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Design and Simulation of a RF Resonant Reactor for Biochemical Reactions

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In this work the development of a multi-tube reactor for chemical processing, running in a microwave irradiated field, is presented. Considering the need of operating with well-known and reproducible experimental conditions, the aim was to design a resonant cavity inside which the tubes with the fluid to be processed are positioned. The irradiated fluid is exposed to constant microwave power since the system works in resonance conditions, therefore the field intensity and power absorption can be accurately calculated and mapped. The cavity was designed by the authors using proper commercial software for 3D electromagnetic simulation, and then the reactor operation was tested by another commercial multiphysics simulation software. The results here presented show the proper geometrical characteristics of the cavity and of the internal tubes to work at 2.45 GHz of frequency while the irradiation power can be varied depending on the needs of the process. The reactor can work with different homogeneous systems, both chemical and biological (enzyme reactions). The future development will be the construction and the real operation of the designed apparatus in order to confirm the simulation results.

1. Introduction

Microwaves are known for their ability to enhance chemical processing thanks to their heating capacity. In fact, chemical and biochemical reactions are related to electrical forces between the charged part of the reacting molecules, i.e. electrical interactions at microscopic scale; thus an external electromagnetic field can interact with such reactions (Buchachenko, 1994), and many findings of these interactions were reported in the literature, about both thermal and non-thermal kind (Foster, 2000), on chemical (Carta and Desogus, 2013) and biological (Carta and Desogus, 2010) reactions, even for very low power levels (Carta et al., 2006).
The effectiveness of non-thermal interactions during chemical, biochemical and biological processes under microwave irradiation cannot be easily demonstrated, because of the inherent difficulties in conducting such experiments. In fact, non-thermal effects (if they exist) operate concurrently with thermal ones, and it is hard to distinguish between them. However, as it results from most of the studies reported in the literature, microwaves power has not been monitored, or was high enough to give a temperature rise in the medium, so making difficult to quantitatively determine thermal and non-thermal microwave effects. In such studies, even the electromagnetic field distribution was not monitored (Gong et al., 2010). So, the real action of microwaves in chemical and biochemical processing has not yet been fully understood, that is because the mechanism of the radiation effect on the enzyme, which are very fragile and temperature sensitive molecules, and whether it is thermal or non-thermal, is still unclear. Actually, the action of an external electric field modifies dipolar orientation of molecules, modifying active sites of the enzyme, enhancing the efficiency and the specificity of enzymatic reactions (Gong et al., 2010).
Aim of this work was to design and analyse the behaviour of a microwave resonant cavity, to be used as a biochemical (enzyme) reactor, working at the frequency of 2.45 GHz, evaluating the influence of the electromagnetic exposition on the reacting processes, especially on enzyme homogeneous catalysed

reactions performed in a polar medium; in particular, the enzymatic hydrolysis of sucrose into glucose and fructose was chosen as a case study.

2. Design and simulation software

The cavity was designed using CST® Microwave Studio, a software for the numerical resolution of high frequency electromagnetic problems which makes use of Finite Integral Technique (FIT). Using this method it is possible to obtain exact equations between average values of the fields and the behaviour of any device can be studied in time or frequency domain. Whilst, utilizing COMSOL Multiphysics®, a software for the numerical simulation of several coupled physical problems through Finite Element Method (FEM), the process operation was simulated.

3. Cavity Design

In order to evaluate the effects of the exposition to electromagnetic fields, in controlled and known conditions, both for chemical compounds and biological molecules, a suitable exposure apparatus is required, consisting in a resonant cavity in which the reacting mixtures can circulate. To explain the working conditions of a resonant cavity, and the design criteria for this, it is needed to start from the concept of waveguide, of which the resonant cavity represents a particular case. Waveguides are devices properly used for confining an electromagnetic field inside a spatial region, forcing it to propagate in a fixed direction, conventionally chosen coincident with the axial direction z. To be more precise, a waveguide is a driving structure with a transverse section which is simply connected and invariant with z, e.g. a metal hollow tube.
Solving Maxwell's equation in the phasor domain, it is possible to describe how the electromagnetic field propagates and distributes along the z-axis of the cylindrical waveguides or transverse to it. So that:

$$\begin{cases} -\dfrac{\partial \mathbf{E}_t}{\partial z} = j\omega\mu \mathbf{H}_t \times \mathbf{i}_z - \nabla_t E_z \\ -\dfrac{\partial \mathbf{H}_t}{\partial z} = j\omega\varepsilon\, \mathbf{i}_z \times \mathbf{E}_t - \nabla_t H_z \\ \nabla_t \cdot \left(\mathbf{i}_z \times \mathbf{E}_t\right) = j\omega\mu H_z \\ \nabla_t \cdot \left(\mathbf{H}_t \times \mathbf{i}_z\right) = j\omega\varepsilon E_z \end{cases} \tag{1}$$

in which **E** and **H** are respectively the electric and the magnetic field, ω is the angular pulse, ε and μ are respectively the electric and the magnetic permittivity, which describe the characteristics of the dielectric material filling the waveguide (air in the present case), and finally j is the imaginary unit. Furthermore, as everything is constant with z, ∇_t is:

$$\nabla_t = \frac{\partial}{\partial x}\mathbf{i}_x + \frac{\partial}{\partial y}\mathbf{i}_y \tag{2}$$

where $\mathbf{i}_x$ and $\mathbf{i}_y$ are the unit vectors directed along, respectively, x and y axis. From the system in (1), factorized solutions of the following type must be found:

$$\begin{cases} \mathbf{E}_t(x, y, z) = V(z)\mathbf{e}(\mathrm{x}, \mathrm{y}) \\ \mathbf{H}_\mathrm{t}(\mathrm{x}, \mathrm{y}, \mathrm{z}) = I(z)\mathbf{h}(x, y) \end{cases} \tag{3}$$

which represent the system modes, and where V(z) and I(z) are scalar mode functions, while **e** and **h** are vector mode functions. To find the solutions of the system in (3), further conditions have to be assumed on the longitudinal components of field. If $E_z = H_z = 0$ is assumed, both the electric and the magnetic field would result to be transverse to z direction, thus the modes are transverse electromagnetic (TEM) modes. It can be demonstrated that, for a waveguide with a simply connected transverse section, TEM modes cannot exist. Other solutions are the modes with only one transverse field, which are the transverse electric (TE, with only $E_z = 0$) and the transverse magnetic (TM, with only $H_z = 0$) modes.
If we now consider the latter case (TM, with $H_z = 0$) for the case of a cylindrical waveguide, it is convenient to solve the problem in cylindrical coordinates. The system in (3) leads to an eigenvalue problem (Fanti et al., 2015a), and could be solved numerically. The most effective approach is probably the Finite-Difference Frequency-Domain (FDFD) method (Fanti and Mazzarella, 2010a), which can be applied both to scalar (Fanti et al., 2016a) and to vector problems (Zhao et al., 2000). As a matter of fact, the FDFD approach (Simone et al., 2016), namely the direct discretization of the differential eigenvalue problem (Fanti et al., 2013a), is the simplest numerical strategy to compute eigenvalues (Fanti et al., 2013b) and modes of metallic hollow waveguides (Fanti et al., 2013c). So, it is possible to determine waveguide modes, which propagate above the

cut-off frequency and the corresponding resonant cavity can be designed knowing the diameter and the resonant frequency (Fanti et al., 2015b), which is 2.45 GHz, as can be derived from the following equation:

$$f_{nml} = \frac{c}{2\pi\sqrt{\varepsilon_{r\_avg}}}\sqrt{\left(\frac{x_{nm}}{a}\right)^2 + \left(\frac{l\pi}{h}\right)^2} \tag{4}$$

with x_{nm} the m-th zero of the n order Bessel's function used when evaluating modes; c is the speed of light in vacuum; ε_{r_avg} and μ_r are respectively the averaged relative electric permittivity and the relative magnetic permeability of the material filling the cavity; a is waveguide radius; d is the section of the cavity and, finally, l is the length of the cavity. As a matter of fact, the materials under test are exposed in aqueous solution, so that the cavity must include a suitable container for them. In order to test the effectiveness in chemical processes, it was decided to expose a continuous flow of solution, using a reactor made of eight plexiglass tubes allocated into the cavity (Figure 1). The reactor was centred with respect to the cavity, ensuring a uniform absorption of the electromagnetic radiation by the liquid. An external pumping system had to be used, so that the tubes diameters were chosen as to significantly reduce the dispersion of the field outside the cavity. Since the dielectric properties of the fluid under test were essentially the same as those of pure water, the fluid was considered (from the electromagnetic point of view) as water, using the Debye model with temperature-dependent parameter (Ray, 1972). Moreover, it was considered the presence of different materials in the system, so that the dielectric constant can be volume averaged as follows:

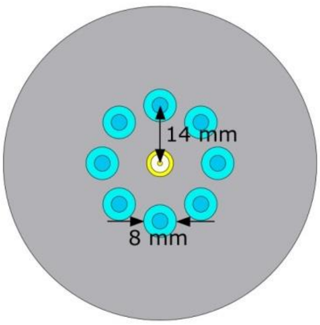
$$\varepsilon_{r\_avg} = \frac{V_a + V_w \cdot \varepsilon_{rw} + V_p \cdot \varepsilon_{rp}}{V_a + V_w + V_p} \tag{5}$$

wherein V_a, V_w , and V_p are the internal volumes filled with air, water, and plexiglass, respectively (V_a+V_w +V_p=2πah is the total cavity volume); ε_{rw} and ε_{rp} are the dielectric permittivity of water and plexiglass.

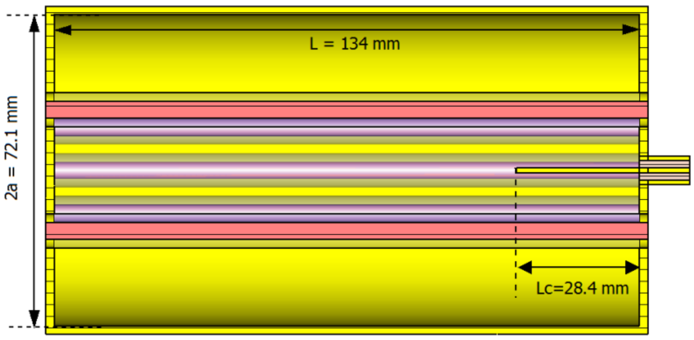
It was chosen for the cavity cylindrical side a commercial size, with a diameter 2a = 72.1 mm (twice the diameter of a cavity designed in a previous work (Desogus et al., 2016). The height h of the cavity, having resonant frequency at 2.45 GHz, is equal to 102.3 mm, neglecting the inhomogeneous distribution of water (and the spatial variation of the electric field). But the imaginary part of the dielectric constant of water, i.e. the loss factor, cannot be neglected at 2.45 GHz, therefore the resonant frequency of the cavity of Figure 1 with h = 102.3 mm is different and so equal to 3.046 GHz. Because the application at hand requires a cavity tuned at (or very close to) 2.45 GHz, a tuning of the cavity length h was performed, obtaining as final value h = 134 mm, and the reflection coefficient behavior of the final cavity is reported in Figure 2.

The cavity length was chosen to excite a mode independent from the azimuthal coordinate, in order to irradiate in the same way all the tubes. The chosen mode corresponds to the TM_{012} of the empty cavity.

The reactor was centred with respect to the cavity, ensuring a uniform absorption of the electromagnetic radiation by the liquid. Moreover, the irradiated liquid is flowing, therefore inhomogeneous microwave exposition is prevented and well mixing conditions are created.



(a)



(b)

Figure 1: Sketch of the reactor in the resonant cavity: a) bottom and top view, b) side view

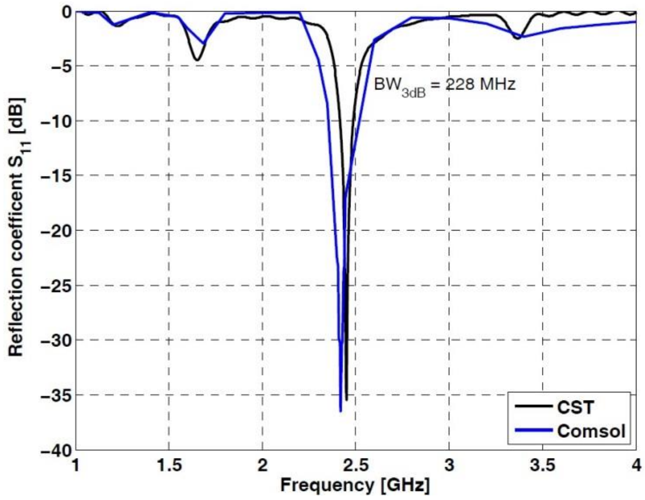


Figure 2: Return loss with probe length Lc=28.4 mm

4. Results

Regarding the distribution of the electric field, the longitudinal distribution is not constant but, since the irradiated liquid is flowing, to create well mixing conditions is needed for preventing an inhomogeneous microwave exposition. The transverse and longitudinal configuration of the field can be observed in Figure 3.
The operating conditions made possible to operate in the laminar flow regime, hence it is possible to analyze the heat transfer in the fluid by the following energy conservation equation:

$$\rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \left(-k \nabla T\right) = Q \tag{6}$$

in which ρ represents the fluid density, C_p the heat capacity at constant pressure, T the temperature, k the thermal conductivity and Q the specific heat power generated by a generic heat source.
Finally, considering the very low concentrations, the solute mass transfer, using the approximation of transport of diluted species, was taken into account by the convection-diffusion equation in the form:

$$\nabla \cdot \left(-D_i \nabla M_i\right) + \mathbf{u} \cdot \nabla M_i = R_i \tag{7}$$

in which D_i is the diffusion coefficient, M_i the mole concentration and R_i the generation rate for i; the latter was chosen and described by a suitable kinetic model (Casu et al., 2016), also considering the enzyme inactivation (Fanti et al., 2016b).
Multyphisics simulation was carried out for different working microwave power in the range 1÷300 W and for fluid average axial velocity ranging from $5.0 \cdot 10^{-5}$ to $1.5 \cdot 10^{-1}$ m s^{-1}. The main finding was the fact that no significant deviation from the resonance frequency was registered, but the working conditions of the cavity strongly influence on the temperature in the system, which is a key parameter in chemical and biochemical kinetic experiments, as it can influence the process evolution rate or it can irreversibly damage the enzyme molecules.

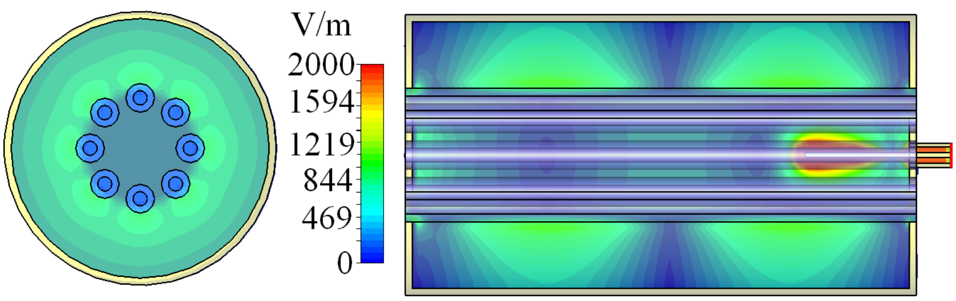


Figure 3: Electric field inside the cavity at 2.45 GHz: a) transverse view; b) longitudinal view

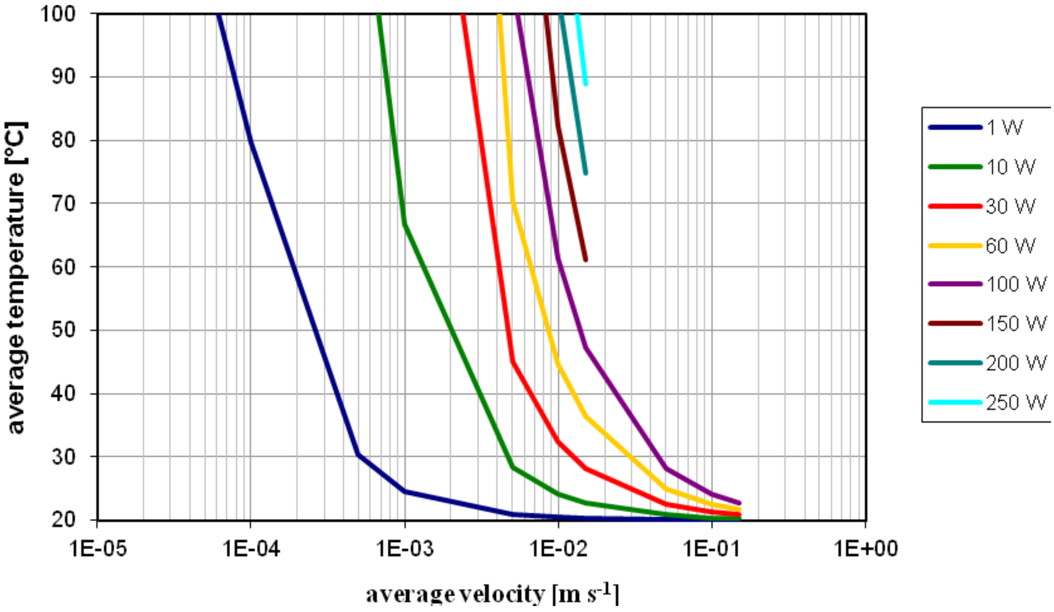


Figure 4: Outlet average temperature of the fluid for different incident microwave powers and average fluid velocities (inlet temperature fixed at 20 °C)

It should be considered that in the sucrose hydrolysis, catalysed by invertase enzyme, the temperature should not overcome 60 °C, since at higher temperatures the enzyme loses most of its activity after 60 min (Vrábel et al., 1997). Therefore, as it van be observed in Figure 4, a useful working region below this temperature threshold was found for P=1 W and velocities in the range $2.0 \cdot 10^{-4} \div 1.5 \cdot 10^{-1}$ m s^{-1}. For increasing power, the available velocity range shrinks, so that velocity has to be increased and then the process will be carried out with more fluid passages inside the cavity. Anyway, the maximum suitable microwave power is 100 W with velocities in the reduced range between $1.0 \cdot 10^{-2}$ and $1.5 \cdot 10^{-1}$ m s^{-1}.

5. Conclusions

In this article, the design and characterization of a resonant cavity reactor, operating at 2.45 GHz, and its possible use as an enzyme reaction apparatus, are described. A multiphysic simulation made possible to study all the interacting phenomena in such a reactor. The field distribution, and so the energy absorption rate, are substantially homogeneous in the tube azimuthal direction, despite the presence of the flowing fluid, which is characterized by a high value of the dielectric constant. Longitudinally the field presents a much more inhomogeneous distribution, however the fluid motion (in the laminar regime) inside the tubes allows all the fluid elements to be subjected to the same irradiation conditions throughout the entire experiment, which consists in several re-circulations of the reacting solution.

Reference

Buchachenko A.L., Frankevich E.L., 1994, Chemical Generation and Reception of Radio- and Microwaves. VCH Publishers Inc., New York, United States.

Carta R., Desogus F., 2010, The effect of low-power microwaves on the growth of bacterial populations in a plug flow reactor, AIChE J. 56, 1270-1278.

Carta R., Desogus F., 2013, The enhancing effect of low power microwaves on phenol oxidation by the Fenton process, J. Environ. Chem. Eng. 1, 1292-1300.

Carta R., Desogus F., Errico M., 2006, Effect of microwave radiation on the growth rate of Bacillus clausii at 37°C, CHISA 2006 – Proceedings of the 17th International Congress of Chemical and Process Engineering, August 27-31 2006, Prague, Czech Republic, Paper ID: 70283.

Casu S., Fanti A., Djuric N., Desogus F., Mazzarella G., 2016, Microwave resonant cavity as a reactor for the enzymatic hydrolysis of sucrose, Proceedings of the 15th IEEE Mediterranean Microwave Symposium (MMS 2015), November 30-December 02 2015, Lecce, Italy, Paper ID: 119001.

Desogus F., Casu S., Muntoni G., 2016, Design of a chemical reactor under microwave irradiation in resonance conditions, ECOS 2016 – 29th International Conference on Efficiency, Cost, Optimization, Simulation, and Environmental Impact of Energy Systems, June 19-23 2016, Portorož, Slovenia, Paper ID: 592.

Fanti A., Mazzarella G., 2010a, Curvilinear finite difference approach to the computation of modes of circular and elliptic waveguides, IEEE Proceedings of the International Conference on Applied Electromagnetics and Communications (ICECom 2010), September 20-23 2010, Dubrovnik, Croatia, Paper ID: 5729772.

Fanti A., Mazzarella G., 2010b, Finite difference single grid evaluation of TE and TM modes in metallic waveguides, IEEE Proceedings of the Loughborough Antennas and Propagation Conference, November 08-09 2010, Loughborough, UK, 517-520.

Fanti A., Mazzarella G., Montisci G., 2012, Curvilinear vector finite difference approach to the computation of waveguide modes, Adv. Electromagnetics, 1, 29-37.

Fanti A., Montisci G., Mazzarella G., Casula G.A., 2013a, Effective analysis of ridged circular waveguides with a curvilinear frequency-domain finite-difference approach, ACES J. 28, 1100-1110.

Fanti A., Simone M., Mazzarella G., 2013b, High order FDFD computation of all waveguide modes using a single grid, IEEE Proceedings of the Loughborough Antennas and Propagation Conference, 11-12 November 2013, Loughborough, UK.

Fanti A., Mazzarella G., Montisci G., Casula G.A., 2013c, VFD approach to the computation TE and TM modes in elliptic waveguide on TM grid, ACES J. 28, 1205-1212.

Fanti A., Deias L., Casula G.A., Montisci G., 2015a, A fourth order FDFD approach for the analysis of sectorial elliptic waveguides, ACES J. 30, 488-495.

Fanti A., Casu S., Desogus F., Montisci G., Simone M., Casula G.A., Maxia P., Mazzarella G., Carta R., 2015b, Evaluation of a microwave resonant cavity as a reactor for enzyme reactions, J. Electromagnet. Wave. 29, 2380-2392.

Fanti A., Simone M., Deias L., 2016a, Analysis and optimization of elliptic ridged waveguide with FDFD technique and PSO algorithm, ACES J., 31, 860-867.

Fanti A., Casu S., Desogus F., Djuric N., Mazzarella G., 2016b, Design and optimization of a microwave irradiated and resonant continuous biochemical reactor, Radio Sci. 51, 1199-1212.

Foster K.R., 2000, Thermal and nonthermal mechanisms of interaction of radio-frequency energy with biological system, IEEE T. Plasma Sci. 28, 15-23.

Gong G., Liu D., Huang Y., 2010, Microwave-assisted organic acid pretreatment for enzymatic hydrolysis of rice straw, Biosyst. Eng. 107, 67-73.

Ray P.S., 1972, Broadband complex refractive indices of ice and water, App. Optics, 11, 1836-1844.

Simone M., Fanti A., Casula G.A., Montisci G., Mazzarella G., 2016, Combined PSO-FDFD optimization of rectangular ridged waveguides, ACES J. 31, 114-151

Vrábel P., Polakovic M., Stefuca V., Báleš V., 1997, Analysis of mechanism and kinetics of thermal inactivation of enzymes: evaluation of multitemperature data applied to inactivation of yeast invertase, Enzyme Microb. Tech. 20, 348-354.

Zhao Y.J., Wu K.L., Cheng K.K.M., 2000, A compact 2-D full-wave finite-difference frequency- domain method for general guided wave structures, IEEE T. Microw. Theory 50, 1844-1848.