

Design and Optimization of a Multi-Purpose, High-Power Ultrasonic Reactor

L.Spicci

Everywave Srl, Via Martiri delle Foibe 2/1, 35010, Vigonza (PD), Italy

Introduction

Today many industrial production lines of fluid products require special treatments, such as: deagglomeration, dispersion, homogenization, emulsion, special mixing or catalysis of chemical reactions. Such effects can be obtained through cavitation in a closed ultrasonic reactor, in which it is possible to reach very high sonication intensity. Speaking of a 'flow-cell' type reactor, the ultrasonic power must be enough to process the product in the time available, so very high power ratings of the order of kW or even tens of kW may be necessary.

As reported in the present paper, COMSOL Multiphysics® was used to design the special reactor, consisting in: a high-power piezoelectric converter, a cylindrical flow cell, and a special sonotrode, with 'tuned rings'. A 'tuned ring' sonotrode is very complicated to design because the geometry of the rings must be determined in order to have both high-pressure field levels in the surrounding fluid, both limitation of spurious resonances modes. Moreover, the flow cell and the piezo-transducer must be optimized with great care, in order to have maximum efficiency and minimum thermal losses. Therefore the system was designed with a parametrized piezo/structural/acoustic COMSOL Multiphysics® model and a complete optimization process was performed.

The simulation results were up to the required level of efficiency and very high ultrasonic pressure values can be obtained in the reactor.

Finally, a reactor prototype was built and used for a sonochemical application project. The results from the chemical reaction module are reported too.

High power Ultrasound and Cavitation

Sonochemistry and ultrasonic processing of fluid products are based on the phenomenon of cavitation.

While cavitation is the most well-known phenomenon linked to the passage of ultrasound through a liquid medium, it is also perhaps the least understood [1].

Cavitation in a liquid occurs due to the stresses induced in the liquid by the passage of a sound wave; in fact the sound waves consist of compression and decompression: if the pressure during the decompression cycle is sufficiently low, the liquid can be torn to pieces to leave small bubbles.

These cavitation bubbles (similar to those seen from the action of a propeller of a boat on water) are the heart of the sonochemistry systems. Being subject to

the stresses induced by sound waves, the bubbles grow during a decompression phase and contract or even implode during a compression phase. The bubbles can be filled with steam and gas and can produce radicals during implosions. It is these implosions that are the high-energy part of sonochemistry: each of these imploded bubbles can be seen as a micro-reactor, with actual temperatures reaching an estimated 5000 ° C and pressures of several hundred atmospheres [2],[3].

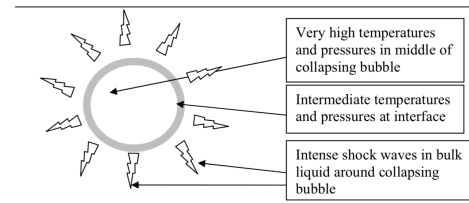


Figure 1: cavitation

These extreme conditions are believed to be responsible for manipulating the kinetics of reactions. Moreover, at the moment of the collapse of the bubbles, powerful shock waves occur. These shocks are believed to be responsible for breaking nearby solids (which may be the walls of reactive solids) and also lead to the generation of shear forces and vortices [1] which in turn can lead to an increase in turbulent energy dissipation.

In industrial applications such as deagglomeration, dispersion, homogenization, emulsion, the strength of ultrasonic mixing can be explained as a special phenomenon of turbulence, due to the shock waves generated by the implosion of cavitation bubbles, which can lead to large increases in the mass transfer coefficient with respect to traditional mixing systems. Of course shock waves originated from cavitation are related to the intensity and frequency of the ultrasonic wave.

It should be noted that some bubbles, depending on their size and applied ultrasonic conditions, cannot collapse and instead undergo growth and shrinkage at a frequency equal to that of the sound wave.

Cavitation is classified mainly as two types, transient and stable.

The type of cavitation that occurs mainly depends on the energy introduced: at higher intensities (10W/cm²), transient cavitation predominates, while at lower energy levels (1-3W/cm²) stable cavitation takes place. The two types of cavitation translate into bubbles that show very different behaviors.

Transitory cavitation bubbles exist for a maximum of a few acoustic cycles and expand at a radius of at least twice their initial size, before collapsing, after which they disintegrate into smaller bubbles or dissolve in most of the solution, under the action of large forces due to surface tension. The life of such bubbles is too small and mass transfer is not assumed to occur across their borders. Their collapse results in extreme temperatures and pressures close to collapsing surfaces.

Stable cavitation bubbles oscillate, usually not linearly, on an equilibrium size for many acoustic cycles. These bubbles exist for time scales long enough to allow mass diffusion and thermal diffusion, with the consequence that vapor evaporation and condensation will continue to occur. The oscillation of the size of the stable bubbles results in a slightly milder temperature rise [1].

Some of the factors that influence cavitation are the following [4]:

- Presence and nature of dissolved gases: they act as nucleation sites for cavitation, soluble gases decrease cavitation effects and vice versa.
- Temperature: the increase in temperature causes a decrease in the sonochemical effect because high temperatures lead to bubbles that largely contain steam, which reduces the ultrasonic energy produced by cavitation.
- Pressure: the increase in pressure causes an increase in the sonochemical effect due to the greater intensity required to cause cavitation.
- Choice of solvent: cavities are formed more easily when solvents with high vapor pressure, low viscosity and low surface tension are used.
- Ultrasonic frequency: low frequency ultrasounds produce more violent cavitation, leading to higher temperatures and pressures. Instead high frequency can increase the number of free radicals (highly reactive species) in a system, although cavitation is less violent due to the fact that more cavitation events may occur.

Simplified model for Sonochemistry models

As regards the acceleration of a chemical reaction caused by ultrasounds, a possible approximation can be considered, as follows.

As previously reported, the acceleration of chemical reactions due to ultrasound is generated by the cavitation effect that takes place in the solvent and is responsible for very high microscopic pressures and temperatures.

If one focuses only on the thermal effect of cavitation (neglecting sonoluminescence, pressure shock waves, formation of radicals and other effects), it is possible to describe the acceleration of reaction with the Arrhenius equation. Indeed, turning to reaction kinetics (assumed of 1st order), if the pressure of the

local ultrasonic field exceeds the Blake pressure value (of the order of 0.1MPa), it is possible to consider the following interaction [5]:

$$-R_{rx} \left[\frac{mol}{m^3s} \right] = [(\hat{p} > p_{G,Blake})\beta k_{son}c] + [(1 - \beta)k_1c] \quad \text{Eq.1}$$

Where: R_{rx} is the reaction rate, $p_{G,Blake}$ is the Blake pressure, β is the cavitation volume fraction, c is the concentration, k_{son} , k_1 are the reaction constants with and without ultrasound.

In Eq.1 it is possible to observe that the reaction consists of a part relating to the areas 'without cavitation' and a part relating to the areas 'with cavitation'.

Therefore it is possible to describe the reaction acceleration with the following Arrhenius equations:

$$k_{son} = A \cdot e^{\frac{-E_a}{RT_{max}}}, \quad k_1 = A \cdot e^{\frac{-E_a}{RT_{liq}}}, \quad T_{max} = \frac{T_{liq}\hat{p}(\gamma-1)}{P_v} \quad \text{Eq.2}$$

Where: T_{max} is the temperature at a point of cavitation collapse, T_{liq} is the temperature of the liquid, p is the acoustic pressure and P_v is the vapor pressure of the solvent.

So it's possible to identify the following link:

Ultrasound >> cavitation >> temperature increase >> Modified Arrhenius equation

as a simplified modeling criterion for many possible Sonochemistry simulations.

Thus, if one is developing a chemical reaction FEM and has to define the effect of ultrasound through cavitation, a way is to consider a 'tuned' thermal power source within the chemical model. That approach was used in the final part of the work, where the results from the acoustic model were transferred to a chemical reaction model where a special experiment was modelled and analysed.

Ultrasonic Reactor

The 3D model of the ultrasonic reactor is reported in figure 2 (with virtual slot to see the sonotrode inside).

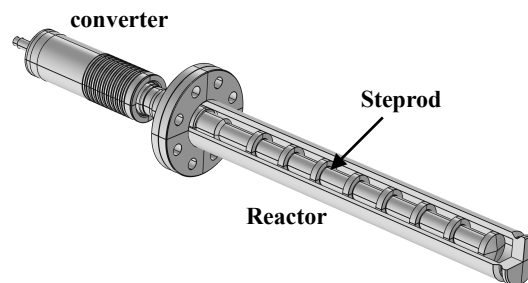


Figure 2: ultrasonic reactor

The system consists of three parts (see fig.2) :

- 20kHz piezoelectric transducer or ‘converter’
- Sonotrode with ‘tuned rings’, named ‘steprod’
- Cylindrical reactor or ‘flow-cell’

The electromechanical transducer or ‘converter’ is based on a standard ‘Langevin structure’, but with many design details and innovations to get the maximum efficiency. It is based on a stack of six Hard-PZT-8 piezoelectric rings, pre-stressed through a central bolt and operating electrically parallel, mechanically series.

As regard the special sonotrode with tuned rings named ‘steprod’, it is a very complicated part to design because the geometry of the rings on the rod must be studied carefully to guarantee a high level of pressure field in the surrounding fluid and, on the other hand, to limit spurious resonances close to the main one, which are generated by the complex geometry.

Also the geometry of the surrounding cylindrical reactor is important for the optimization of the main resonance and for the homogeneity of the pressure field in the fluid.

The electro-mechanical system is therefore critical to design and optimize, in order to yield very high acoustic power densities, as required for the industrial applications.

Finally, the voltage generator that drives the converter is of fundamental importance for the system efficiency. Indeed, the voltage generator is a high technology device (Titako generator, Unitech Srl [6]), equipped with a smart electrical impedance analyzer that ensures in real time the best operating conditions when the acoustic load on the transducer varies : such generator is autonomously able to perform a search for the optimal operating point by varying the control frequency of the transducer and detecting the corresponding minimum electrical impedance Z_{min} and maximum $\cos(\varphi)$.

Model description

A detailed FEM for the ultrasonic reactor was built using COMSOL Multiphysics® 5.4, making use of Solid Mechanics, Piezoelectric, Acoustics and Chemical Reaction module for the final part.

First a brief description of the Structural & Piezoelectric model is reported.

Axial symmetry was exploited to reduce model dimensions and computation time. Mesh on all domains was chosen as free tetrahedral and element size was always less than a fifth of signal wavelength.

As already mentioned, the electro-mechanical converter is based on a prestressed stack of six Hard-PZT-8 piezoelectric rings that work electrically

parallel, mechanically series. Hard PZT-8 type ceramic is chosen as active medium, due to its exceptionally high efficiency and Q factor.

A sketch of such transducer is reported in figure 3. Two very important parts to design in such device are the metallic masses that enclose the piezoelectric stack, since they are responsible for : tuning, efficiency and vibration amplitude symmetry (or desired asymmetry) of operation. They are generally called ‘backmass’ and ‘frontmass’ and, in the present design, are made of Aluminum and Titanium respectively. The frontmass must also include a mechanical suspension system, in order to decouple radial undesired vibration modes.

In the present work, the converter was designed to operate with a resonance frequency of 20kHz.

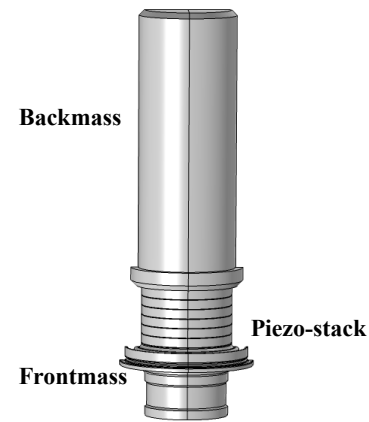


Figure 3: 20kHz ultrasonic converter (without cover)

As regard piezoelectricity, the constitutive equations for the material are [7], in *stress-charge* form :

$$\begin{cases} \mathbf{T} = [\mathbf{c}^E] \mathbf{S} - [\mathbf{e}'] \mathbf{E} \\ \mathbf{D} = [\mathbf{e}] \mathbf{S} + [\boldsymbol{\epsilon}^S] \mathbf{E} \end{cases} \quad \text{Eq.3}$$

where \mathbf{T} is the stress vector, \mathbf{c} is the elasticity matrix, \mathbf{S} is the strain vector, \mathbf{e} is the piezoelectric matrix, \mathbf{E} is the electric field vector, \mathbf{D} is the electric displacement vector, $\boldsymbol{\epsilon}$ is the dielectric permittivity matrix. The superscripts indicates a zero or constant corresponding field. Eq.(3) take into account both piezoelectricity, both mechanical and electrical anisotropy of the material.

Once these matrices have been specified, COMSOL recognizes which equations domains are to be used inside the FEM elements.

Piezoelectric Material and Electrostatics were imposed on the six piezoceramic rings inside the transducer, were ground and electric potential were set alternately to get electrical parallel connection.

Next the special sonotrode was designed and optimized.

The ‘tuned rings’ of the ‘steprod’ are needed to increase the coupling surface and get stronger cavitation in the surrounding fluid, but need to be designed carefully, along with the sonotrode total length, to perfectly match the converter resonance frequency.

Some zooming of the complete axial-symmetric mechanical model are reported in figure 4, with meshed surfaces :

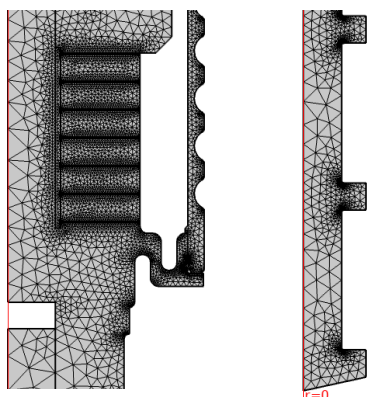
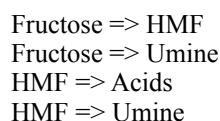


Figure 4: axial-symmetric mesh : piezo stack and

Then the cylindrical reactor (or ‘flow cell’) surrounding the steprod was designed, so that the acoustic domain could be determined and analysed. Of course the acoustic-structure interaction is automatically set on the steprod surface.

In the Acoustic module it is possible to study the pressure field generated by the steprod, to check for the required pressure level for industrial applications. Moreover, it is possible to set a power loss in the fluid, due to cavitation, that can be used in the Chemical Reaction module as heat source/reaction accelerator (as described in previous paragraph).

The chemical reaction module was developed to study a specific reaction, as follows. An important application for the reactor is the dehydration reaction of monosaccharides to give *Hydroxymethylfurfural* ‘HMF’, in particular for aqueous monophasic systems using fructose as the starting substrate. The acid-catalyzed dehydration reaction of fructose to give HMF includes several secondary reactions. However, the main by-products in aqueous medium are formic acid and levulinic acid and the condensation polymeric compounds, the ‘umines’, corresponding to the following reactions:



In particular, together with the HMF, the umines are by-products of considerable importance for the final product application.

Here is a picture of the Chemical Reaction model tree, along with Transport, Heat transfer and Fluid flow modules :

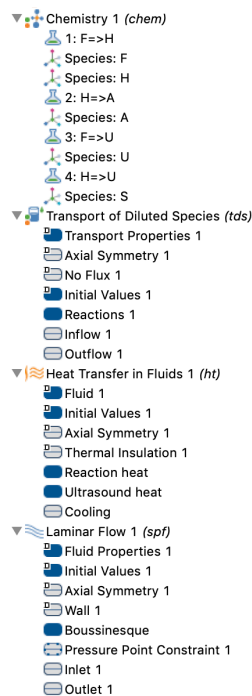


Figure 5: Chemical model tree : F=Fructose, H=HMF, A=acids, U=umines, S=solvent

Of course activation energy, frequency factor, enthalpy and initial concentration was specified for each species.

Solvent is water and reactor volume is approx. 1 liter. Forced fluid flow was taken into account (inlet, outlet in laminar flow and Transport modules, fig. 5) as the reactor is going to work as a flow-cell in the specific industrial application with inflow in the lower part and outflow on top (close to converter).

Simulation Results

The most important results of simulations are reported here.

The following data are the result of the complete optimization process, which is not described for the sake of brevity.

First the frequency analysis for the mechanical vibration of converter+steprod assembly is reported, so that the main resonance frequency is defined.

Driving power is approx. 1.5kW for the following results.

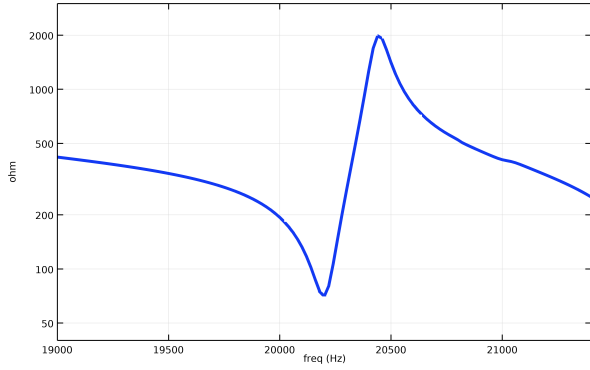


Figure 6: electrical impedance

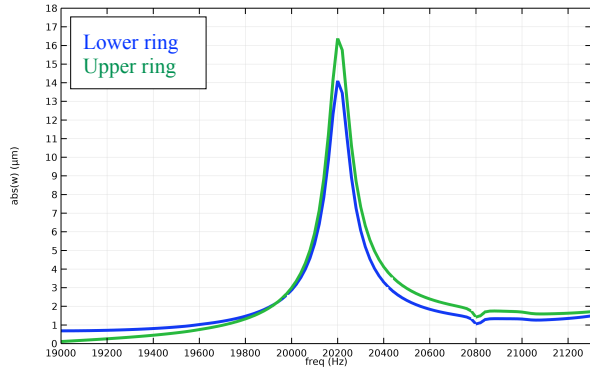


Figure 7: vibration amplitude

Clearly a strong resonance is present at 20.2kHz, as required. The electrical impedance is approx. 80Ω and vibration amplitude is approx. $15\ \mu\text{m}$.

Next, in the acoustic domain it's possible to check the Pressure map in the fluid, at resonance frequency, with 2kW driving power, as follows :

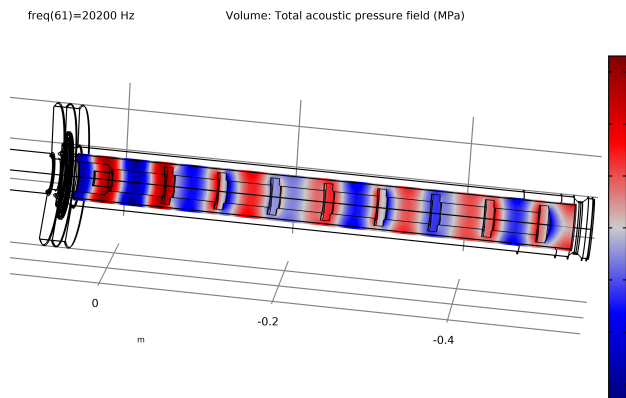


Figure 8: Pressure field

More than 3MPa of ultrasonic pressure amplitude are available at 20kHz (with max values close to the rings) which is enough to get strong cavitation phenomena in the fluid.

Finally and most important, the chemical reaction results should indicate if the reactor is capable to trigger the chemical synthesis reaction of HMF from fructose solution.

Starting with a fructose concentration of $100\text{mol}/\text{m}^3$ and accounting for the cavitation generated by ultrasound as heat source, it is possible to get the following reaction kinetics, parametrized with respect to selected fluid flow and ultrasound power values :

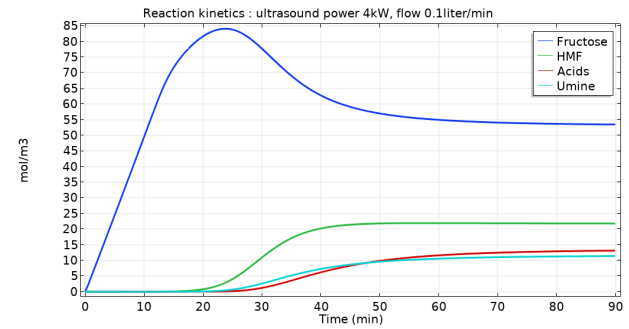
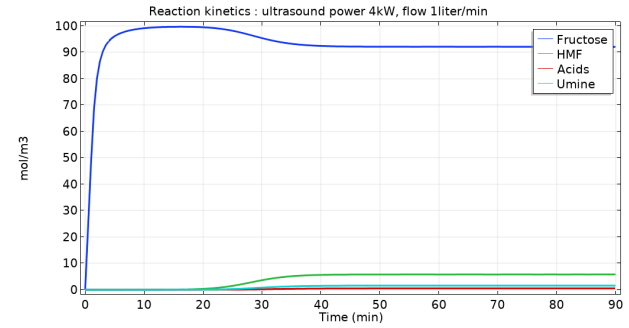
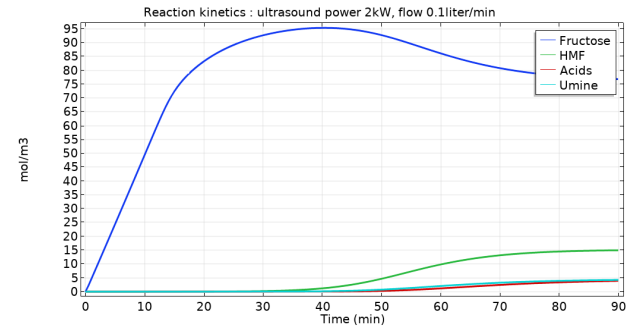
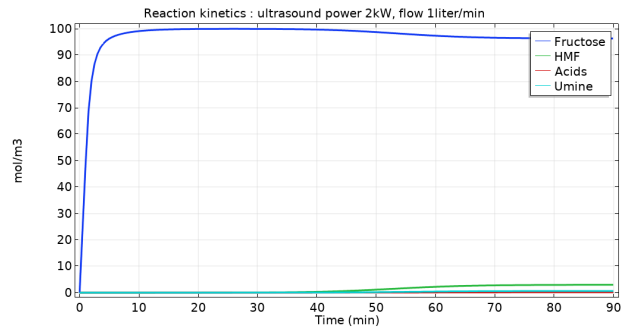


Figure 9: HMF synthesis kinetics for different values of flow (0.1; 1 liter/min.) and ultrasonic power (2; 4kW)

As it's clear from figure 9, products yield is highly dependent on fluid flow and ultrasound power which is equivalent to say that indeed the ultrasonic field can trigger and control the chemical reaction.

The best HMF and umine yield and lower reaction time occurs, as can be guessed, for max. ultrasonic power (4kW) and lower fluid flow (that corresponds to a longer reaction time). In this case, product concentrations get stationary after 40min. of sonication with stronger HMF yield.

Of course a larger ultrasonic power and a lower fluid flow both increase product yield and reduce reaction time, as can be seen from figure 9.

Finally, products concentration 3D maps are very interesting, as they show how chemical reaction is stronger, as desired, close to the steprod rings. As an example, the HMF concentration (after a significant reaction time) follows.

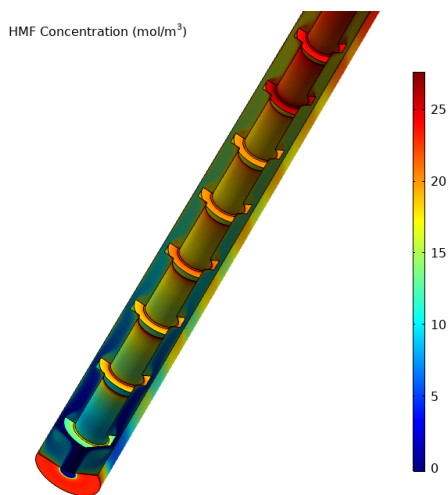


Figure 10: HMF concentration after 80min., with fluid flow = 0.1 liter/min., ultrasonic power = 2kW

Prototype and experimental results

A prototype was manufactured according to the FEM design, in order to validate the model and to perform the chemical reaction described above.

The prototype can be seen in figure 11, with the steprod visible inside a plexiglass tank filled with water, instead of the flow-cell steel reactor.

As can be seen from the Titako generator screen, resonance frequency was 20.3kHz, in very good agreement with simulation results.

Moreover, a very high level of cavitation was present at driving power above 500W during testing and it was clearly stronger close to the sonotrode rings, as expected. On the Titako generator it was possible to record the electrical impedance Z_{min} and $\cos(\varphi)$ at resonance, with values of 120 Ω and 0.8 respectively (figure 11). Last value corresponds to a good power transfer efficiency.

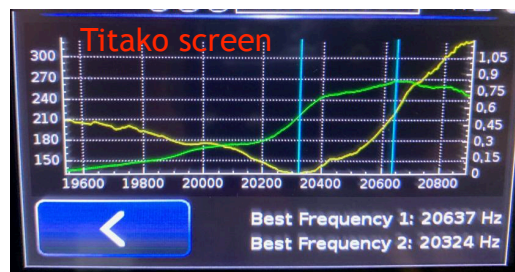


Figure 11: Experimental testing on prototype

Finally, complete Sonochemical reaction tests will be performed by the end of the year, but 'batch' test already confirmed that the reactor is capable of triggering and controlling the HMF synthesis reaction.

Conclusions

COMSOL Multiphysics® was used to design a multi-purpose ultrasonic reactor, consisting in a high-power piezoelectric converter, a cylindrical flow cell and a special sonotrode with 'tuned rings'.

The system was designed with a parametrized piezo/structural/acoustic multiphysic model and a complete optimization process was performed.

The simulation results were up to the required level of efficiency and very high levels of cavitation could be obtained in the reactor, in order to trigger special chemical reactions.

Such results were validated with experimental testing on a complete prototype.

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