Modeling Temperature Field Dynamics During Microwaves-Assisted Extraction of Active Principles from Vegetables

Vasile Lavric* and Ioan Calinescu

Faculty of Applied Chemistry and Material Science, University Politehnica of Bucharest,
1-7, Gh. Polizu St., Bucharest, 011061, Romania
*E-mail: lavric.vasile@gmail.com

Introduction

Microwave (MW) technology gained attention as a process intensification method in the last few decades, due to some unique advantages: volumetric and selective heating[1-4]. The former is responsible for the high heating rates, characteristic to MW interactions with polar/ionic liquids, while the latter is a peculiarity of MW heating of heterogeneous mixtures – depending upon their dielectric properties, one phase could heat-up faster than the other; no other heating technique is capable of such discriminative heating.

Subjected to an electromagnetic field in the MW domain (300 MHz – 300 GHz), absorbing materials may suffer dielectric losses due to interactions with the electric field (EF), based on ionic conduction and dipole rotation, which lead to heating. In an alternating EF, charged carriers (ions, electrons, protons) are subjected to a forced convective transport in opposite directions (electrophoretic migration), which should follow the EF. These forth and back movements of ions are responsible for a supplemental friction between themselves and with the rest of the molecules, which generates heat. Polar molecules attempt to align to the alternating EF, colliding with neighboring molecules (oscillating or not), thus generating heat[4].

A liquid with only polar molecules (i.e., pure water) will experience smaller dielectric losses with the increase of temperature[2]; the kinetic energy of the molecules increases, thus diminishing the relative gain in energy due to oscillations. When ions are present in the liquid phase, they should be in balanced concentration, for the sake of neutrality. Although their kinetic energy increases with temperature as well, when in an oscillating EF, the opposite ions must move in opposite directions, therefore their collisions between themselves and with the surrounding molecules will increase, accordingly. So, dielectric losses will increase, as well, as opposite to the pure polar liquids. Therefore, as a salted solution is subjected to a microwave field, the heating is initially dominated by the contribution of polar molecules, and, as the temperature increases, the ionic conduction will prevail, after a specific threshold value. The relative contribution of these two heating mechanisms depends on the mobility and concentration of the ions, and on the relaxation time of the polar molecules[5].

The efficiency of MW heating depends on frequency and temperature of the liquid/solid phase, being directly proportional to the dielectric loss tangent, $\tan(\delta) = \varepsilon''/\varepsilon'$, where δ is the loss angle, ε' is the dielectric constant, proportional to the amount of energy absorbed, while ε'' is the effective dielectric loss (loss factor), indicating the ability of a medium to dissipate the absorbed energy as heat. Both factors depend upon MW frequency, *f*, and temperature, *T*:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (2\pi f)^2 \tau^2}, \tag{1}$$

$$\varepsilon'' = \frac{2\pi f \tau \cdot (\varepsilon_S - \varepsilon_\infty)}{1 + (2\pi f)^2 \tau^2} + \frac{\sigma}{2\pi f \varepsilon_0}. \tag{2}$$

When ions are present in solutions, the ionic losses, which are functions of conductivity, σ, and free space permittivity, ε_0, are added to the dielectric loss; data for water and aqueous solutions are well documented and interpreted[6,7].

Both static and high-frequency permittivity, ε_s and ε_∞, respectively, vary linearly with temperature, while the relaxation time, τ, follows an Arrhenius-like dependency:

$$\varepsilon_S = a_S \cdot T + b_S \tag{3}$$

$$\varepsilon_\infty = a_\infty \cdot T + b_\infty \tag{4}$$

$$\tau = \tau_0 \cdot \mathrm{e}^{E_\tau / T} \tag{5}$$

Unfortunately, there are no simple, additive rules to compute the permittivity for mixtures of liquids, but rather complex relationships. According to Ref.[8], Kraszewski relationship, in which the volume fractions, x_i, are used as weights, gives better results:

$$\sqrt{\varepsilon^*} = x_1\sqrt{\varepsilon_1^*} + x_2\sqrt{\varepsilon_2^*}\,. \tag{6}$$

The permittivity of vegetable materials depends on frequency, temperature, humidity/moisture (M) as well as ash (A) contents. For the current operating MW frequency (2.45 GHz), the relationships for both dielectric constant and loss factor are of empirical nature. The second order polynomials[9] in T, M and A, with the polynomial coefficients (c_i) are found through regression upon experimental data:

$$\begin{aligned}\varepsilon = \varepsilon' - j\varepsilon'' = c_0 + c_1T + c_2M + c_3A + c_4T\cdot M\\ + c_5T\cdot A + c_6M\cdot A + c_7T^2 + c_7M^2 + c_9A^2\end{aligned} \tag{7}$$

The selective heating and its effects upon heat and mass transfer is key in understanding the intensification of the microwave assisted extraction (MAE)[3]. When the temperature increases over a threshold value, specific to each vegetable, the matrix heats faster than the surrounding liquid, and, as such, thermally-induced structural damages may appear, causing cell-rupture[1] (various mechanisms being proposed for the latter).

To the best of the authors' knowledge, there is no possibility of measurement of this selective heating. In the present paper, we analyze the favorable conditions for the selective heating to act, and model the temperature field dynamics during the MAE process using a mono-mode applicator in Comsol®.

Results

The applicator with the standing electric wave

The monomode MW applicator, in which vegetables are discontinuously processed in ethanol/water solutions (50/50 %vol.), to extract active principles, is, in fact, a hollow metallic rectangular prism (cuboid), with width and height corresponding to WR 340 guide (see Fig. 1). On the left of the applicator in Fig. 1 is the inlet rectangular port for the TE_{10} mode. The length of the applicator is designed to ensure a standing wave, through reflection on the right metallic wall shown in Fig. 2. The working space is delimited by a cylinder, placed central to the waveguide, having on top another cylinder through which the test tube could be introduced into the working space (Fig. 1). This geometry ensures that the electric wave exiting the working space is very low, non-harmful to the operator in the present case, maximum 5 V/m (Fig. 2).

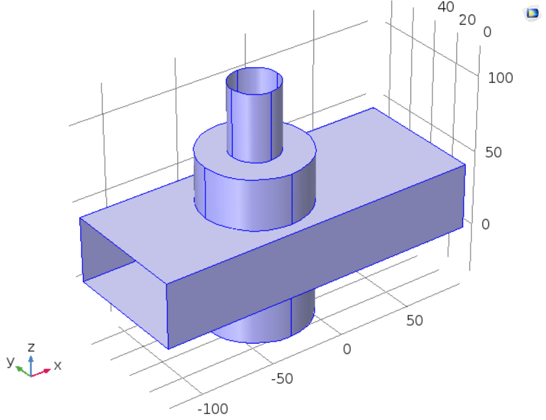

Figure 1: The geometry of the applicator.

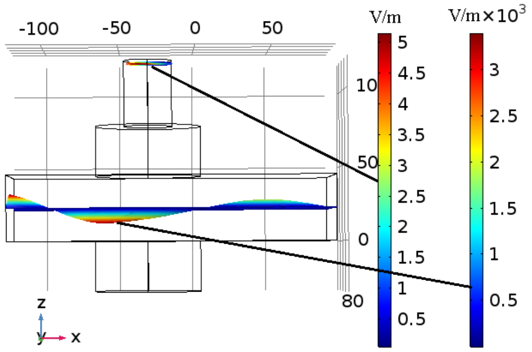

Figure 2: The standing wave in the empty applicator.

The key role of this geometry is to concentrate the E field in the test tube filled with 10 ml of water/ethanol solution, placed in the center of the waveguide (Fig. 3).

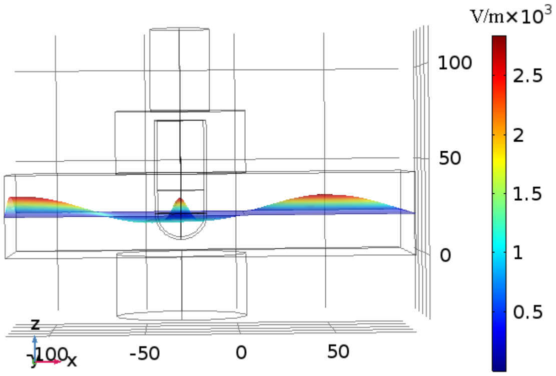

Figure 3: The E-field concentration in the test tube with the liquid phase placed in the working space

The present modeling study of the interactions between the microwaves and the liquid/solid suspension, for which the permittivity dependency upon temperature is considered, has three stages:

a) stressing the heating dynamics of the liquid phase only, disregarding natural convection;
b) emphasizing the selective heating of the solid phase (vegetable) placed in the water/ethanol solution, disregarding natural convection;
c) highlighting the way natural convection, induced by the non-uniform heating of the liquid phase under gravity, changes the dynamics of the heating of liquid/solid phases.

The operating mode is adiabatic, thus avoiding the decrease of the liquid temperature due to heat transferred to the thermal agent. This decrease could hinder the vegetable selective heating – if a difference in temperatures of solid and liquid phases would appear, it could be attributed to the delay in the heat transferred form the solid to the liquid, the latter being cooled down faster by the thermal agent, than the vegetable by the surrounding liquid.

Heating dynamics of the liquid phase (natural convection disregarded)

Not only the temperature modifies, during the heating of the liquid phase (Fig. 4), but also the E field, due to the change with temperature of the solution permittivity (Fig. 5). Quite remarkably, the intensity of the E field, expressed as the electric field RMS norm, EFN, increases as the temperature of the liquid phase raises, up to 4.3x10^3 V/m, significantly higher than the intensity of the E field in the empty applicator (see Fig. 2). Due to the adiabatic operating regime, the maximum temperature increases heavily (Fig. 4), but the lack of convective mixing creates large temperature gradients in the liquid volume (Fig. 6).

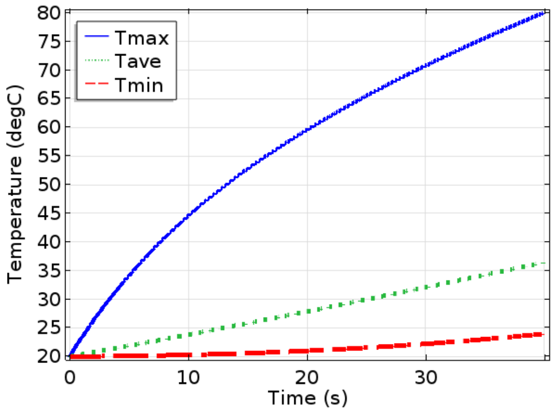

Figure 4: The temperature time profile for the liquid phase – T_{max} represents the maximum, T_{ave}, the average, and T_{min}, the minimum of temperatures

Due to the specific way the liquid phase is heated, a small hotspot developed in the center of the liquid phase, where the intensity of the microwave field is maximum, overheated near the boiling point of the mixture. The surrounding liquid, much larger in volume, has a temperature near the average value, while the rest is barely heated to 3-4 degrees (Fig. 6).

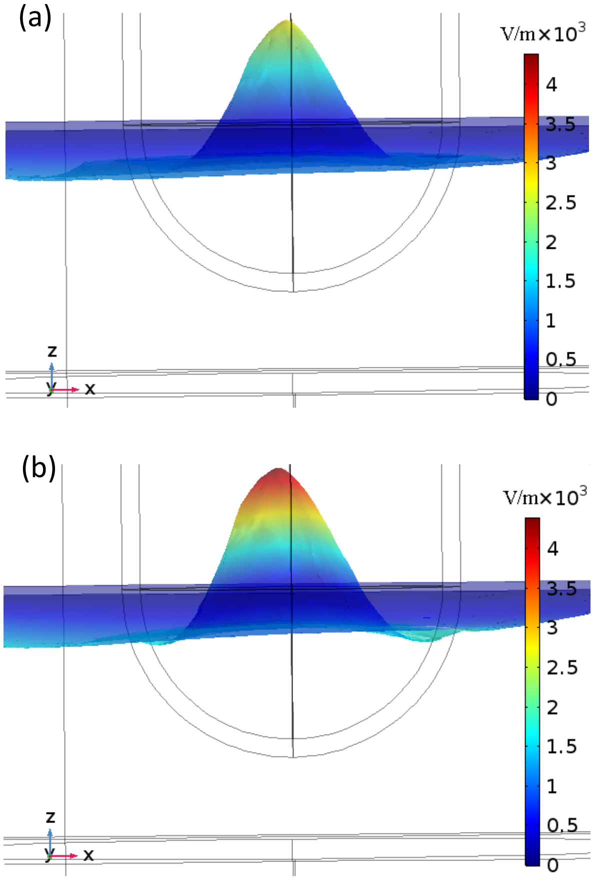

Figure 5: The E-field distribution change with temperature (a) at the beginning of the process, and (b) at the end of the process.

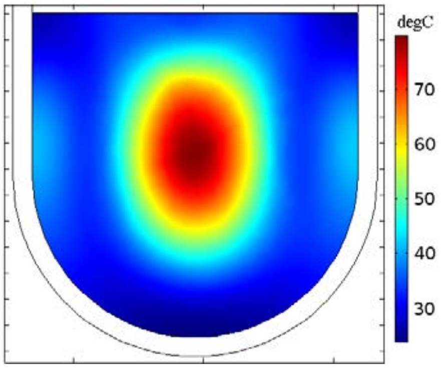

Figure 6: A ZX cut plane through the liquid phase temperature, to emphasize the gradients of temperature and the specific heating in the microwave field at the end of the process.

As the temperature of the liquid increases, its specific absorption rate (SAR) decreases, due to the decrease of the loss tangent; therefore, the heating rate becomes lower and lower, for the overheated region (Fig. 7, SAR_{max}), although the intensity of the E field increases with temperature (Fig. 8, EFN_{max}), but not as fast as the loss tangent decreases. The regions where temperature is close to the average value (Fig. 6) experience an increase of SAR (Fig. 7, SAR_{ave}), since the decrease of the loss tangent is compensated by the increase of the intensity of EF (Fig. 8, EFN_{ave}). Thus, on average, the heating rate tends to increase – see the curves for the maximum and average/minimum temperatures (Fig. 4).

Selective heating of vegetable (natural convection disregarded)

To study if the selective heating occurs, a sphere of vegetable material with 0.5-mm diameter, for which the permittivity is dependent on temperature, was placed in the center of the liquid phase, where temperature increased faster. Since the natural convection is disregarded, there will be no sleep velocity between the solid and the liquid phases. Therefore, heat is transferred only through diffusion between the two phases.

The grain of vegetable is too small to change the behavior of the liquid phase, for which the temperature profiles remain the same. The temperature of the vegetable material follows closely the maximum liquid temperature, due to the position where the grain was placed (Fig. 9).

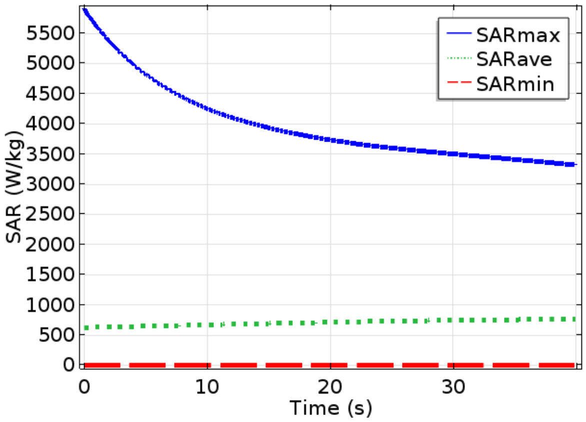

Figure 7: SAR profiles for the liquid phase.

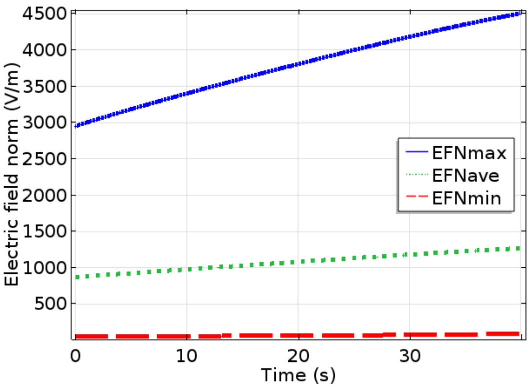

Figure 8: EFN profiles for the liquid phase.

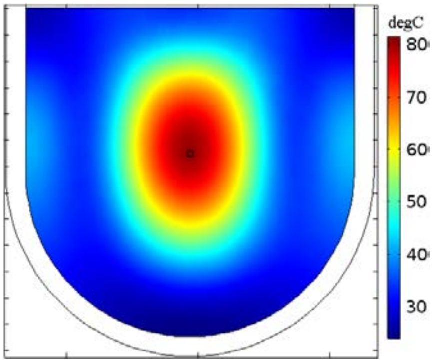

Figure 9: A ZX cut plane through the liquid/solid phases, the latter placed where the microwave irradiation is maximum.

To emphasize the selective heating, six points were chosen in the liquid phase, near the surface of the sphere, on the *x*, *y*, and *z* axes, which pass through its center – North (TN), South (TS), West (TXW), East (TXE), Front (TYW) and Rear (TYE) (Fig. 10). In these points, the temperature is recorded, together with the temperature in the center of the grain, TC (Fig. 11). The temperature profiles show that, although the selective heat is active, with the temperature in the center of the grain being higher than any temperature of the liquid surrounding it, the gap is rather small, maximum 0.66 K, quite close to the one quoted in the literature[6].

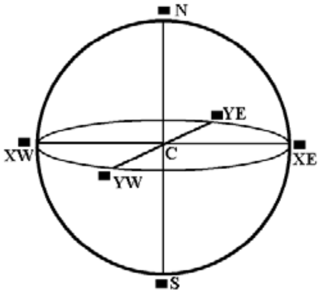

Figure 10: The whereabouts of the points for probing the temperature in the liquid surrounding the vegetable grain and in its center.

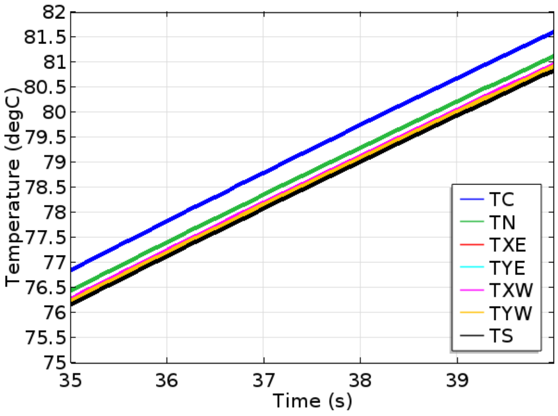

Figure 11: The temperatures in the center of the grain and in the points surrounding it, for the last 5 s of the simulation.

To have a clearer picture of this gap, the difference between TC and the average temperature of the six surrounding points

$$T_{L,ave} = \left(TN + TS + TXE + TXW + TYE + TYW\right)/6\,,$$

is presented in Fig. 12.

At the beginning of the process, when the dielectric properties of the liquid phase are higher than that of the vegetable (as shown in Fig. 13 for the dielectric loss tangent profiles), the difference between the temperature of grain and of the surrounding liquid is negative, since the latter heats-up faster. But, as the temperature of the vegetable material grows over the threshold, the selective heating starts acting, so the difference becomes positive and increases over 0.65 K.

The selective heating of the solid phase (natural convection considered)

Any fluid placed in a confined space and subjected to heating (direct or through a heat transfer area) develops, under the influence of gravity, a specific internal movement, known as natural convection – rotating cells generating local mixing. When heating is produced by microwaves, (a) the fluid in the rotating cells moves from the middle of the test tube towards the walls, and (b) the fluid gets thermally stratified (Fig. 14), due to the place where the E field is concentrated (Fig. 9).

This local mixing makes the fluid better homogenized and, although the average temperature time trajectory remains the same as when the natural convection is disregarded, the minimum temperature gets higher in time, while the maximum temperature stays significantly lower. After 40s of heating, the temperature surrounding the vegetable is slightly under 40^{0}C (Fig. 15, see Fig. 4 for comparison).

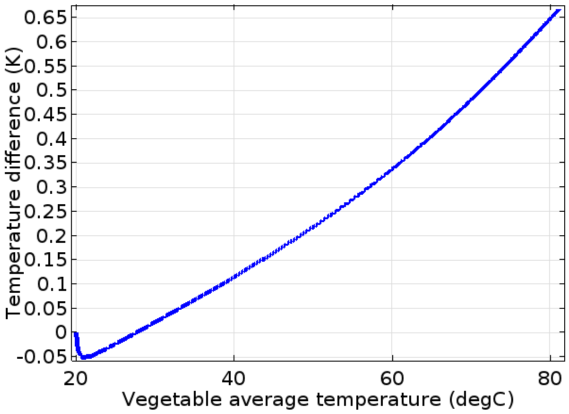

Figure 12: Difference between TC and $T_{L,ave}$ and the vegetable average temperature.

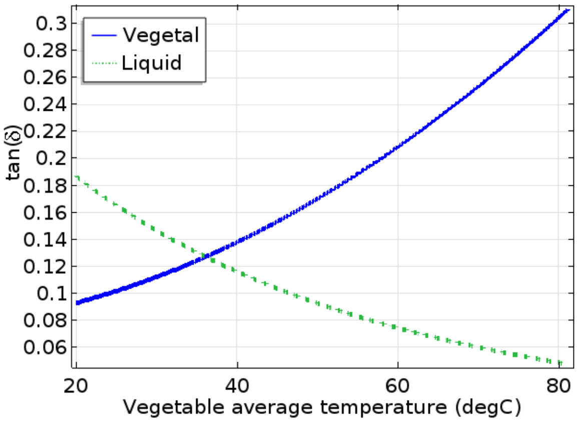

Figure 13: Loss tangent for vegetable and the liquid surrounding it, computed at $T_{L,ave}$.

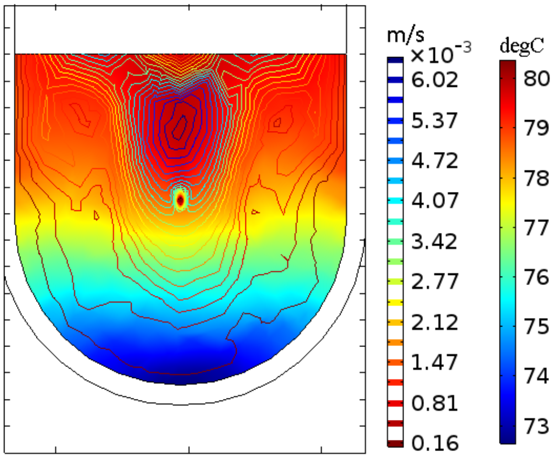

Figure 14: The temperature map with the velocity current lines.

Therefore, to reach the same final temperature for the vegetable as in the former case, the irradiation time should be prolonged to 160 s. As the result of natural convection, the liquid overheated zone occupies the top, the under-heated, the bottom, and the property of the vegetable to concentrate the E field is more apparent (Fig. 14). The selective heating is present and more important (up to 0.76 K), due to the increased temperature difference between the vegetable grain and the surrounding liquid (Fig. 16).

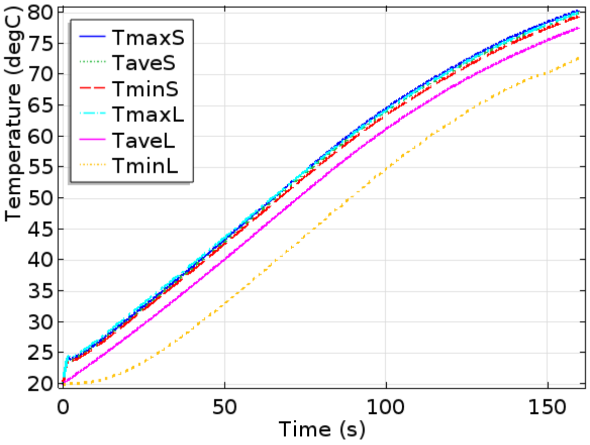

Figure 15: The temperature time profile for the liquid phase subjected to natural convection (see notations in Fig. 4).

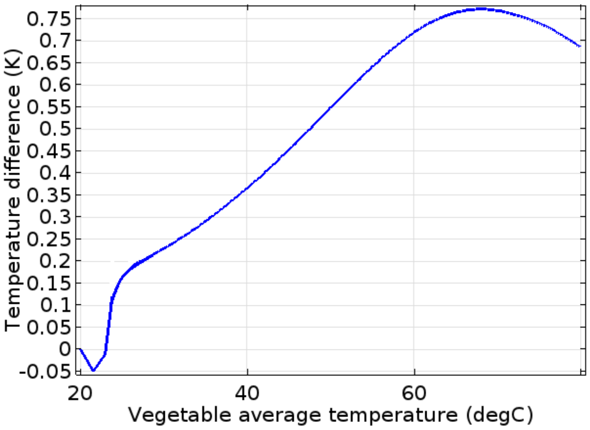

Figure 16: Difference between TC and $T_{L,ave}$ and the vegetable average temperature.

At the beginning of the process, the liquid still gets heated faster, but the vegetable starts being preferentially heated at lower temperatures than in the previous case. At the end of the process, EFN starts decreasing faster for the solid than for the surrounding liquid, which, in combination with the heat transfer from the solid to the liquid, determines a decrease in temperature difference between phases (Fig. 17).

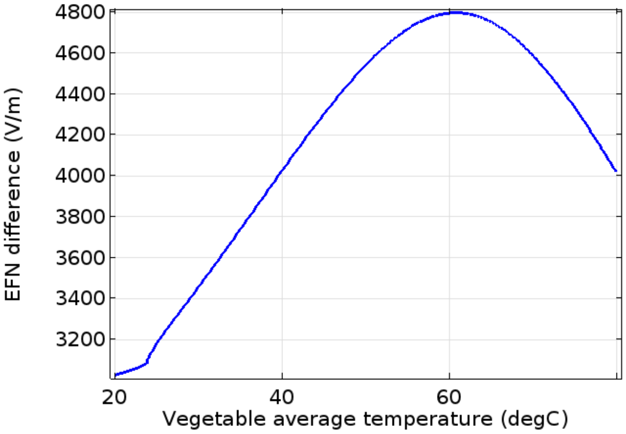

Figure 17: Difference between the E field in the center of the vegetable and the averaged E field in the liquid surrounding it (see Fig. 10) against the vegetable average temperature.

Conclusions

The temperature field dynamics during the microwaves assisted extraction of active principles from vegetables was modeled in Comsol®, first disregarding, then considering natural convention effects. The selective heating of vegetable was emphasized, which depends strongly upon the local temperature field and fluid dynamics.

For further reading:

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About the Authors

Prof. Vasile Lavric (University POLITEHNICA of Bucharest) graduated from University POLITEHNICA of Bucharest with an M.Sc. in chemical engineering and obtained the Ph.D. at the same university, in the domain of bioengineering. His research interest covers several domains like time scales of (bio)chemical processes, systems optimization and optimal control, process integration and intensification, artificial neural networks and evolutionary algorithms, biological/biochemical/chemical reactors. He co-authored over 100 peer-reviewed papers in these areas. In 1998 he was the recipient of the "Nicolae TECLU" award of the Romanian Academy's Chemical Division for "The applications of artificial neural networks in chemical engineering". He coordinated numerous fundamental and applied research projects.

E-mail: lavric.vasile@gmail.com

Prof. Ioan Calinescu (University POLITEHNICA of Bucharest) received his chemical engineering education (M.Sc. and Ph.D.) from University POLITEHNICA of Bucharest. His research interest includes the use of microwave, electron-beam and ultrasound in intensifying processes related to biomass processing and biofuels production, as well as removing various pollutants from the gaseous or liquid media. He co-authored over 85 peer-reviewed papers in these areas. He is a doctoral supervisor with 15 PhD students who supported his doctoral thesis under his guidance. He has coordinated numerous research projects funded by government or industrial companies.

E-mail: ioan.calinescu@upb.ro