

Cristina LEONELLI^{a,*}, Witold ŁOJKOWSKI^b, Paolo VERONESI^a

^a MAG-Microwave Application Group at the Department of Engineering “Enzo Ferrari”, University of Modena and Reggio Emilia, Italy

^b Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland

* Corresponding author: cristina.leonelli@unimore.it

TEMPERATURE PROFILE WITHIN A MICROWAVE IRRADIATED BATCH REACTOR

© 2018 Cristina Leonelli, Witold Łojkowski, Paolo Veronesi

This is an open access article licensed under the Creative Commons Attribution International License (CC BY)



<https://creativecommons.org/licenses/by/4.0/>

Key words: microwave, modeling, temperature profile, nanoparticles, synthesis.

Summary: The finite element method has been used here to investigate the volumetric temperature distribution differences between conventional and microwave heating for a rotating batch reactor containing water-based solutions.

It was shown that the temperature distribution is much narrower with microwave heating compared to conventional heating, leading to conditions favourable for process intensification, and uniform particle growth. This effect is particularly pronounced for the first 60 seconds of heating.

Thus, some of the claimed „non-thermal” microwave effects could be explained considering the different temperature distribution in the reaction volume for the two types of reactors, i.e. they can be ascribed to purely thermal effects.

The computer simulations included 3D modeling, coupling with fluid-dynamics, heat transfer, and electromagnetic analysis, with insertion of a large number of not perturbative “virtual” temperature probes in the reactors.

Rozkład temperatury w reaktorze mikrofalowym z ogrzewaniem mikrofalowym

Słowa kluczowe: mikrofałe, modelowanie, rozkład temperatury, nano cząstki, synteza.

Streszczenie: Metoda elementów skończonych została wykorzystana do zbadania rozkładu temperatury w obracającym się pojemniku reakcyjnym napełnionym roztworem wodnym. Porównano rozkład temperatury przy nagrzewaniu konwencjonalnym i mikrofalowym.

Pokazano, że rozrzut temperatury jest znacznie mniejszy dla ogrzewania mikrofalowego niż konwencjonalnego. Przyczynia się to do intensywności reakcji, jej selektywności i jednorodności w syntezie nanocząstek. Jest to szczególnie widoczne w ciągu pierwszych 60 sekund procesu.

Zatem niektóre twierdzenia o „efekcie mikrofalowym” mogą być wyjaśnione różnicami w rozkładzie temperatury w obu typach reaktorów.

Symulacje komputerowe obejmowały modelowanie 3D, sprzężenia z dynamiką płynów, przepływem ciepła i obliczeniem pola elektromagnetycznego. Wirtualne czujniki temperatury były rozmieszczone w reaktorze.

Introduction

Very often, the microwave (MW) irradiation of chemical environments has brought unexpected results, so that a “non-thermal” effect of this technology was indicated as “the” responsible. Some papers report about incredibly high yields, but most of the “magic” of microwave heating technique, also termed the

Bunsen burner of the 21st century, has to be sought in unreliable temperature measurements. When accurate measurement of temperature using fibre optic temperature probes were performed, the influence of the electromagnetic field on the specific chemical reactions under truly identical conventional heating conditions were accurately evaluated [1–2]. Most of the organic reactions heated under MW irradiation gave similar

yields to heat resistance or bath oil reactors. The few syntheses that presented higher yields and, most of all, higher selectivity under MW where accurately investigated [3] and, in most cases, the higher heating rate in MW irradiation was considered responsible for these advantages.

Despite the above mentioned difficulties, application of microwave irradiation is considered as a valuable alternative in the synthesis of organic compounds, polymers, inorganic materials, and nanomaterials. It emerged as the only technique capable to produce powders of inorganic compounds characterized by a mono-modal grain size distribution with very small dispersion. Additionally, MW synthesis enhances crystalline phase formation compared to the amorphous one, and the crystalline phase selectivity is another property which is often associated to the previous one.

The present paper formulates a theory to explain both phenomena, starting from the simulated volumetric temperature distribution inside a stirred reaction vessel. A fully coupled thermal and electromagnetic model, including convection and imposing load rotation has been used, in order to simulate the real experimental conditions occurring during microwave heating in a single mode applicator or oil bath heating. A validated model of this kind allows obtaining the volumetric distribution of temperature, which is a piece of information which is not accessible by conventional temperature measurement techniques. Therefore, it allows one to compare the temperature distribution depending on the heat source used. This is the first paper to our knowledge that reports the investigation of temperature profiles in 3D EM and thermal coupled modeling including load rotation simulating solution stirring.

1. Batch reactor model

A software-based model was established to simulate transient heating by microwave or conventional heating (oil bath, hot plate, resistance,...) of a closed batch reactor that typically might be used for chemical synthesis.

For batch systems, finite element methodology was employed to couple fluid-dynamics, heat transfer, and electromagnetic analysis by the insertion of multitudinous virtual temperature probes (at least one per cubic millimetre) into the reactors. This facilitated investigation of possible differences in the distribution of volumetric temperature between conventional and microwave heating. Numerical simulation was chosen since an analogous experimental approach could have perturbed the system under investigation, thereby precluding reliable practical results.

A closed polytetrafluoroethylene (PTFE) vessel of wall thickness 5 mm, filled with an aqueous solution to within 10 mm of the top, is employed in the model. The vessel is positioned at the centre of a rectangular single mode microwave applicator, based upon WR340 waveguide geometry (WR340 is an acronym used to indicate the dimensions of the section in inches, equivalent to 86 mm x 43 mm). Microwaves are introduced at one side (port) of the applicator, while the opposite port is closed by a fixed short circuit. The temperature distribution during the first 60 s of microwave or conventional heating was assessed.

This arrangement simulates an experimental system that is typically used in a single mode applicator, including rotation of the load (vessel plus saline solution) at 10 to 100 revolutions per min (rpm). Identical geometry was used for modeling conventional heating. The saline water or salts solution was chosen to be representative of nanopowders/nanoparticles preparation starting from soluble salts, hence a very high dilution was used [4].

The physico-chemical properties of the reference load are presented in Table 1.

Table 1. Properties of materials associated with the reference load

Property	Vessel	Solution
<i>Name</i>	<i>PTFE</i>	<i>Diluted water solution</i>
Relative permittivity (real), ϵ'	2.33	$15.09 \cdot 10^{-5} T^3 - 0.0148 T^2 + 4.5343 T - 357.69$
Relative permittivity (imaginary), ϵ''	0.0001	$-3.55 \cdot 10^{-5} T^3 + 0.0371 T^2 - 12.997 T + 1521.66$
Specific heat [J/kg K]	1050	4200
Thermal conductivity [W/m K]	0.24	$0.0015 T + 0.1689$
Viscosity [Pas]	n.a.	Interp: $1.79 \cdot 10^{-3}$ @ 274 K; $2.78 \cdot 10^{-4}$ @373 K
Electrical conductivity [S/m]	0	$5.5 \cdot 10^{-6}$
Density [kg/m ³]	2200	Interp: 999.841@ 274 K; 958.4@373 K

Source: Authors.

Polynomial interpolating functions for permittivity were obtained from published data for brine solutions. [5] Other properties were interpolated from the Comsol Multiphysics material database and agreed with literature values. [6]

The model, implemented in Comsol Multiphysics 3.3, involved two-way coupling, since most of the properties of the materials are temperature-dependent and would have affected the electromagnetic field distribution in the microwave reactor. The starting temperature was specified as 273.15 K. Simulated microwave heating was applied with an input power of 200 W at 2.45 GHz. Simulated conventional heating employed a constant inward flux from the outer walls of the vessel. The input power density was such as to provide the same average temperature level in the load after 60 s of heating by either conventional or microwave means.

Solutions of the model under these transient conditions provided data for the temperature-time

evolution of the load during the first 60 s of conventional or microwave heating. The calculated standard deviation of the temperature values in the whole of the load, excluding the PTFE vessel, facilitated the assessment of thermal homogeneity. The scattering parameters (reflection coefficient indicated as $|S_{11}|$) of the microwave system were also calculated to provide an indication of the percentage of the incident power transferred to the load [7].

Figure 1 shows the rise in temperature with time and the associated increase of reflection coefficient. Due to the change of permittivity of the load as a function of temperature and hence time, $|S_{11}|$ initially varied from 0.77 to a final value of 0.87 during the 60 s of microwave exposure, as shown in Figure 1. This approximately corresponds to a reflection of 60–75% of the incident power, indicating that only 25–40% of that was transferred to the load. In practice, impedance matching devices may be employed to increase microwave absorption by the load, but that aspect was considered to lie beyond the present scope.

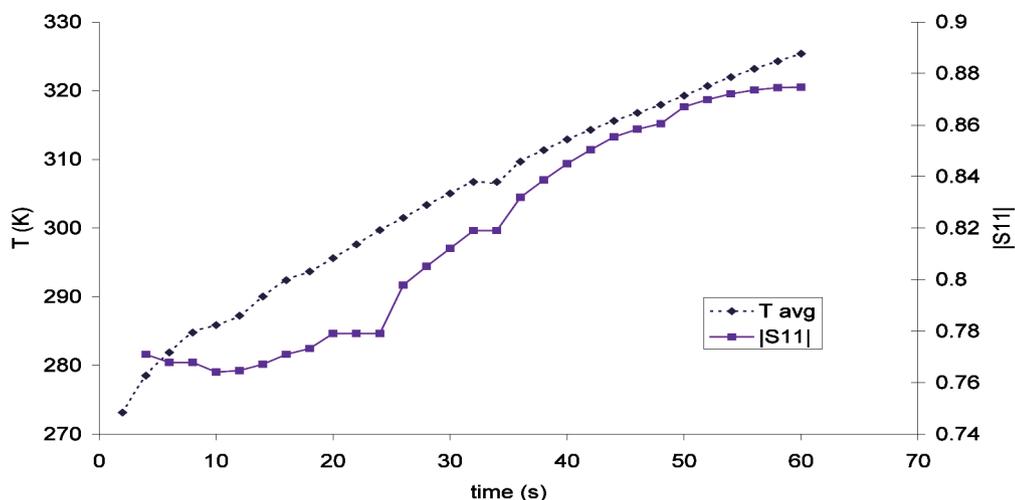


Fig. 1. Average load temperature (T_{avg}) and reflection coefficient ($|S_{11}|$) as a function of microwave heating time (forward power, 200 W; load rotating at 10rpm)

Interestingly, the heating rate (slope of the temperature/time curve in Figure 1) is progressively decreasing as a consequence of the lower efficiency of the system: Warm water has a lower tangent loss value than cold water, that is to say it heats up more slowly. This effect is particularly evident when comparing the early stages of heating (5 s) with the last ones.

The electric field intensity, temperature distribution, and velocity field distribution in the load after 60 s of heating are shown in Fig. 2. The E field appears to be

higher at the centre of the vessel, as shown in the mid-longitudinal section. It is also reported that the liquid motion, represented here with velocity field (grey lines), indicates the presence of turbulences in the vessel contents and its consequent stirring effect.

The standard deviation of temperature, evaluated in the overall volume of the saline solution as a function of heating time, for microwave or conventional heating is shown in Fig. 3.

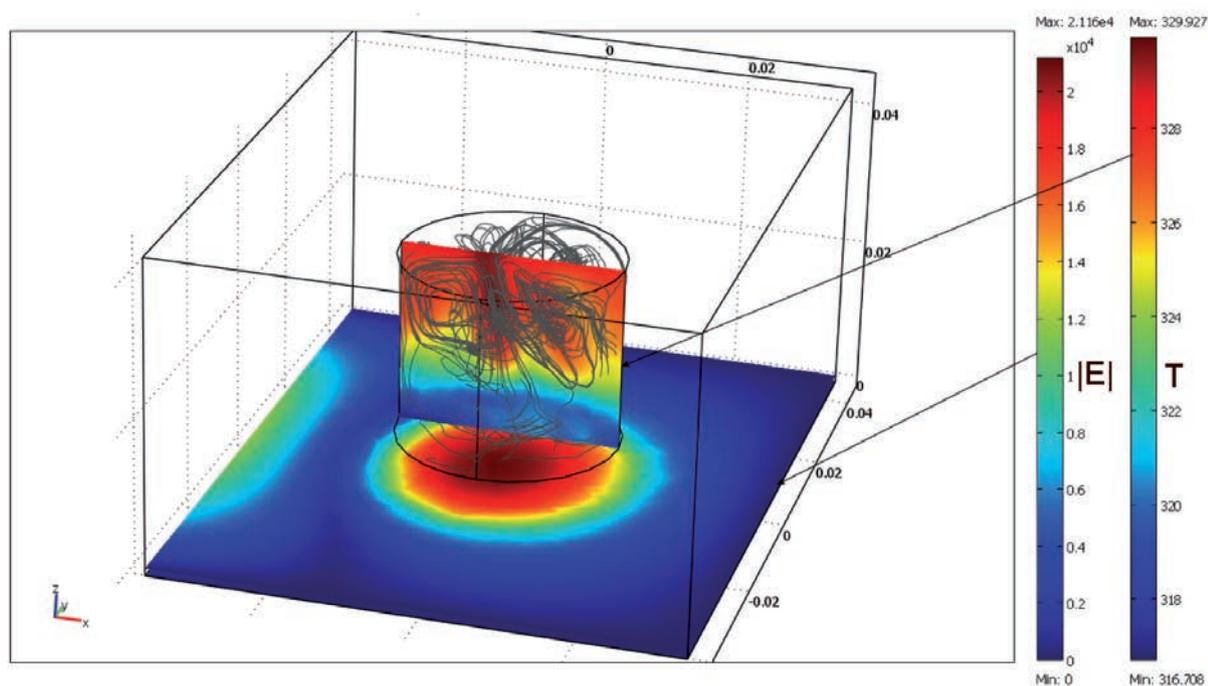


Fig. 2. Electric field intensity ($|E|$, in V/m) at the reaction vessel bottom and temperature distribution (T , in K) in the mid longitudinal section of the load after 60 s of microwave heating. The lines show the liquid velocity field (streamlines)

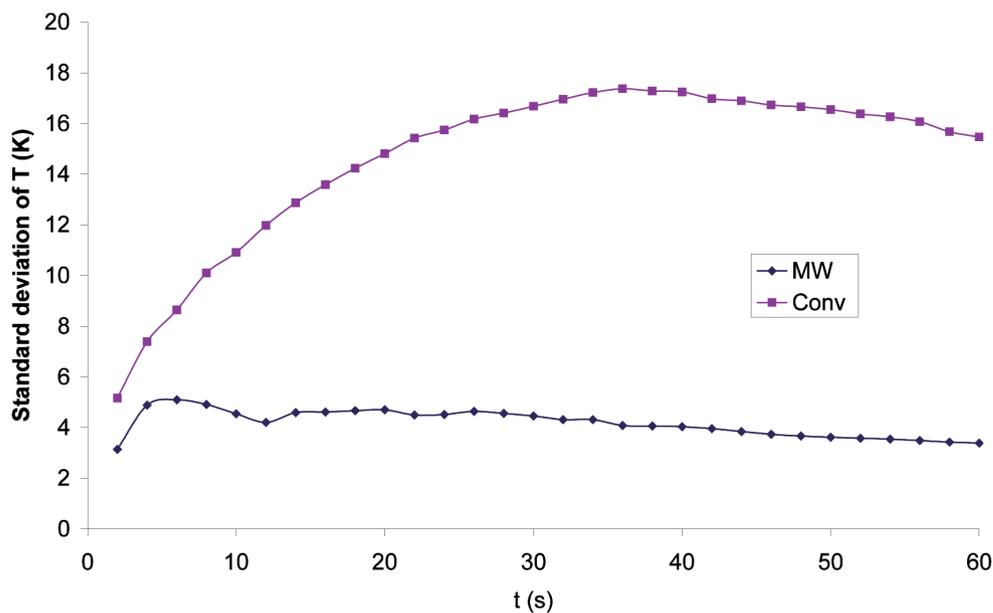


Fig. 3. Standard deviation of temperature in the load volume, during the first 60 s of microwave (MW) and conventional (Conv) heating, 10 rpm

2. Discussion

The microwave region of the electromagnetic spectrum lies between infrared and radio frequencies with the majority of the equipment employed in chemistry operating at 2450 MHz with

a corresponding wavelength of 12.2 cm in air. [8] At this frequency, the photon energy is lower than 10^{-3} eV, which means that it is three orders of magnitude lower than the binding energy of atoms in molecules; therefore, microwaves are not considered ionizing radiation. [9] The origin of the heat generated by

microwave radiation is due to oscillation of dipoles, which are particularly intense in highly polar solvents such as water and its solutions, and they do not rupture of molecular bonds [7].

In this paper, we have presented the results of a simulation describing the temperature evolution as a consequence of microwave and matter interaction when matter is highly polarisable as water and absolutely non-polarisable as a PTFE vessel. Due to the different nature of the vessel material and reaction media, the microwave radiation can pass through the vessel's walls without any significant energy loss and become attenuated and absorbed by the reaction media which starts to heat up.

To explain why microwave processes typically produce narrower particle size distribution and single phase nano-crystalline materials than analogous conventionally heated counterparts, we simulated temperature distributions within microwave and conventionally heated continuous flow and batch reactors, under comparable conditions, with the insertion of virtual temperature probes, which do not perturb the heating process [10].

Heating profiles for simulated batch reactions indicated that, under the modelled conditions, the temperature throughout the bulk volume of the load was more homogeneous for the early stages of microwave heating. As heating proceeds, the difference in the calculated volume variance of temperature decreases, still being less in the case of microwave heating.

After longer processing times, conventional heating might be expected to afford enhanced thermal homogeneity when the influence of wall temperature on the thermal gradient would decrease with temperature increase. On the other hand, microwave heating initially would proceed more rapidly than conventional heating, but the rate of temperature rise would be expected to decrease as heating proceeds.

Three concurrent factors favour thermal homogeneity associated with microwave heating, notwithstanding a non-homogeneous electric field intensity distribution in the load:

- The volumetric heating of the sample (microwave penetration depth at 2.45 GHz in diluted solutions is higher than 10 mm);
- Heat generation homogeneity, due to the exposure of new regions of the sample to the zone of maximum electric field intensity as the sample rotates; and,
- The decreasing conversion of microwave energy into heat occurring in sectors of the load at higher temperature (permittivity variation of water as a function of temperature) [11].

Figure 2 shows that the field intensity is higher inside the vessel than on its border, so that a slightly higher temperature can be expected for the vessel interior than close to its walls. It is also seen that there are turbulences in the vessel contents, so that a stirring effect is present and the reagents are continuously mixed.

Conversely, with conventional heating, heat sources are located at the load boundaries (vessel walls) and are not significantly affected by small changes in temperature of the load. With microwave heating, however, the volume itself acts as a distributive heat source that can vary with the properties of the load.

Figure 3 shows that, indeed, for MW heating, the standard temperature deviation is up to 5 K at the beginning of the heating process and decreases to 3 K after 60 seconds; however, for conventional heating, it rises with time from 5 K up to 16 K.

Data from the simulation of the first 60 seconds of microwave and conventional heating in batch reactors enabled the calculation of the cumulative temperature distribution in the load through the virtual temperature probes hypothetically located within each mm^3 of reaction volume. Cumulative temperature distribution is a measure of the deviation of temperature for a period of time over the mean level. The results are shown in the upper part of Fig. 4.

Data from the simulation of the first 60 seconds of microwave and conventional heating in batch reactors enabled the calculation of the cumulative temperature distribution in the load through the virtual temperature probes hypothetically located within each mm^3 of reaction volume. The results are shown in the upper part of Fig. 4, where two hypothetical nucleation and growth curves (bottom part) are also reported accounting for the nanoparticles formation.

The data in Fig. 4 may help to account for some phenomena typically associated with microwave heating and often ascribed to microwave “non-thermal” effects. The narrower temperature distribution in microwave heating can correspond to the conditions of maximum nucleation rate and minimum growth rate, meaning that many small particles are formed. Conversely, the broader temperature distribution by conventional heating shows that part of the system can also undergo growth, i.e. particles are nucleated, and some of them progressively grow in size, leading to a broader particle size distribution in comparison with the previous case. Significantly, a narrow energy distribution is one of the main requirements for process intensification, as reported by Van Gerven and Stankiewicz [12].

It can be assessed that, when considering a partially overlapping processes of nucleation and growth, as it is in the majority of the cases, the calculated temperature distribution can explain the cause of the narrower particle size distribution observed in hydrothermal synthesis of nanoparticles with respect to conventional hydrothermal synthesis [13–16].

It should be pointed out, however, that the obtained temperature distributions are dependent upon the type of reactor, vessel motion, and the nature of the reactants, and this could also explain the poor reproducibility of results in studies conducted with slightly different reactors or conditions.

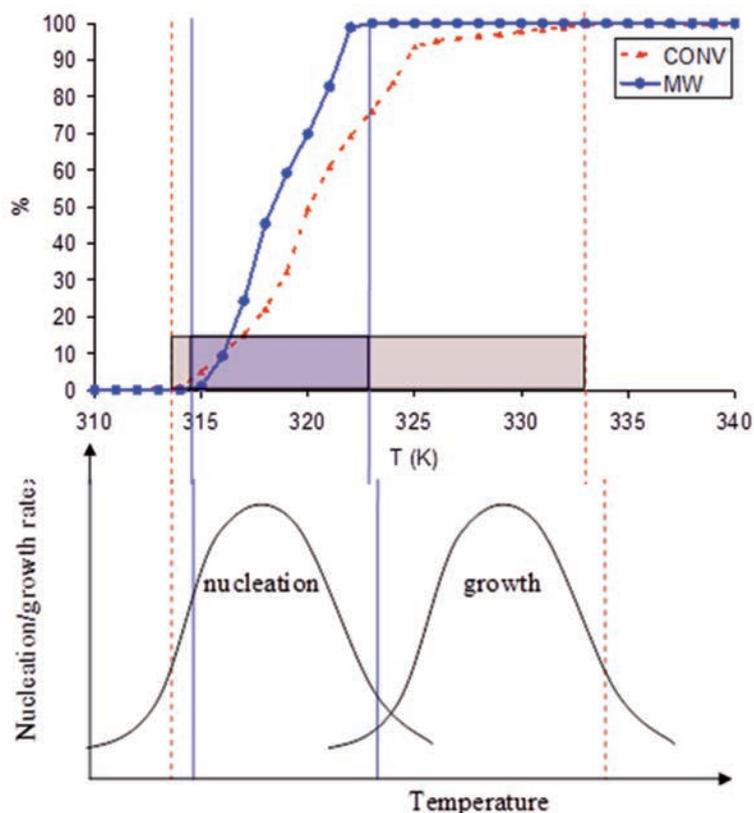


Fig. 4. (top) cumulative temperature distribution curve after 60 s of conventional (dotted line) and microwave (continuous line) heating and colour bars indicating the width of the temperature distribution in the reactor; (bottom) illustration of nucleation and growth rate curves as a function of temperature. Vertical lines show the energy/temperature level with respect to the transformation rate

Conclusions

The finite element method has been used here to investigate the volumetric temperature distribution differences between conventional and microwave heating. This method proved to be efficient in describing the temperature profile within a reaction media either during microwave irradiation or conventional heating (convection and conduction). The computer simulations included 3D modeling, coupled with fluid-dynamics, heat transfer, and electromagnetic analysis, with the insertion of a large number of not perturbative “virtual” temperature probes in the reactors. The numerical simulation was performed for microwave heating of a rotating batch reactor containing water-based solutions.

The simulation’s results show that the temperature distribution is much narrower, at least for the first 60 seconds, with microwave heating compared to conventional heating, leading to conditions favourable for process intensification, reaction selectivity, and uniform particle growth.

Thus, some of the claimed “non-thermal” microwave effects in inorganic syntheses could be

explained considering the different temperature distribution in the reaction volume for the two types of reactors, i.e. they can be ascribed to purely thermal effects, as already published for organic reactions. [17]

References

1. Kappe C.O., Pieber B., Dallinger D.: Microwave effects in organic synthesis: Myth or reality? *Angewandte Chemie, International Edition*, 2013, 52, pp. 1088–1094.
2. Gawande M.B., Shelke S.N., Zboril R., Varma R.S.: Microwave-assisted chemistry: synthetic applications for rapid assembly of nanomaterials and organics. *Accounts of Chemical Research*, 2014, 47(4), pp. 1338–1348.
3. Herrero M.A., Kreamsner J.M., Kappe C.O.: Non-thermal microwave effects revisited: On the importance of internal temperature monitoring and agitation in microwave chemistry. *Journal of Organic Chemistry*, 2008, 73(1), pp. 36–47.

4. Rizzuti A., Corradi A., Leonelli C., Rosa R., Pielaszek R., Lojkowski W.: Microwave technique applied to the hydrothermal synthesis and sintering of calcia stabilized zirconia nanoparticles. *Journal of Nanoparticle Research*, 2010, 12(1), pp. 327–335.
5. Stogryn A.: Equations for calculating the dielectric constant of saline water. *IEEE Transactions on Microwave Theory and Techniques*, 1971, 19(8), pp. 733–736.
6. Eves E.E., Yakovlev V.V.: Analysis of operational regimes of a high power water load. *Journal of Microwave Power and Electromagnetic Energy*, 2002, 37(3), pp. 127–144.
7. Metaxas A.C.: *Industrial Microwave Heating*. London: Peter Peregrinus Ltd. - on Behalf of the Institution of Electrical Engineers, 1950.
8. Ondruschka B., Bonrath W., Stuerger D.: Development and design of laboratory and pilot scale reactors for microwave-assisted chemistry. In: Loupy A. (ed.): *Microwaves in Organic Synthesis*, 2nd edition. Weinheim (Germany): Wiley-VCH, 2006, pp. 62–107.
9. Schnabel W.: Sub-terahertz radiations including radiofrequency (RF) and microwave radiation. In: Schnabel W.: *Polymers and electromagnetic radiation*. Weinheim (Germany): Wiley-VCH, 2014, pp. 5–54.
10. Gharibeh M., Tompsett G., Lu F., Auerbach S.M., Yngvesson K.S., Conner W.C.: Temperature distribution within zeolite precursor solutions in the presence of microwave. *The Journal of Physical Chemistry. B*, 2009, 113(37), pp. 12506–12520.
11. Von Hippel A.: *Dielectric Materials and their Applications*. MA, USA: MIT Press, 1954.
12. Van Gerven T., Stankiewicz A.: *Structure, Energy, Synergy, Time – The Fundamentals of Process Intensification*. *Industrial & Engineering Chemistry Research*, 2009, 48(5), pp. 2465–2474.
13. Caponetti E., Martino D.C., Saladino M.L., Leonelli C.: Preparation of Nd:YAG nanopowder in a confined environment. *Langmuir*, 2007, 23(7), pp. 3947–3952.
14. Corradi A.B., Bondioli F., Ferrari A.M., Focher B., Leonelli C.: Synthesis of silica nanoparticles in a continuous-flow microwave reactor. *Powder Technology*, 2006, 167(1), pp. 45–48.
15. Bondioli F., Leonelli C., Manfredini T., Ferrari A.M., Caracoche M.C., Rivas P.C., Rodríguez A.M.: Microwave-hydrothermal synthesis and hyperfine characterization of praseodymium-doped nanometric zirconia powders. *Journal of the American Ceramic Society*, 2005, 88(3), pp. 633–638.
16. Bondioli F., Corradi A. B., Ferrari A.M., Leonelli C.: Synthesis of zirconia nanoparticles in a continuous-flow microwave reactor. *Journal of the American Ceramic Society*, 2008, 91(11), pp. 3746–3748.
17. Strauss C.R., Rooney D.W.: Accounting for clean, fast and high yielding reactions under microwave conditions. *Green Chemistry*, 2010, 12(8), pp. 1340–1344.

