour filled bubbles.

Since sonochemical effects are based upon the energy produced by cavitation bubble collapse, solvents with high vapour pressures generate vapour filled bubbles whose collapse is cushioned and therefore less violent than cavitation collapse in solvents of low vapour pressure.

Thermal conductivity, compressibility, sound velocity and dissolved material: not yet well documented

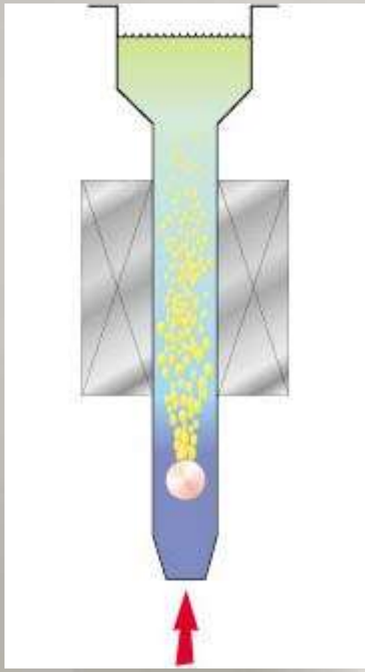
External factors

Bubbled gas

Dissolved gas, or small gas bubbles in a fluid can act as nuclei for cavitation and will lower the cavitation threshold. Ultrasound can also be used to degas a liquid. Thus at the beginning of the sonication of any liquid, gas which is normally entrapped or dissolved in the liquid promotes cavitation and is removed. Manufacturers instructions for the use of ultrasonic cleaning baths always suggest that the instrument is run for a short time until the water in the bath is ultrasonically degassed before using it for cleaning. This is because the bath is not producing its optimum cavitational effects until the gas is removed.

Many research groups deliberately introduce a gas by bubbling it into a sonochemical reaction in order to maintain uniform cavitation. According to theory the energy developed on collapse of these gas-filled bubbles will be greatest for gases with the largest ratio of specific heat $\gamma = c_p/c_v$. The ratio should be high as the collapse temperature is proportional to $(\gamma - 1)$. For this reason monatomic gases (He, Ar, Ne) are used in preference to diatomics (N_2, air, O_2). Gases such as CO_2 are less suitable. Increasing the gas content of a liquid not only leads to more facile cavitation but also to a reduction in the intensity of the shock wave released on the collapse of the bubble. If a soluble gas is used this will also provide a large number of nuclei in the solvent. The greater the solubility of the gas, the greater the amount which penetrates into the cavitation bubble, and the smaller the intensity of the shock wave created on bubble collapse. Furthermore, the smaller the thermal conductivity of the gas, the higher will be the local heating during the collapse.

Bubbled gas



The Gas Sparged Reaction Cell.

The GSR Cell allows gas to be introduced into the process solution directly within the ultrasonic reaction chamber. The steady state ultrasonic energy maximizes the diffusion rates at the liquid/gas interface.

http://www.advancedsonics.com/reaction%20cells.htm

External factors

External temperature

A rise in the ambient temperature decreases viscosity and surface tension as well as increasing the vapour pressure of the solvent. Thus, the cavitation threshold becomes lower and a lower intensity is necessary to induce cavitation. However, the bubble collapse is less violent as more vapour may enter the bubble (as above). A further factor that must be considered is that at higher temperatures, approaching solvent boiling point, large numbers of cavitation bubbles are generated concurrently. These will act as a barrier to sound transmission and dampen the effective ultrasonic energy from the source that enters the liquid medium. If a liquid were sonicated at its boiling point we would therefore not expect to obtain any great sonochemical effects.

External pressure

Increasing the external pressure will mean that a greater rarefaction pressure is required to initiate cavitation. Consequently bubble formation under such conditions will require a higher acoustic intensity than that required under atmospheric pressure. More importantly, raising the external pressure will give rise to a larger intensity of cavitational collapse and consequently an enhanced sonochemical effect.

The physical, chemical and biological effects of acoustic cavitation

Loomis et al. reported for the first time on the physical and biological [*R.W. Wood and A.L. Loomis, Phil. Mag. **4** (1927) 414****] as well as chemical effects [****W.T. Richards and A.L. Loomis, J. Am. Chem. Soc. **49** (1927) 3086****] of acoustic cavitation.***

The action of cavitation, either pulsation (stable bubble) or violent collapse (transient bubble), has dramatic effects in a solvent. There are three different theories about cavitation collapse - the hot-spot, the electrical and the plasma theory. But, for each theory, there is no doubt that the origin of sonochemical effects is cavitation.

The most popular and widely accepted theory is the so-called hot-spot theory.
conditions: temperatures of 2000 – 5000 °K and pressures of 1800 – 3000 atm inside the collapsing cavity were deduced from experimental data. Furthermore, the heated gas in the collapsing bubble is surrounded by a liquid shell at a temperature of 1500 – 2000 °K.

The plasma theory developed by Lepoint et al. [a) F. Lepoint-Mullie, **T. Lepoint** and R. Avni, J. Phys. Chem., **100** (1996) 12138.b) F. Lepoint-Mullie D. DePauw, **T. Lepoint**, P. Supiot and R. Avni, J. Phys. Chem.,**103** (1999) 3287, 3346] assumes that the cavitational collapse creates a microplasma highly charged with energy inside the collapsing bubble.

The electrical theory developed by Margulis [M.A. Margulis, Sonochemistry and Cavitation, Gordon & Breach, London, 1996] focuses on the development of strong electrical fields during an asymmetric collapse in the bubble. Such collapse results in an electrical discharge produced as the bubble fragments.

Physical effects inside the bubble

Within a few µs from the start of collapse (depending on the frequency and intensity) the motion of the imploding bubble walls reaches the speed of sound.

Heat conduction cannot keep up with the temperature increase due to the resulting adiabatic heating.

Numerical calculations of the adiabatic heating result in values for the gas temperatures inside the bubble of several thousand Kelvin and pressures of 1000 – 4000 atm depending on the conditions applied. Thus, extreme conditions are generated within a short-lived microcavity.

Suslick [K.S. Suslick, "Ultrasound, Its Chemical, Physical and Biological Effects", VCH, Weinheim, 1988, K.S. Suslick, D.A. Hammerton and R.E. Cline, J. Am. Chem. Soc. 108 (1986) 5781, K.S. Suslick, W.B. McNamara III and Y. Didenko, in "Sonochemistry and sonoluminescence", eds L.A. Crum, T.J. Mason, J. Reisse and K.S. Suslick (Eds.), Kluwer, Dordrecht, 1999] was able to verify the extreme conditions inside an acoustic bubble experimentally.

He studied the sonochemical decomposition of iron pentacarbonyl using sonoluminescence as a spectroscopic probe. From these measurements temperatures of around 5000 °K were estimated for the gas phase of the hot spot generated in the cavitation event. The liquid shell temperature was estimated to be around 1900 °K during a period of less than 100 ns. Therefore, cooling rates of more than 10^{10} °K/s were deduced for this process. The pressure inside the collapsing bubble was calculated from experimental data to reach 1700 atm [K.S. Suslick and K.A. Kemper, in "Bubble dynamics and interface phenomena" eds J.R. Blake, J.M. Boulton-Stone and N.H. Thomas, Kluwer, Dordrecht, 1994].

Physical effects inside the bubble

Assuming an adiabatic collapse, the temperature inside the bubble the pressure and temperature at the end of the bubble collapse p and T may be calculated according to following equation :

$$P = [P_v + P_{g0}(R_0/R_{max})^3]\,(R_{max}/R)^{3\gamma}$$

$$T = T_\infty\,(R_{max}/R)^{3(\gamma-1)}$$

Where:

P_v is the vapor pressure;

$P_{g0} = p\infty + (2\sigma/R_0) - P_v$ is the gas pressure in the bubble at its ambient state;

R_0 is the ambient bubble radius;

γ is the ratio of specific heats capacities (c_p/c_v) of the gas/vapor mixture;

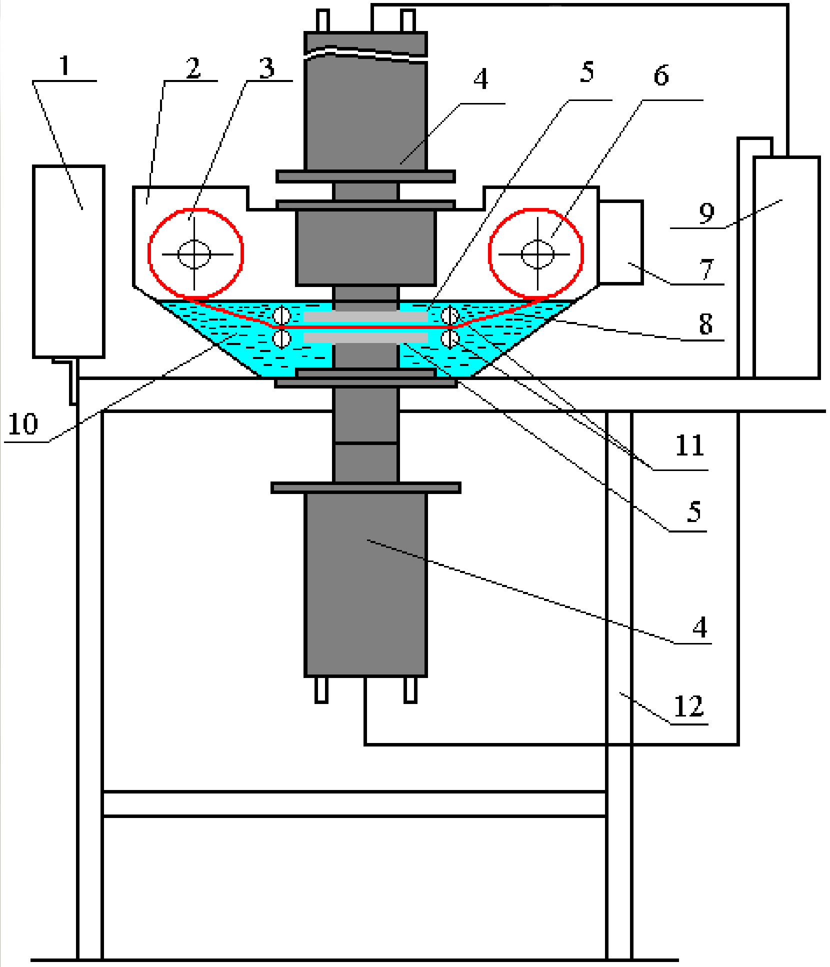
T_∞ is the bulk liquid temperature;

R_{max} is the maximum radius of the bubble.

An optimum bubble temperature of about 5200 ± 200 K and pressure of about 250 ± 20 MPa were found for a range of 20–1000 kHz

Slimane Merouani, Oualid Hamdaoui, Yacine Rezgui, Miloud Guemini, Theoretical estimation of the temperature and pressure within collapsing acoustical bubbles, Ultrasonics Sonochemistry 21 (2014) 53–59.

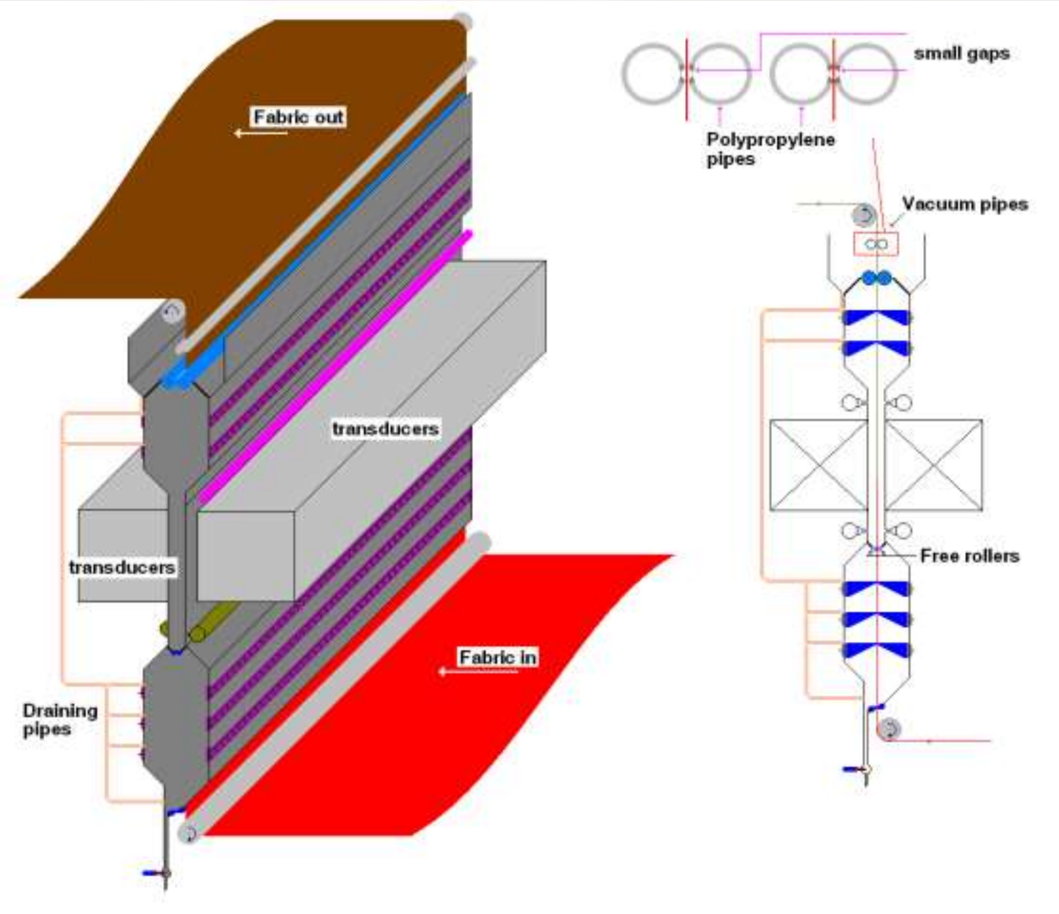
Ultrasonic textiles finishing



Legend:

1 – control panel;
2 – reactor;
3 – releasing spool;
4 – magnetostrictive transducers;
5 – sonotrode system;
6 – winding spool;
7 – motor;
8 – fabric;
9 – ultrasonic power supply generator;
10 – solution of reagent;
11 – directing rollers;
12 – frame.

Ultrasonic textiles finishing



SONO final report

http://cordis.europa.eu/docs/results/228/228730/final1-publishable-report-with-figures.pdf

Ultrasonic textile's new properties

On 03 December 2015:

Mircea Vinatoru, Timothy Mason and Jamie Beddow

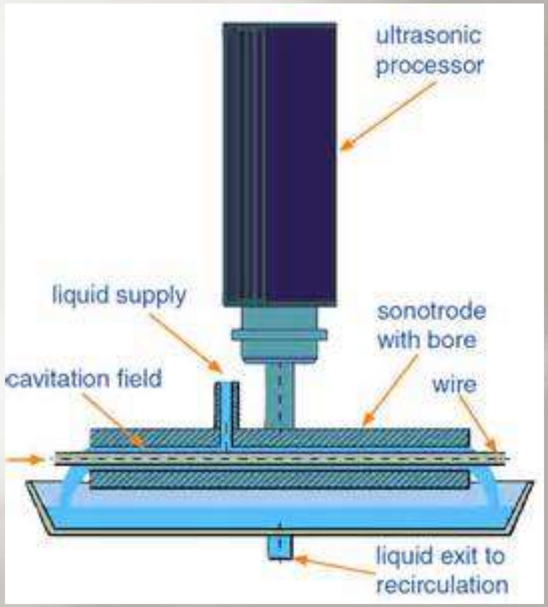
We got the WO patent: 2016/087864 A1

FOR:

Method for producing antimicrobial yarns and fabrics by nanoparticle impregnation

The invention relates to a method for producing an antimicrobial fabric or yarn, said method comprising the steps of immersing a fabric or yarn in an aqueous solution of a metal salt whilst simultaneously subjecting said solution to ultrasonic radiation; and removing the fabric or yarn from said solution and subsequently converting the metal salt in situ in the fabric or yarn into metal oxide nanoparticles, preferably via chemical and heat treatment. Fabrics and yarns obtained or obtainable by such method are also provided. In a further aspect the invention provides an apparatus for performing such method.

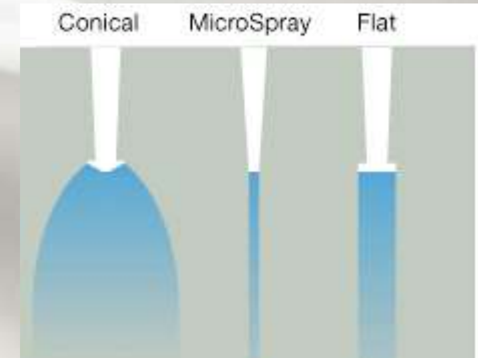
Cleaning general surface cleaning; washing of soil and ores

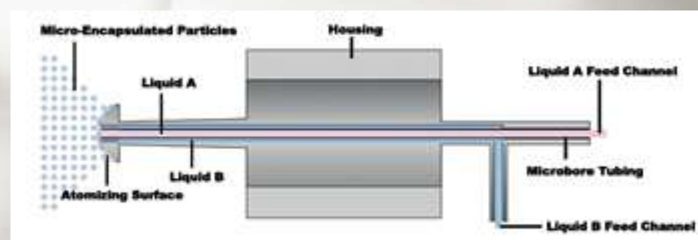


Homogenisation emulsification liquids

Emulsification of vegetable oil with methanol to make biodiesel

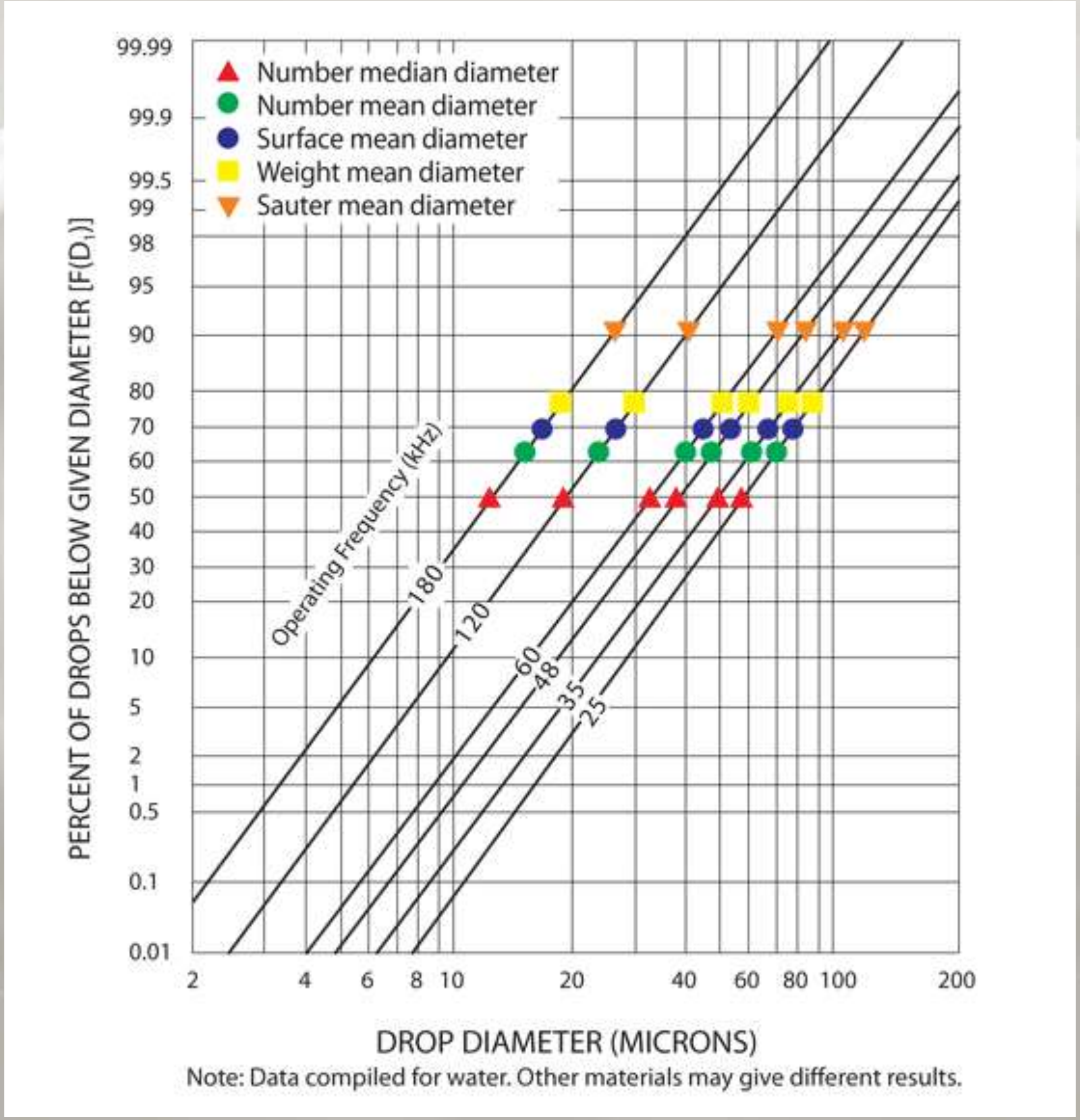
Homogenisation/Spraying *atomisation of liquids*





http://www.sono-tek.com/

Homogenisation/Spraying atomisation of liquids



http://www.sono-tek.com/drop-size-and-distribution/

Homogenisation/Spraying atomisation of liquids

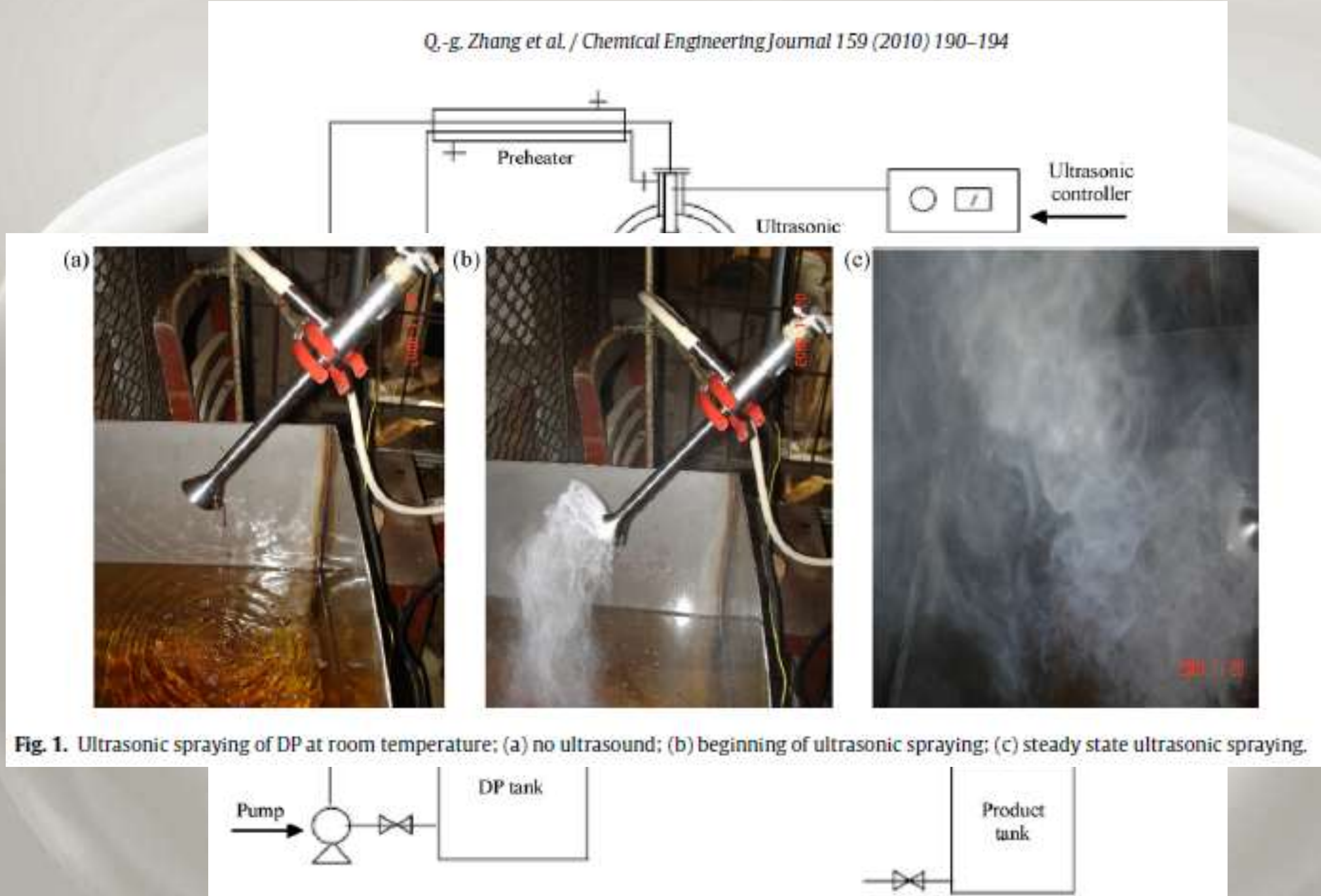


Fig. 1. Ultrasonic spraying of DP at room temperature; (a) no ultrasound; (b) beginning of ultrasonic spraying; (c) steady state ultrasonic spraying.

Scheme 1. Equipment of DP dehydrogenation using ultrasonic or common spraying.

Qui-ge Zhang, Ling-wu Bi, Zhen-dong Zhao, Yuan-ping Chen, Dong-mei Li, Yan Gu, Jiang Wang, Yu-xiang Chen, Cai-ying Bo, Xian-zhang Liu, Application of ultrasonic spraying in preparation of p-cymene by industrial dipentene dehydrogenation, Chem. Eng., 159, 1-3, May 2010, 190-194

Ultrasonic Spray Dry Unit

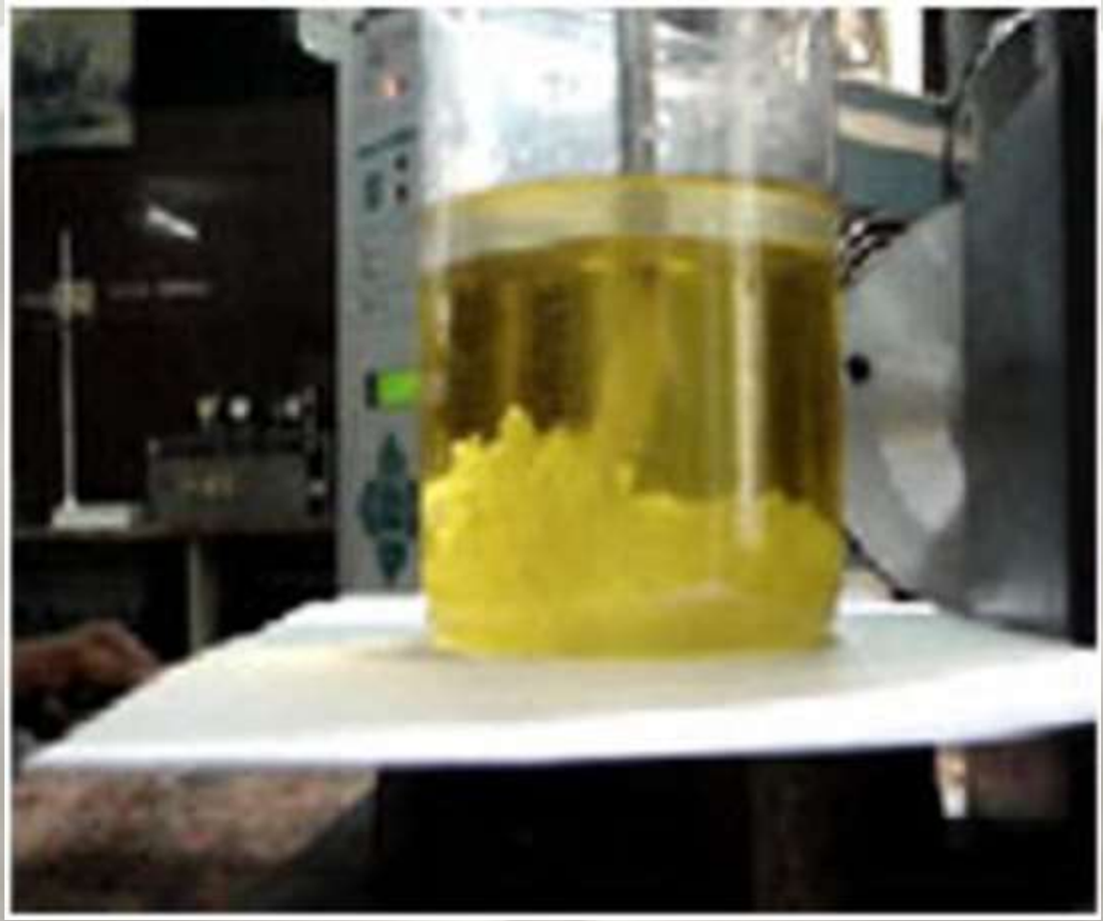
https://www.youtube.com/watch?v=bn_ZD5R27O4

SYNETUDE Company
France

Sake improved using ultrasonic atomization

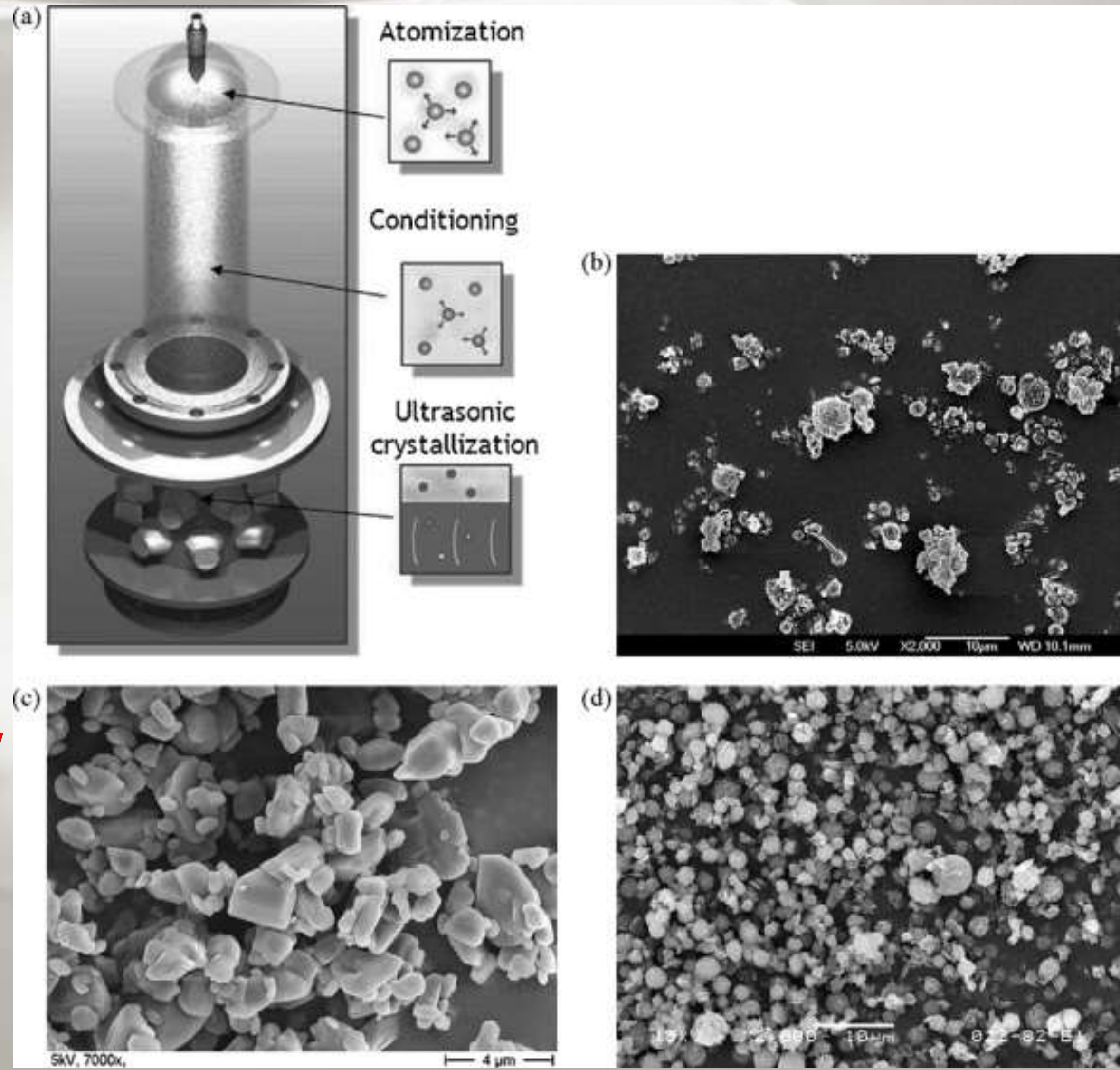
S. S. Nii, K. Matsuura, Application of ultrasonic atomization to production of a high-quality Japanese sake and ethanol-enrichment from its aqueous solution,
Mater. Integr. 18 (2005) 12–16 (in Japanese).

Separation crystallisation



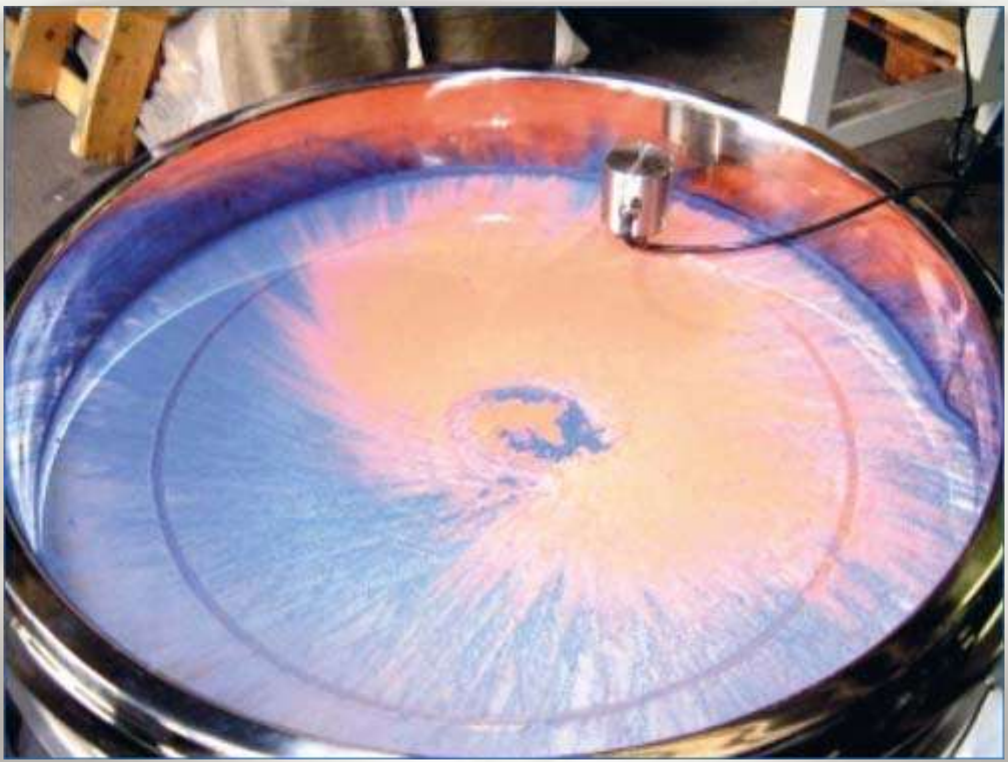
http://mumbai.all.biz/ultrasonic-crystallization-g324141#.WGY-xxt97cs

Ultrasonic crystallisation (courtesy of Prosonix, UK): (a) schematic SAX process; (b) corticosteroid prepared normally; (c) corticosteroid prepared normally then micronized; (d) corticosteroid prepared by the UMAX system



G. Ruecroft, et al., Process for improving crystallinity, WO2010/007447 (2010).

Separation sieving



http://www.sodeva.com/en/ultrasonic-sieving-soniscreen/

Too small. Could create filtrations problems

Too big. Ultrasonic extraction will be inefficient

< 0.1 mm

> 0.5 mm

0.1 – 0.5 mm

The right particles sizes should be established for each particular herb

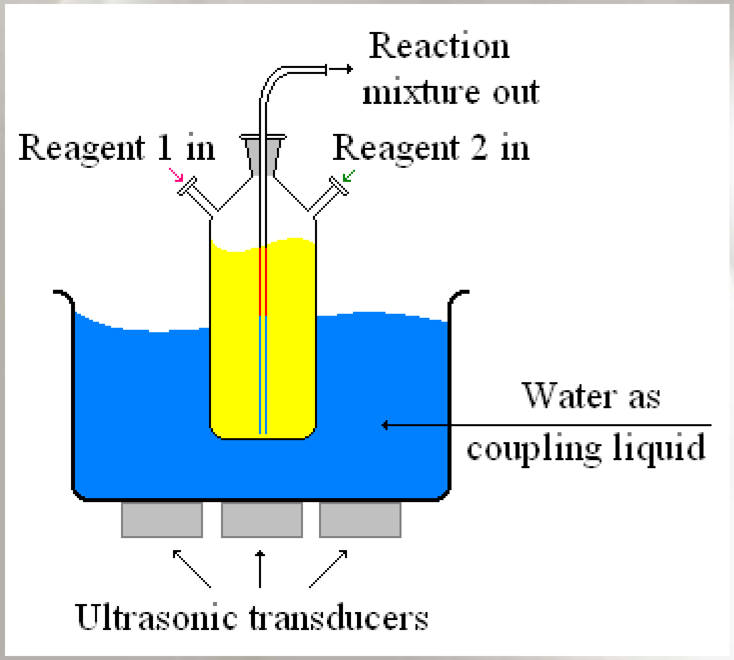
https://www.youtube.com/watch?v=6xxEcyPxjwA

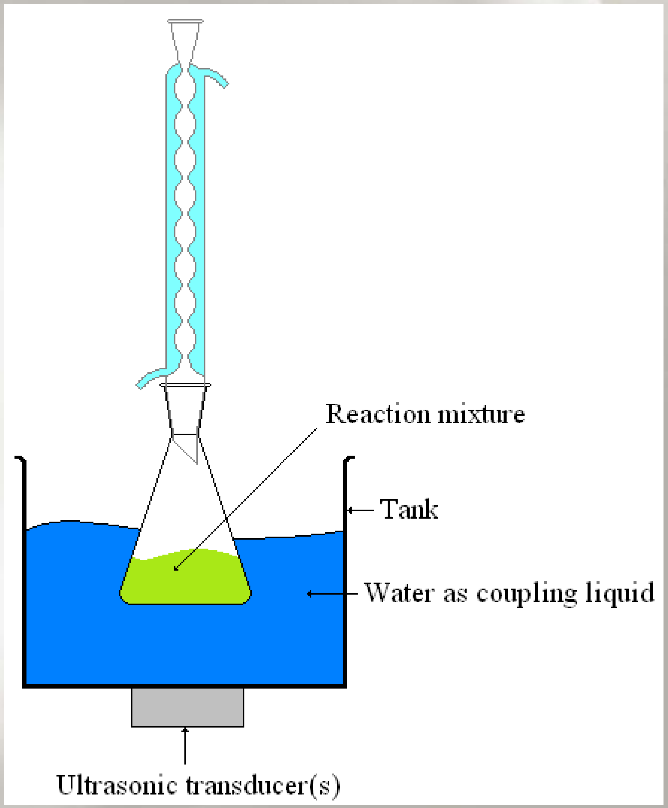
Separation filtration

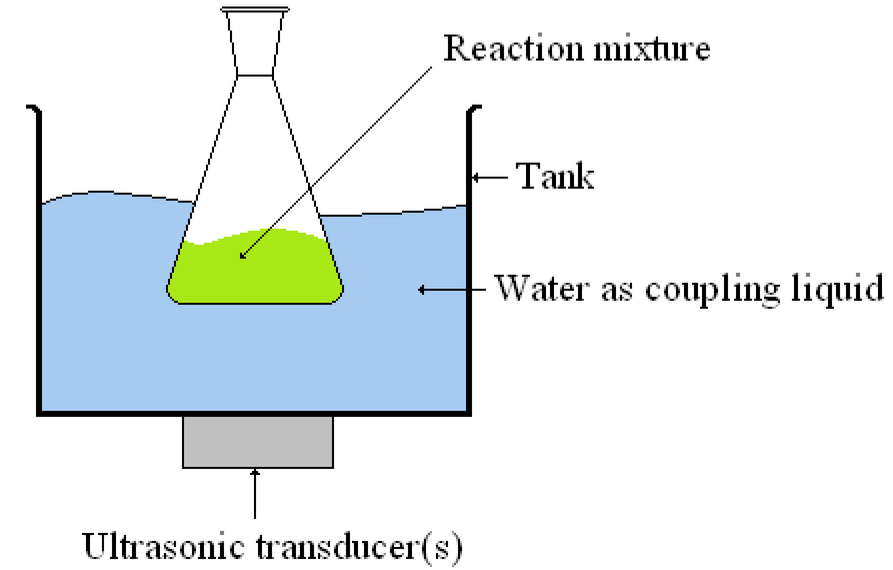
http://acoustics.org/pressroom/httpdocs/167th/4aPA3_McCarthy.html

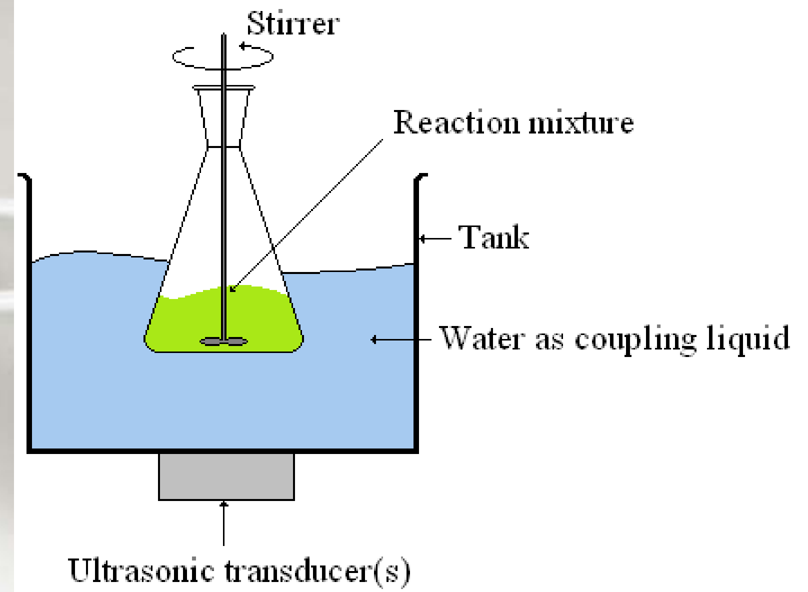
Degassing treatment of HPLC eluents

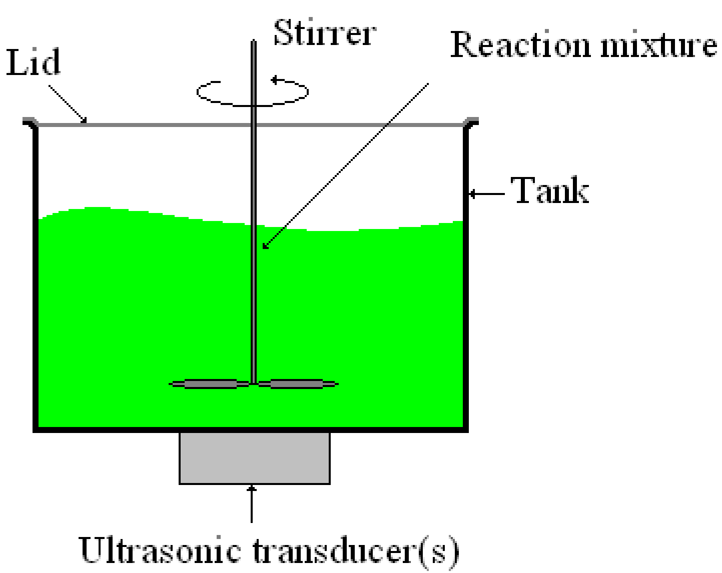
Using an ultrasonic cleaner for chemical reactions

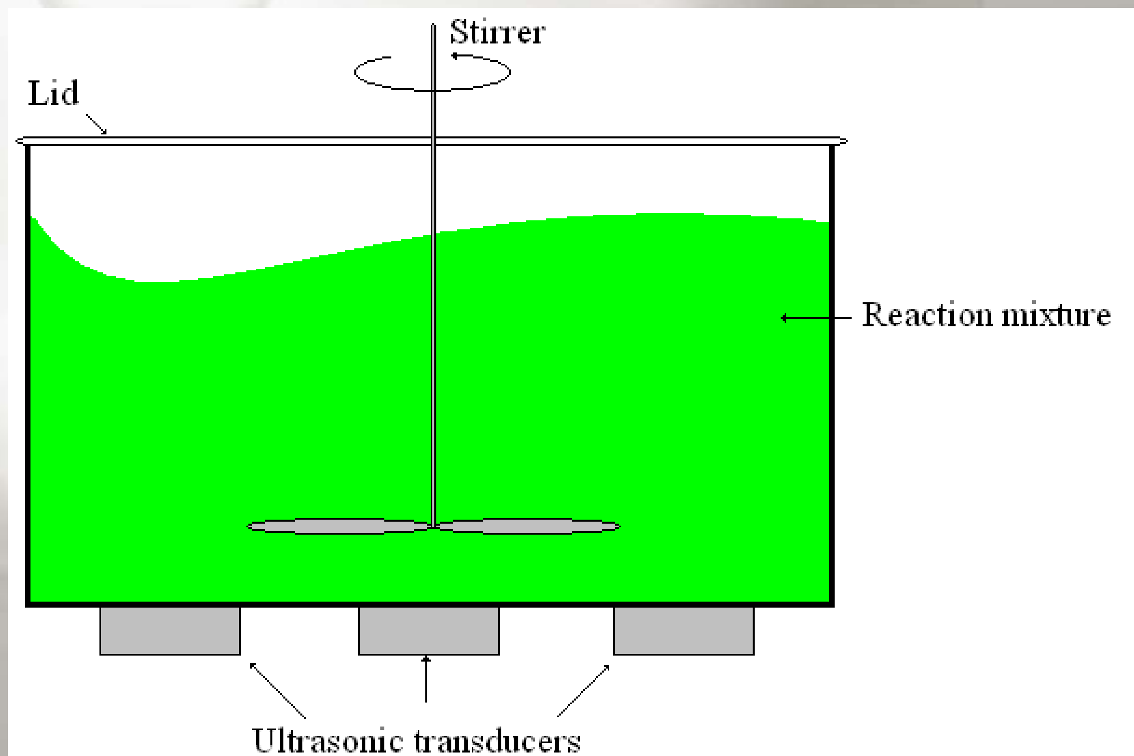

Reaction
mixture out
Reagent 1 in
Reagent 2 in
Water as
coupling liquid
Ultrasonic transducers


Reaction mixture
Tank
Water as coupling liquid
Ultrasonic transducer(s)


Reaction mixture
Tank
Water as coupling liquid
Ultrasonic transducer(s)


Stirrer
Reaction mixture
Tank
Water as coupling liquid
Ultrasonic transducer(s)


Lid
Stirrer
Reaction mixture
Tank
Ultrasonic transducer(s)


Stirrer
Lid
Reaction mixture
Ultrasonic transducers

Bio-refinery

Fuels

Solvents

Bulk chemicals

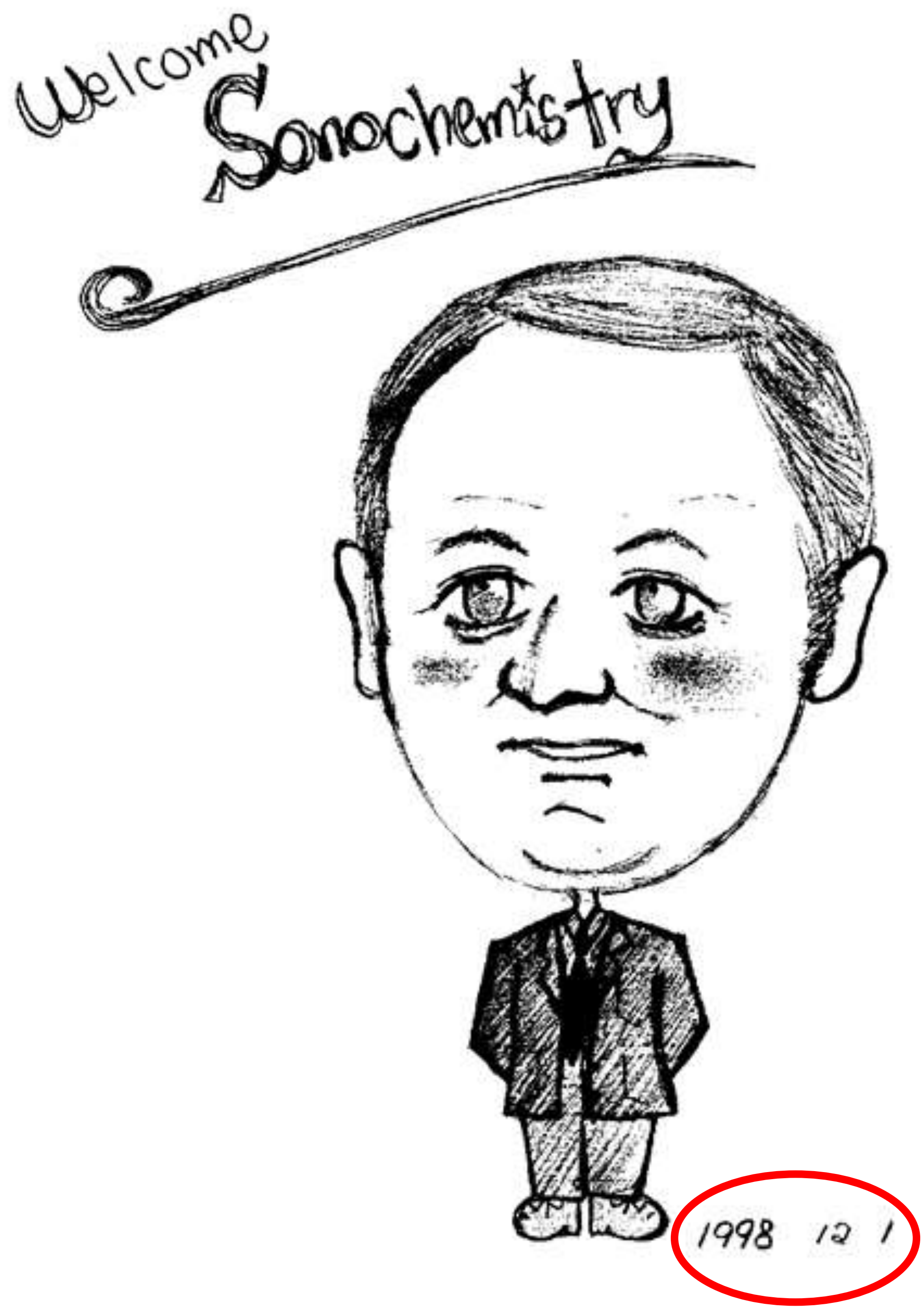
Plastics

Fibers

Fine chemicals

Oils

Adapted after:
Dr. Jeff Hardy, Green Chemistry Teaching Associate, The University of York, Department of Chemistry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