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Microwave Material Processing—A Review

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Microwave heating is caused by the ability of the materials to absorb microwave energy and convert it to heat. This article represents a review on fundamentals of microwave heating and their interaction with materials for various applications in a comprehensive manner. Experimental studies of single, multimode, and variable frequency microwave processing were reviewed along with their applications. Modeling of microwave heating based on Lambert's law and Maxwell's electromagnetic field equations have also been reviewed along with their applications. Modeling approaches were used to predict the effect of resonances on microwave power absorption, the role of supports for microwave heating, and to determine the nonuniformity on heating rates. Various industrial applications on thermal processing have been reviewed. There is tremendous scope for theoretical and experimental studies on the athermal effects of microwaves. Some of the unresolved problems are identified and directions for further research are also suggested. © 2011 American Institute of Chemical Engineers AICHE J, 58: 330–363, 2012

Keywords: microwave heating, modeling, experimental, thermal applications, athermal applications

Introduction

Microwaves are part of the electromagnetic spectrum with the wavelength ranging from 1 m to 1 mm, which corresponds to a frequency range of 300 MHz to 300 GHz. The most commonly used frequencies for domestic and industrial heating purposes are 915 MHz and 2.45 GHz. These frequencies correspond to significant penetration depth within most of the materials and hence are suitable for most laboratory reaction conditions.¹ Microwaves can be generated by a variety of devices such as magnetrons, klystrons, power grid tubes, traveling wave tubes, and gyrotrons, and the most commonly used source is the magnetron which is more efficient, reliable, and available at lower cost than other sources.² Microwaves find applications for thermal purposes such as drying, cooking of food materials, sintering of ceramics, and so on and for athermal purposes such as microwave-assisted reactions,^{3–8} and in the field of communication, including broadcasting and radar. In this review, we focus our attention on the thermal applications and the athermal effects of microwave-assisted reactions, and not on telecommunication applications. The status of development in experimental studies, modeling, and thermal and athermal applications are reviewed. Based on the current status of research, suggested directions for future work are derived. We also point out some areas where a more active cooperation between the industry and the academia would be beneficial.

Microwave heating

Microwave heating is caused by the ability of the material to absorb high frequency electromagnetic energy (micro-

waves) and convert it to heat. Microwave heating is due to dipolar polarization of the molecules which are permanently polarized due to chemical bonding, and they are realigned in presence of high frequency electric field. Because of high frequency, the realignment occurs a million times per second resulting in internal friction of molecules causing a volumetric heating of the material. Generally, materials can be classified into three types based on their interaction with microwaves. (1) Opaque or electrical conductors where microwaves are reflected and do not penetrate. (2) Transparent or low dielectric loss materials, in which microwaves are neither reflected nor absorbed, but are transmitted through the material with little attenuation. (3) Absorbers or high dielectric loss materials which absorb microwave energy to a certain degree based on the value of the dielectric loss factor and convert it to heat.⁹ The factors that affect microwave heating and its heat distribution are dielectric properties, penetration depth, operating frequency, operating mode (single or multimode), placement inside the oven, load geometry, and oven geometry.

Dielectric Properties. Dielectric properties are one of the important properties to assess the viability of heating effect due to the microwaves and hence knowledge of the material dielectric properties is necessary. The ability of a dielectric material to absorb microwaves and store energy is given by the complex permittivity ϵ^* .

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

where dielectric constant (ϵ') signifies the ability of the material to store energy and dielectric loss (ϵ'') represents the ability of the material to convert absorbed energy into heat. The ratio of the dielectric loss to the dielectric constant is known as the loss tangent ($\tan \delta$) which is given as,¹⁰

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$$\tan \delta = \frac{\kappa''}{\kappa'} = \frac{\epsilon''}{\epsilon'} \quad (2)$$

where κ' and κ'' are relative dielectric constant and relative dielectric loss respectively, which are given as $\kappa' = \epsilon'/\epsilon_0$ and $\kappa'' = \epsilon''/\epsilon_0$. Hence, with values of dielectric constant and large values of loss tangent or dielectric loss, materials couple with microwave with great efficiency. In addition, the dielectric properties of a material depend upon the temperature, frequency, purity, chemical state, and the manufacturing process.

Penetration Depth. Knowledge of the penetration depth is useful to quantify the interaction of microwave with materials. The penetration depth is defined as the distance from the surface of the material at which the power drops to e^{-1} from its value at the surface. The penetration depth is given by

$$D_p = \frac{1}{\alpha} = \frac{1}{2\pi f} \left(\frac{2}{\mu' \mu_0 \epsilon_0 \kappa'} \right)^{1/2} \left[((1 + \tan^2 \delta)^{1/2} - 1) \right]^{-1/2} \quad (3)$$

With free space velocity, $c = (\mu_0 \epsilon_0)^{-1/2}$ and $\mu' = 1$; Eq. 3 can be given as,

$$D_p = \frac{c}{\sqrt{2\pi f} \left[\kappa' \left\{ \sqrt{1 + (\kappa''/\kappa')^2} - 1 \right\} \right]^{1/2}} \quad (4)$$

where α is the attenuation factor, c is the velocity of light, f is the frequency, μ' is the magnetic permeability, ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m), and μ_0 is the permeability of free space ($\mu_0 = 4\pi \times 10^{-7}$ H/m). Further, it is found that the penetration depth increases with larger wavelengths or with decreasing frequencies. At frequencies below 100 MHz, the penetration depth is of the order of meters, which poses an additional problem with the penetration of microwave energy unless the loss factors are exceedingly high. However, at frequencies near the microwave regime, the penetration depths are correspondingly smaller than the size of the processing material and hence that may result in microwave heating of the material.¹ The heating effect may be neglected for samples with penetration depth larger than that of sample dimension. Similarly, if the penetration depth is smaller than the dimension of the sample, penetration of microwave energy will be limited, thus making uniform heating impossible.²

Microwave heating finds application in various fields due to its high heating rates, reduced processing time, and significant energy savings. Besides, no direct contact between the material and the energy source is required for heating. Microwave applications involve environmental friendly usage, safer handling, and improved quality of materials, so on.¹¹ Because of its various advantages, microwave has found applications in low- and high-temperature processes. Low-temperature applications include food processing applications such as melting of frozen foods, pasteurization of milk products, concentration of fruit juice, destruction of unwanted microorganisms, removal of moisture, biomedical applications, and heating of certain reacting systems. High-temperature applications include sintering of metals and ceramics, melting of glass and metals, pyrolysis reactions, and so on. Despite these advantages, microwave also has limitations such as the lack of dielectric data over a range of

temperatures and the inability to heat transparent materials in the microwave frequency range.⁹ Furthermore, for some of the dielectric materials whose dielectric loss increases with temperature, microwave heating can cause uneven heating and “hot spots” or thermal runaway.^{1,2}

Experimental Details

A typical microwave heating apparatus consists of three main components: (i) microwave source such as magnetrons, in which microwaves are generated, (ii) applicator in which the microwave energy is transferred to the materials, (iii) transmission lines or waveguides, which are used to couple energy of the microwave source to the applicators.¹² Microwave applicators are generally classified into single-mode cavities and multimode cavities.

Single-mode microwave applicators and applications

Single-mode microwave applicators are used to focus the microwave field precisely at a given location with the help of proper design. The transverse electric (TE or H) waves and transverse magnetic (TM or E) waves are commonly used for single-mode cavities which are designed either rectangular or circular cross section. The electric intensity in the direction of propagation is zero for the TE wave whereas for the TM wave, the magnetic intensity in the direction of propagation is zero. It may be noted that, TE and TM waves in a waveguide can have different field configuration, which are derived from the mathematical solution of the electromagnetic wave either in the rectangular or cylindrical waveguide. Each field configuration is called a mode which is recognized by the indexes m and n (which is expressed as TE_{mn} and TM_{mn}), where m and n are the eigenvalues of the wave solution.^{2,12} A few applications on single-mode applicators are illustrated below.

Material Processing with Phase Change. Ratanadecho and coworkers^{13–15} used a TE_{10} mode microwave system operating at a frequency of 2.45 GHz, for the applications of melting frozen packed beds^{13,14} and drying of multilayered capillary porous materials.^{15,16} Figure 1 shows the experimental setup for microwave of TE_{10} mode operating at a frequency of 2.45 GHz.¹³ It was found that the direction of microwave melting of frozen packed beds (water and ice) strongly depend on the structure of layered packed beds due to the difference between dielectric properties of water and ice.^{13,14} Moreover, in drying of multilayered capillary porous materials such as glass bead and water, the variation in particle size and initial moisture content influenced the degree of penetration and the rate of microwave power absorbed within the sample.^{15,16} Similarly, Antti and Perre¹⁷ used single-mode microwave for drying of wood samples and they found that the power distribution differs between dry wood and moist wood, as dry wood absorbed less energy than moist wood. Microwave heating of dielectric materials such as water layer and saturated porous medium was performed in the TE_{10} -dominated mode, and it was found that the sample with smaller volume had higher rise in temperature due to larger heat generation rate per unit volume.¹⁸

Environmental and Mineral Processing Applications. Microwave-assisted processes using single-mode cavity were used for environmental applications such as pyrolysis of oil contaminated drill cuttings and gas-stripping processes.^{19,20} Single-mode microwave system (2.45 GHz) of varying power 0–1 kW was used for pyrolysis and gas-stripping

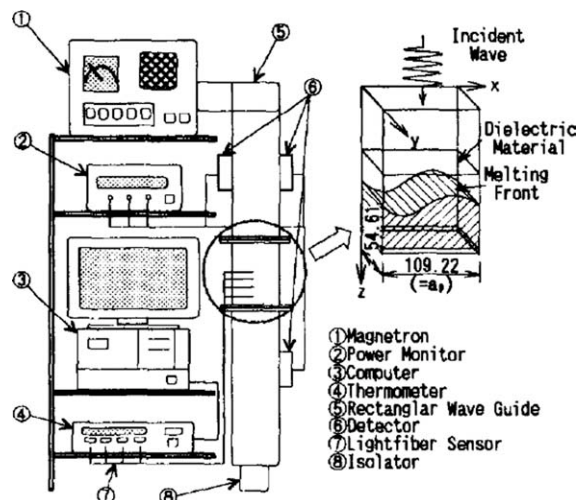


Figure 1. Schematic diagram of experimental setup for microwave heating using TE_{10} mode¹³ (Reproduced from Ref. 13, with permission from Elsevier).

operations. High microwave power level and high electric field strength were the two major factors which determine the mechanism of oil removal.¹⁹ In addition, 75% of the contaminant removal was achieved by microwave-assisted process with great improvement in the desorption kinetics.²⁰ Similarly, 95% removal of polyaromatic hydrocarbons from contaminated soils can be achieved with the help of microwave heating under moderate processing conditions and complete remediation of the soils was possible at high microwave powers or long residence times.²¹ In mineral processing, microwave heating was used for the purification of single-wall carbon nanotubes at different temperatures. The microwave system for purification consists of a tuned TE_{103} single-mode cavity driven by a 1.5 kW, 2.45 GHz power supply. It was found that after microwave-assisted purification, less than 0.2 wt % of catalyst metals was found to remain in the samples.²²

Ceramic and Metal Sintering Applications. Microwave sintering of nanocrystalline alumina and titania compacts were successfully performed in a single-mode (TE_{103} rectangular waveguide) microwave set up operated at a frequency of 2.45 GHz.²³ Similarly, with the help of tubular susceptor, microwave sintering of Y-ZrO₂, Ce-ZrO₂, and Al₂O₃ were carried out in a single-mode microwave furnace with a power output continuously adjustable from 0 to 1 kW. It was shown that microwave processing has advantages over conventional sintering with respect to sintering time, production cycle time, and energy consumption.²⁴ It may be noted that various materials exhibit different trends in both H and E fields. The heating effect due to H field was more effective than that due to E field for a high electric conductive sample such as powdered metal sample and conversely, heating effect of E field was superior for low conductive samples or pure ceramic samples such as alumina.^{25,26} Comparative studies on microwave sintering of copper powder using single-mode and multimode applicators operated at 2.45 GHz illustrate that sintering kinetics in a single-mode applicator was faster compared to those of a multimode applicator.²⁷

Applications of Continuous Flow Microwave Processing. Microwave heating of materials can be achieved in a continuous flow system as shown in Figure 2.²⁸ A continu-

ous microwave thermal processor (continuous microwave belt drier) was used for the application of drying dielectric and cementitious materials.^{28,29} Microwave power was generated by means of 14 compressed air-cooled magnetrons of 800 W each for a maximum of 11.2 kW. The magnetron was arranged in a spiral around the cylinder cavity, and the microwave power was then directed into the drier by means of waveguides. The sample to be dried was passed through the drier on an air-permeable microwave transparent conveyor belt which can operate up to 2 m/min. The continuous microwave system was found to be faster and reproducible and it ensured high product quality and consumed low specific energy compared to fixed sample microwave system.^{28,29} The drying of wood was also performed in a continuous flow system using microwaves, and the dried specimens had a better heat and moisture distribution and microstructure arrangement because of uniform energy absorption.³⁰

Multimode microwave applicators and applications

Multimode microwave applicators are closed volume, totally surrounded by conducting walls and have a large cavity to permit more than one mode (pattern) of the electric field.³¹ They are often used for processing bulk materials or arrays of discrete materials. Unlike single-mode applicators, multimode applicators are less sensitive to product position or geometry, adaptable to batch or continuous flow and are suited for hybrid heating.² As a batch process, this type of

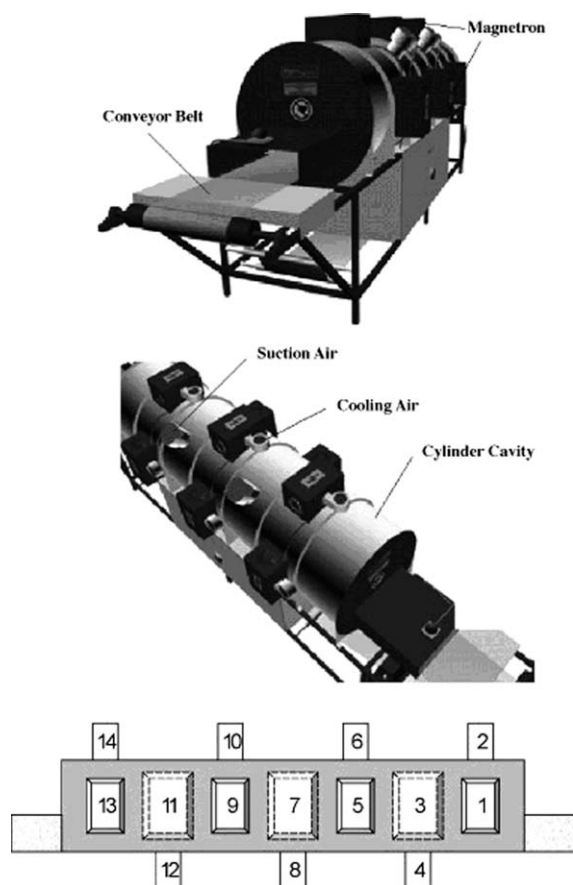


Figure 2. Experimental setup for microwave heating using continuous microwave belt drier²⁸ (Reproduced from Ref. 28, with permission from Elsevier).

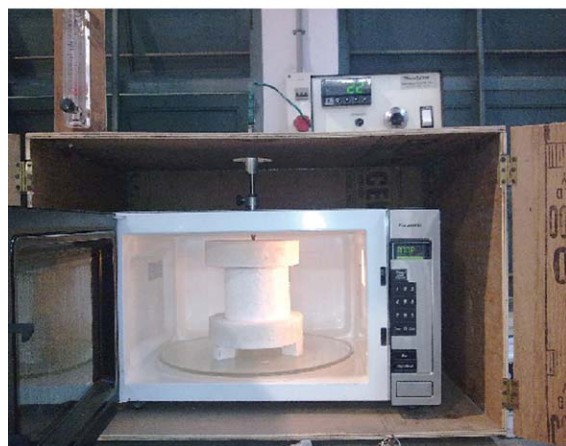
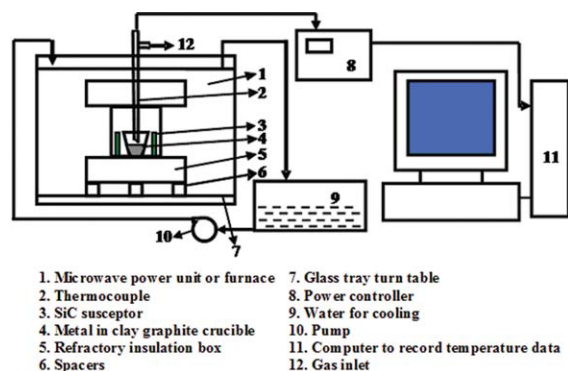


Figure 3. Schematic diagram of experimental setup for melting of metals using multimode microwave oven⁴⁰ (Reproduced from Ref. 40, with permission from Elsevier).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

applicator is used in domestic microwave ovens. The uniformity of microwave field can be improved either by increasing the size of the cavity or operating at a higher frequency. The size of the applicator required to achieve uniformity can be reduced at higher frequencies due to the shorter wavelengths. Hence, multimode ovens are operated at 2.45 GHz to create greater uniformity. Uniformity can be improved either by providing a turn table or by using mode stirrers. Mode stirrers are reflectors provided near the waveguide input, which reflect waves off the irregularly shaped bodies, and the electromagnetic field would be continuously redistributed.¹² A few applications on multimode microwave applicators are illustrated below.

Metallurgical Applications. Gupta and Wong³² used a 900-W multimode microwave oven operated at a frequency of 2.45 GHz for powder metallurgical applications such as sintering of aluminium, magnesium, lead-free solder, and synthesis of magnesium nanocomposites (Mg/Cu, Mg/SiC, Mg/Al₂O₃, Mg/Y₂O₃) through hybrid microwave sintering.^{33–36} SiC powder was used as a susceptor material (contained within a microwave transparent ceramic crucible) which absorbs microwave energy readily at room temperature, and the material can be heated up quickly, providing a more uniform temperature gradient within the heated material. Temperature measurements were done using a sheathed K-type thermocouple. It was found that the use of hybrid microwave sintering demonstrated greater potential in the

reduction of sintering time and that also has the ability to sinter highly reactive magnesium under ambient conditions without the use of protective atmosphere.^{32–36} Apart from the time and energy savings, microwave sintering of metal powders and composites such as PM copper steel and WC/Co illustrate that the microwave sintered samples has better uniform microstructure, better hardness, and exhibited more resistance against corrosion and erosion.^{37–39} In the same manner, melting of metals such as tin, lead, aluminium, and copper were accomplished using multimode research microwave oven. Microwave oven was operated at a frequency 2.45 GHz, with power varying from 500 to 1300 W. Figure 3 shows the schematic diagram of the setup used for the microwave melting of metals.⁴⁰ It was found that the microwave melting was twice faster and more energy efficient than conventional melting. Figure 4 shows the results for comparative studies of microwave and conventional melting of metals.⁴⁰

Applications in Food Processing. Microwave is very widely used as a household appliance for food preparation

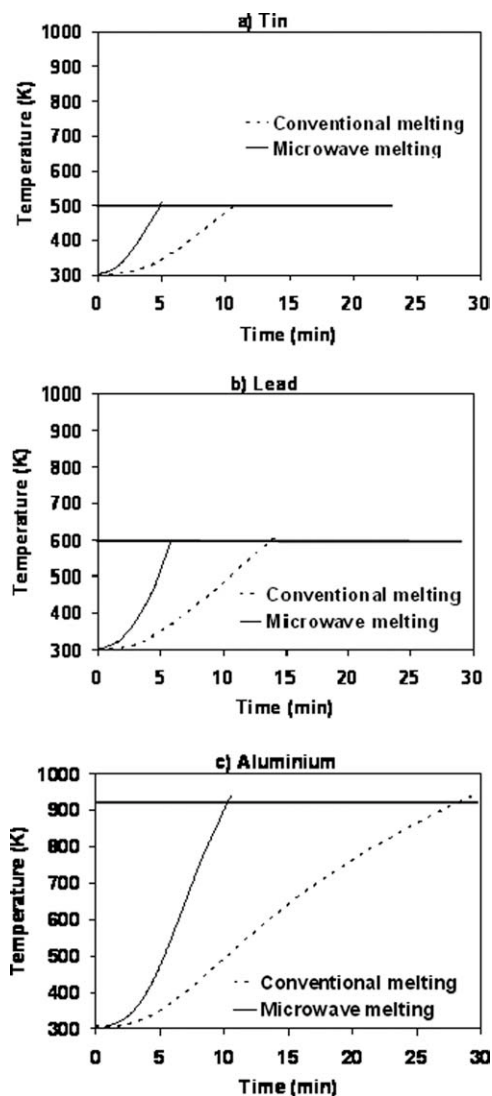


Figure 4. Comparison of microwave melting with conventional melting for (a) tin, (b) lead, and (c) aluminium⁴⁰ (Reproduced from Ref. 40, with permission from Elsevier).

and reheating applications. In food processing, multimode microwave experiments were carried out to determine the effect of power levels, power cycling, load geometry, and dielectric properties of thawing of food in a microwave oven.^{41,42} It was found that the microwave flux at the surface and its decay were affected by the changes in the power level whereas power cycling has the same effects as continuous power.⁴¹ Thawing time was found to increase linearly with the volume and an effective increase in the thawing rate was observed with decrease in the load aspect ratio.⁴² Similarly, microwave thawing of frozen layer (water layer and ice) and microwave drying of unsaturated porous material were carried out by using 2.45 GHz microwave oven and the results show that the increase in electric field intensity input led to an increase in heating rate as well as thawing and drying rate.^{15,43}

Ceramic and Polymer Applications. In ceramic processing, microwave sintering of ceramic materials such as alumina/zirconia system and mullite/zirconia system were carried out in a 900 W, 2.45 GHz microwave oven, and it was found that the densification was enhanced up to 46% due to the addition of zirconia.⁴⁴ Similarly, enhancement in densification up to 60% was observed with the microwave sintering of amorphous alumina powder.³ For microwave sintering of NiO-Al₂O₃ system, enhanced diffusion associated with the anisothermal conditions were observed when samples were exposed to the microwave field. Anisothermal heating arises due to the differences in the microwave absorption in which the individual phases heat up to different final temperatures.⁴⁵ Commercial microwave oven operating at 2.45 GHz frequency was used to synthesize sorbents or catalysts such as dealuminated Y zeolite supported CuO sorbent, and it was found that the temperature and time required to prepare sorbents by the microwave heating method were far lower or shorter than those corresponding to the conventional methods.⁴⁶

Drying of silica sludge was carried out in a domestic microwave oven with power output adjustable between 0 and 1000 W. An aluminium stirrer was placed in the microwave oven, to dissipate microwave energy more uniformly in the cavity. The optimum conditions to achieve high drying rate was found to be a power input of 800 W and a sample weight of 1000 g.⁴⁷ Similarly, in polymer processing, microwave oven were used for the bulk-polyaddition reactions of vinyl acetate, methyl methacrylate, styrene, and acrylonitrile.⁴⁸ In addition, polyesterification reaction between neopentyl glycol and adipic acid were achieved by consuming less microwave energy.⁴⁹

Variable frequency microwave processing

Variable frequency multimode (VFM) processing systems were developed in order to overcome the nonuniformity in microwave power within multimode cavities, which can result in multiple hot spots. Variable frequency microwave furnace consists of a traveling-wave-tube amplifier capable of sweeping the frequency of the microwave field which result in the time-averaged power uniformity within the microwave cavity.^{2,12} In fixed microwave heating, arcing occurs from a charge build-up in conductive materials, due to the presence of standing waves of electric fields during constant frequency microwave operation. Because of time-averaged heating processes, variable frequency microwave eliminates arcing and localized heating problems.^{50,51} Applications on variable frequency microwave processing are outlined below.

Applications of Variable Frequency Microwave Processing. Ku et al.^{52,53} used two variable frequency microwave equipments VW1500 model (operating frequency 6–18 GHz and power level 125 W) and Microcure 2100 model (operating frequency 2–7 GHz and power level 250 W) for various polymeric applications. It was found that for a fixed frequency higher electric field strength can lead to hot spots and thermal runaway for single-mode or multimode cavity. Time-averaged uniform heating was achieved using variable frequency microwaves with precise frequency tuning, thereby optimizing the coupling efficiency.^{52,53}

Variable frequency microwave processing was used for rapid curing of thermoset polymers,⁵⁴ benzocyclobutene and of high-performance polyimide on epoxy-based low-temperature organic substrates. Compared to conventional processing, shorter cure times and lower processing temperatures were achieved with the help of VFM processing.^{55,56} VFM was applied for soldering of tin alloys, and the results showed that the VFM heating was faster and provided more uniform heating profile than conventional heating methods.⁵⁷ VFM has also been used for the synthesis of silver nanoparticles with the help of reducing agents such as ethylene glycol or diethylene glycol, and it was found that VFM led to a more homogeneous nucleation due to uniform heating.⁵⁸ Although variable frequency microwave have great advantage by providing power uniformity, they tend to be expensive for a given power level, since the cost of the traveling wave tubes are high.^{12,53}

Theoretical investigations and modeling approaches

Microwave heating involves the propagation of electromagnetic waves within the sample medium. The heat generation within materials is due to dipole interactions via dielectric loss. Heat transport is mainly governed by conduction for solid substances and convective transport is important for liquid heating. The following sections discuss modeling in heat transfer and the modeling approaches for electromagnetic propagation within samples based on Lambert's law and Maxwell's equations respectively. Further, few applications based on modeling have been reviewed in subsequent sections.

Modeling for heat transport

Temperature distributions in samples exposed to microwaves are predicted by solving the appropriate energy balance equation. Based on heat transport due to conduction, the governing partial differential equation for the temperature in the sample as a function of space and time obtained by an energy balance is

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q(x, T) \quad (5)$$

where ρ , C_p , k are material density, specific heat capacity, and thermal conductivity, respectively. The microwave power, $q(x, T)$ is a spatially distributed heat source term given by

$$q = \frac{1}{2} \omega \epsilon_0 \kappa'' E^2 \quad (6)$$

Here, ω is the angular frequency, and E is the electric field intensity

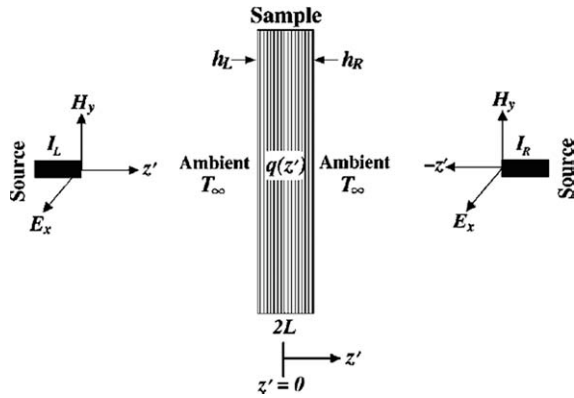


Figure 5. Representation of 1-D sample with internal heat source $p(z)$ due to absorption of microwave from left and right sides⁵⁹ (Reproduced from Ref. 59, with permission from John Wiley and Sons).

If the material has temperature dependent dielectric properties, the microwave power is temperature dependent, and the equations for the electric field must be solved simultaneously with the energy balance equation, Eq. 5. If heat is transferred from the boundaries of the sample to the surroundings by convection and radiation, the boundary condition is

$$\mathbf{n} \cdot k \nabla T = h(T - T_\infty) + \sigma_h \epsilon_h (T^4 - T_\infty^4) \quad (7)$$

where \mathbf{n} is the outward pointing unit normal on the surface of the sample, T_∞ is the ambient temperature, h is the heat transfer coefficient, ϵ_h is the emissivity of the sample, and σ_h is the Stefan Boltzmann constant.

Closed Form Solutions: Various Time Scales. The energy equations obtained for the evolution of temperature within the semiinfinite slab of length $2L$ when exposed to uniform plane microwave radiations of intensities I_L (from left side) and I_R (from right side), respectively (see Figure 5) is given by⁵⁹

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z'^2} + q(z'), \quad -L \leq z' \leq L \quad (8)$$

The above equations were determined based on the assumptions of constant density (ρ), heat capacity (C_p) and thermal conductivity (k) and the slab is initially maintained at temperature T_0 . The equations accounting for heat loss to ambient is given as

$$k \frac{\partial T}{\partial z'} = h_L(T - T_\infty) \quad \text{at } z' = -L \quad (9)$$

$$-k \frac{\partial T}{\partial z'} = h_R(T - T_\infty) \quad \text{at } z' = L \quad (10)$$

where T_∞ is the ambient temperature, q is the volumetric heat generation term due to microwaves, h_L and h_R are left and right side heat transfer coefficients. Equations 8–10 can be written in dimensionless form as

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial z^2} + N_G p(z), \quad -1 \leq z \leq 1 \quad (11)$$

$$\frac{\partial \theta}{\partial z} = Bi_L(\theta - 1) \quad \text{at } z = -1 \quad (12)$$

$$-\frac{\partial \theta}{\partial z} = Bi_R(\theta - 1) \quad \text{at } z = 1 \quad (13)$$

where the dimensionless numbers are defined as,

$$\theta = \frac{T}{T_\infty}, \quad \theta_0 = \frac{T_0}{T_\infty}, \quad \tau = \frac{t}{\alpha}, \quad z = \frac{z'}{L}, \quad p(z) = \frac{q(z'/L)}{q_0},$$

$$\{Bi_i\}_{i=L,R} = \frac{h_i L}{k}, \quad N_G = \frac{q_0 L^2}{k T_\infty} \quad (14)$$

where $\alpha = \rho C_p L^2 / k$ is the thermal diffusion time, $q_0 = I_0 / L$ with $\sqrt{I_0} = \sqrt{I_L} + \sqrt{I_R}$ is the characteristic volumetric heat source and Bi_L and Bi_R are left and right side Biot number, respectively. Using Finite Fourier Transformation, the analytical solution of Eq. 11 can be obtained as,⁵⁹

$$\theta = 1 + \sum_{n=1}^{\infty} \left[\langle 1, \psi_n(z) \rangle (\theta_0 - 1) e^{-\mu_n^2 \tau} + N_G \frac{1 - e^{-\mu_n^2 \tau}}{\mu_n^2} p_n \right] \psi_n(z) \quad (15)$$

where μ_n and $\psi_n(z)$ are n th eigenvalue and eigenfunction, respectively and the closure p_n is the power Fourier coefficient. In Eq. 15, the first term within the bracket denotes the thermal diffusion due to different initial and ambient temperatures, while the second term represents to thermal diffusion due to imposed internal heat sources. Thus, the temperature distributions within the slab depend upon the parameters $\theta_0 - 1$, N_G , and τ .⁵⁹

Simple conduction and convection model of heat transport is not adequate for complex transport processes involving melting, thawing, drying, and so on and the detailed modeling approach for such processes is as follows.

Thawing and Melting of Materials. The energy balance equation for phase change applications such as thawing may be given based on the enthalpy formulation as,⁶⁰

$$\frac{\partial H}{\partial t} + \delta_l \rho C_l \mathbf{U} \cdot \nabla T = \nabla \cdot k_{\text{eff}} \nabla T + q(T), \quad (16)$$

where

$$\delta_l = \begin{cases} 0 & 0 \leq \phi_l < 1, \quad \text{solid and mushy region} \\ 1 & \phi_l = 1, \quad \text{liquid region} \end{cases} \quad (17)$$

In Eq. 16, \mathbf{U} is the fluid velocity, $q(T)$ is the absorbed microwave power, C_l is the heat capacity of the liquid phase and enthalpy $H(T)$ is a function of temperature at a given location in the sample.⁶⁰ The boundary condition (Eq. 7) may be used for the solution of Eq. 16.

Figure 6 shows the analytical model for melting of frozen packed beds.¹³ The boundary conditions for the heat transport equation were assumed to be of perfectly insulated boundary layers (Eq. 18) and the Stefan's equation was used to describe the moving boundary between unfrozen layer and frozen layer (Eq. 19).^{13,14}

$$\frac{\partial T}{\partial n} = 0 \quad (18)$$

$$\left(k_{\text{eff},s} \frac{\partial T_s}{\partial z} - q_{\text{Bou}} \Delta z_{\text{Bou}} - k_{\text{eff},l} \frac{\partial T_l}{\partial z} \right) \left[1 + \left(\frac{\partial z_{\text{Bou}}}{\partial x} \right)^2 \right] = \rho_s L_s S_s \frac{\partial z_{\text{Bou}}}{\partial t} \quad (19)$$

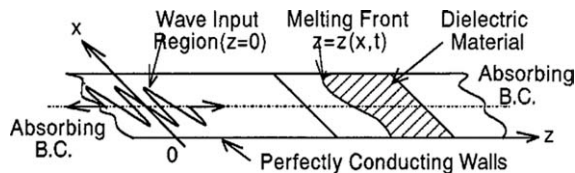


Figure 6. Physical model for microwave melting of frozen packed beds¹³ (Reproduced from Ref. 13, with permission from Elsevier).

where k_{eff} is the effective thermal conductivity, q is the heat flux, L is the latent heat and the subscripts s , l and Bou denote the solid, liquid, and solid-liquid front, respectively. For microwave heating of liquid layers, fluid flow equations were also considered along with heat transport equation (Eq. 5). The governing equation for the momentum transport in the liquid phase for Newtonian fluid using Boussinesq approximation is given by

$$\rho \frac{\partial \mathbf{U}}{\partial t} + \rho \mathbf{U} \cdot \nabla \mathbf{U} = -\nabla P + \mu \nabla^2 \mathbf{U} - \rho_0 \beta (T - T_f) \mathbf{g}, \quad (20)$$

and the continuity equation is

$$\nabla \cdot \mathbf{U} = 0 \quad (21)$$

In Eq. 20, ρ_0 is the density at the reference temperature T_f , P is the pressure, \mathbf{g} is the acceleration due to gravity, μ and β are the viscosity and the coefficient of thermal expansion of the liquid respectively.

Galerkin finite element may be used to solve the coupled enthalpy and momentum balance equations for thawing process along with electric field equations.⁶⁰ Similarly, in melting of frozen packed beds, the coupled nonlinear set of Eqs. 5, 7, and 18–21 can be solved numerically with appropriate boundary conditions by finite volume or finite element method.^{13,14}

Drying of Unsaturated Porous Material. The transport mechanisms involved in the microwave drying of unsaturated porous material are: liquid flow due to capillary pressure gradient and gravity, and vapor flow due to the partial pressure gradient.^{61,62} Figure 7 depicts the analytical model for the microwave drying process.⁶¹ The assumptions involved in the transport model are that the capillary porous material is rigid with no chemical reactions occurring in the sample, local thermodynamic equilibrium prevails, simultaneous heat, and mass transfer occur at constant pressure and nonthermal microwave effects are negligible. The mass conservation equations for liquid, water vapor, air, and gas phases are written as

$$\text{Liquid phase} \quad \rho_l \phi \frac{\partial s}{\partial t} + \rho_l \frac{\partial u_l}{\partial x} = -\dot{n} \quad (22)$$

$$\text{Vapour phase} \quad \frac{\partial}{\partial t} [\rho_v \phi (1-s)] + \frac{\partial}{\partial x} [\rho_v u_v] = \dot{n} \quad (23)$$

where s is the water saturation, ϕ is the porosity, u is the superficial average velocity, and n is the phase change term and subscripts l and v denote liquid and vapor phase.

The generalized Darcy's law for the calculation of superficial average velocity of liquid and gas phases is given as,

$$u_l = -\frac{KK_{rl}}{\mu_l} \left[\frac{\partial p_g}{\partial x} - \frac{\partial p_c}{\partial x} - \rho_l g \right], \quad u_g = -\frac{KK_{rg}}{\mu_g} \left[\frac{\partial p_g}{\partial x} - \rho_g g \right] \quad (24)$$

where p_g and p_c represent gas and capillary pressure respectively, μ_l and μ_g denote the viscosity of liquid and gas phases, respectively, and K_{rl} and K_{rg} represent liquid and gas relative permeabilities respectively, which are given by the set of constitutive relationships for liquid and gas system.⁶¹

The generalized Fick's law for the velocity of water vapor and air phases is given as

$$\rho_v u_v = \rho_v u_g - \rho_g D_m \frac{\partial}{\partial x} \left(\frac{\rho_v}{\rho_g} \right), \quad \rho_a u_a = \rho_a u_g - \rho_g D_m \frac{\partial}{\partial x} \left(\frac{\rho_a}{\rho_g} \right) \quad (25)$$

where the subscripts a and g denote air and gas phase, respectively, and the effective molecular mass diffusion D_m is given as,

$$D_m = \frac{2\phi}{3-\phi} (1-s) D \quad (26)$$

and the capillary pressure p_c is represented by the Leverett's function as,

$$p_c = p_g - p_l = \frac{\sigma}{\sqrt{K/\phi}} J(s_e) \quad (27)$$

Here σ is the gas-liquid interfacial tension, s_e is the effective water saturation and the Leverett function $J(s_e)$ is given by

$$J(s_e) = 0.325(1/s_e - 1)^{0.217} \quad (28)$$

The heat transport equation due to heat conduction and latent heat transfer is represented by

$$\begin{aligned} \frac{\partial}{\partial t} [(\rho C_p)_T T] + \frac{\partial}{\partial x} [\{\rho_l C_{pl} u_l + (\rho_a C_{pa} + \rho_v C_{pv}) u_g\} T] \\ + H_v \dot{n} = \frac{\partial}{\partial x} \left[\lambda \frac{\partial T}{\partial x} \right] + Q \end{aligned} \quad (29)$$

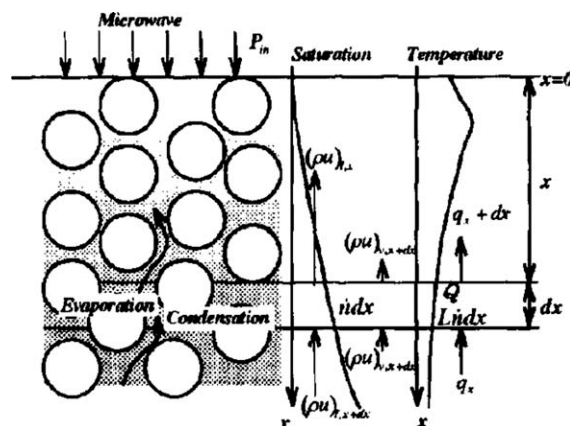


Figure 7. Analytical model for microwave heating of unsaturated porous medium⁶¹ (Reproduced from Ref. 61, with permission from Elsevier).

where

$$(\rho C_p)_T = \rho_l C_{pl} \phi s + [(\rho_a C_{pa} + \rho_v C_{pv}) \phi (1 - s)] + \rho_p C_{pp} (1 - \phi) \quad (30)$$

and the phase change term (\dot{n}) is given by

$$\dot{n} = \frac{\partial}{\partial t} [\rho_v \phi (1 - s)] + \frac{\partial}{\partial x} \left[\rho_v \frac{KK_{rg}}{\mu_g} \rho_g g - D_m \frac{\partial \rho_v}{\partial x} \right] \quad (31)$$

Here, subscript p denotes particle, H_v is the specific heat of vaporization, C_p is the specific heat capacity, λ is the effective thermal conductivity, and Q is the microwave power absorbed term which is given by Eq. 6.

The moisture transport phenomenon is characterized by the mass conservation equations for the liquid phase and for the water vapor in the gas phase [addition of one-dimensional (1-D) Eqs. 22 and 23]

$$\phi \frac{\partial}{\partial t} [\rho_l s + \rho_v (1 - s)] + \frac{\partial}{\partial x} \left[\rho_l \frac{KK_{rl}}{\mu_l} \left(\frac{\partial p_c}{\partial x} + \rho_l g \right) + \rho_v \frac{KK_{rg}}{\mu_g} (\rho_g g) - D_m \frac{\partial \rho_v}{\partial x} \right] = 0 \quad (32)$$

The boundary conditions applicable for the exchange of energy at the open boundary is given by,

$$-\lambda \frac{\partial T}{\partial x} = h_c (T - T_a) + \dot{n} H_v \quad (33)$$

$$\rho_l u_l + \rho_v u_v = h_m (\rho_{vs} - \rho_{v\infty}) \quad (34)$$

where h_c is the heat transfer coefficient, h_m is the mass transfer coefficient, ρ_{vs} is the density of water vapor at the open boundary and $\rho_{v\infty}$ is the reference vapor density in the gas phase surrounding the open boundary.

Similarly, for closed boundary, no heat and mass exchange takes place.

$$\frac{\partial T}{\partial x} = 0, \quad \frac{\partial u}{\partial x} = 0 \quad (35)$$

The system of nonlinear partial difference equations with boundary conditions (Eqs. 29–35) for microwave heating of unsaturated porous material can be solved by using finite difference method.⁶¹

Electromagnetic wave propagation: Lambert's law

Lambert's law is based on exponential decay of microwave absorption within the product, via the following relationship

$$P(x) = P_0 e^{-2\alpha x} \quad (36)$$

where P_0 is the power at the surface; x , the distance measured from the surface; $P(x)$ is the power dissipated at a distance x and α is the attenuation constant which is a function of wavelength of radiation (λ_0), relative dielectric constant (κ') and loss tangent ($\tan \delta$). The attenuation constant is given by the following equation:

$$\alpha = \frac{2\pi}{\lambda_0} \sqrt{\frac{\kappa'((1 + \tan^2 \delta)^{1/2} - 1)}{2}} \quad (37)$$

Lambert's law has been applied to frame simple mathematical models for microwave energy distribution in food products with basic geometries (slabs, spheres, and cylinders), and the effect of changes in product composition with relation to dielectric properties and changes in product size can be predicted.⁶³ Similarly, Campanone and Zaritzky⁶⁴ developed a mathematical model to solve the unsteady state heat transfer differential equations and applied the method to large 1-D systems for which Lambert's law is valid and numerical results were found to be in a very good agreement with experimental data. However, Lambert's law model was unable to give an exact and detailed prediction of temperature distributions during microwave heating.⁶⁴

Electromagnetic wave propagation: Maxwell's field equations

Maxwell's equations that govern the propagation and the microwave heating of a material are given below:

$$\nabla \cdot \mathbf{D} = \nabla \cdot (\epsilon^* \mathbf{E}) = \rho \quad (38)$$

$$\nabla \cdot \mathbf{B} = \nabla \cdot (\mu \mathbf{H}) = 0 \quad (39)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (40)$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (41)$$

where \mathbf{H} and \mathbf{E} are the magnetic and electric field intensities, respectively; \mathbf{J} and $\frac{\partial \mathbf{D}}{\partial t}$ denote the current density and displacement current density, respectively; \mathbf{D} and \mathbf{B} signify the electric flux density and magnetic flux density respectively; μ is the magnetic permeability; and ϵ^* is the permittivity.

The power flow through a closed surface S , of a given volume V can be calculated from the integration of the Poynting vector as given below.¹

$$P = \oint_S (\mathbf{E} \times \mathbf{H}^*) \cdot d\mathbf{S} \quad (42)$$

where $\mathbf{E} \times \mathbf{H}^*$ is the Poynting vector. Using the divergence theorem and the Maxwell's equation yields,

$$\begin{aligned} \oint_S (\mathbf{E} \times \mathbf{H}^*) \cdot d\mathbf{S} &= \int_V \nabla \cdot (\mathbf{E} \times \mathbf{H}^*) dV \\ &= -j\omega \int_V (\mu_0 \mu' \mathbf{H}^* \cdot \mathbf{H} - \epsilon_0 \kappa' \mathbf{E} \cdot \mathbf{E}^*) dV - \int_V \omega \epsilon_0 \kappa'' \mathbf{E} \cdot \mathbf{E}^* dV \end{aligned} \quad (43)$$

The average power obtained from Eq. 42 is given as,^{1,65}

$$P_{av} = -\frac{1}{2} \int_S \text{Re}(\mathbf{E} \times \mathbf{H}^*) \cdot d\mathbf{S} \quad (44)$$

Comparing Eqs. (43) and (44) we obtain,

$$P_{av} = \frac{1}{2} \omega \epsilon_0 \kappa'' \int_V (\mathbf{E}^* \cdot \mathbf{E}) dV \quad (45)$$

If the electric field is assumed to be uniform throughout the volume, then the simplified equation for power absorbed by the material per unit volume may be given as,

$$P_{av} = \frac{1}{2} \omega \epsilon_0 \kappa'' E^2 = 2\pi f \epsilon_0 \kappa'' E_{rms}^2 \quad (46)$$

where E_{rms} refers to the root mean square of the electric field.

Using Maxwell's field equations, modeling of microwave heating may be done using either spatial analysis of field variables (\mathbf{E} , \mathbf{H}) or spatiotemporal field variables.

Spatial Analysis of Maxwell's Equations. Using basic Maxwell's equations and assuming the medium to be homogeneous (i.e. electrical properties have no spatial variation in the medium), the governing equation for electromagnetic wave propagation due to uniform electric field, \mathbf{E}_x (\mathbf{E}_x lies in x - y plane), varying only in the direction of propagation, z axis is given as

$$\nabla^2 \mathbf{E}_x + k^2 \mathbf{E}_x = 0 \quad (47)$$

where $k^2 = \omega^2 \mu \epsilon^*$. The above equation is also referred as Helmholtz or reduced wave equation.

The constant ' k ' is wave number or propagation constant and can be expressed as,

$$k = \omega \sqrt{\mu \epsilon^*} = \frac{\omega}{c} = \frac{2\pi f}{c} = \frac{2\pi}{\lambda} \quad (48)$$

In terms of relative dielectric constant (κ') and relative dielectric loss (κ''), the propagation constant ' k ' is defined as,

$$k^2 = \omega^2 \mu_0 \epsilon_0 (\kappa' + i\kappa'') \quad (49)$$

The electric field can be derived for nonhomogeneous medium with temperature dependent permeability and a more general form of the Helmholtz equation is

$$\nabla \left(\mathbf{E} \cdot \frac{\nabla \kappa^*}{\kappa^*} \right) + \nabla^2 \mathbf{E} + k(T)^2 \mathbf{E} = 0 \quad (50)$$

where κ^* is the complex relative dielectric constant. The first term of Eq. 50 represents the spatial variation of dielectric properties along the direction of electric field vector and for most of 1-D and two-dimensional (2-D) samples exposed to plane waves this term is zero.⁶⁵ The electric field within the medium can be obtained via solving governing equations (Eq. 47 or Eq. 50) with the boundary conditions. The boundary conditions relating the electric and magnetic fields at the interface between two media, 1 and 2, are⁶⁶

$$\begin{aligned} \mathbf{n} \cdot (\kappa_1^* \mathbf{E}_1 - \kappa_2^* \mathbf{E}_2) &= 0 \\ \mathbf{n} \times (\mathbf{E}_1 - \mathbf{E}_2) &= 0 \\ \mathbf{n} \cdot (\mathbf{H}_1 - \mathbf{H}_2) &= 0 \\ \mathbf{n} \times (\mathbf{H}_1 - \mathbf{H}_2) &= 0 \end{aligned} \quad (51)$$

Here \mathbf{n} is the unit outward normal originating in medium 2. These boundary conditions assume that there are no

charges at the interface between the two media. The system of equations (Eqs. 47 or 50 and 5) with the appropriate boundary conditions can be solved by finite element method as discussed in earlier literatures.^{65,67-75}

Equation 47 can be solved analytically for a single medium surrounded by air and in such a case, a closed form solution is available for 1-D samples incident with uniform plane waves⁶⁵ whereas a generalized version, Eq. 50 is used for 2-D samples.⁶⁷

The coupled equations for the propagation of electromagnetic wave through the surrounding free space (Figure 5) is given by⁷⁶

$$\frac{d^2 E_{x,j}}{dz'^2} + \kappa_j^2 E_{x,j} = 0, \quad j = \begin{cases} l & z' < -L \\ m & -L \leq z' \leq L \\ r & z' > L \end{cases} \quad (52)$$

with

$$\left. \begin{aligned} E_{x,l} &= E_{x,m} \\ \frac{dE_{x,l}}{dz'} &= \frac{dE_{x,m}}{dz'} \end{aligned} \right\} \text{ at } z' = -L \text{ and } \left. \begin{aligned} E_{x,m} &= E_{x,r} \\ \frac{dE_{x,m}}{dz'} &= \frac{dE_{x,r}}{dz'} \end{aligned} \right\} \text{ at } z' = L \quad (53)$$

The solution of Eq. 52 can be given as a combination of transmitted and reflected waves

$$E_{x,j} = E_{1,j} e^{i\kappa_j z'} + E_{2,j} e^{-i\kappa_j z'}, \quad j = l, m, r \quad (54)$$

where $E_{1,j}$ and $E_{2,j}$ are transmission and reflection coefficients respectively with

$$E_{1,l} = E_L \quad \text{and} \quad E_{2,r} = E_R \quad (55)$$

Equation 53 can be used to determine other coefficients ($E_{2,l}$, $E_{1,m}$, $E_{2,m}$, $E_{1,r}$) and thus the electric field within the sample can be obtained as

$$E_{x,m} = E_T \frac{\sum_{k=l}^r 2\kappa_k e^{-i\kappa_k L} [\kappa_m \cos\{\kappa_m L(1 + \sigma z)\} - i\kappa_j \sin\{\kappa_m L(1 + \sigma z)\}]}{\kappa_m (\kappa_l + \kappa_r) \cos(2\kappa_m L) - i(\kappa_m^2 + \kappa_l \kappa_r) \sin(2\kappa_m L)} \phi_k \quad (56)$$

where κ_m is the propagation constant of the sample, $\sigma = 1, -1$, and $j = l, r$ for $k = r, l$, respectively, $E_T = E_L + E_R$, and dimensionless variables ϕ_l , ϕ_r , and z are given by

$$z = \frac{z'}{L}, \quad \phi_l = \frac{E_L}{E_L + E_R}, \quad \phi_r = \frac{E_R}{E_L + E_R} \equiv 1 - \phi_l, \quad (57)$$

The distribution of dimensionless absorbed power can be obtained by taking complex conjugate of $E_{x,m}$.⁷⁶

$$Q(z) = \frac{C_q^l(z) \phi_l^2 + C_q^r(z) \phi_r^2 + 2C_q^{lr}(z) \phi_l \phi_r}{C_q^d} \quad (58)$$

where

$$Q(z) = q(z'/L)/Q_0 \quad (59)$$

with

$$Q_0 = \pi f \epsilon_0 \kappa_m'' E_T^2 \quad (60)$$

and

$$C_q^k = c_{q,1}^k \cos(2\kappa_{mR}L(1 + \sigma z)) + c_{q,2}^k \cosh(2\kappa_{mI}L(1 + \sigma z)) + c_{q,3}^k \sin(2\kappa_{mR}L(1 + \sigma z)) + c_{q,4}^k \sinh(2\kappa_{mI}L(1 + \sigma z)), \quad k = l, r \quad (61)$$

$$C_q^{lr} = c_{q,1}^{lr} \cosh(2\kappa_{mI}Lz) - c_{q,2}^{lr} \sinh(2\kappa_{mI}Lz) + c_{q,3}^{lr} \cos((\kappa_{lR} - \kappa_{rR})L - 2\kappa_{mR}Lz) + c_{q,4}^{lr} \cos((\kappa_{lR} - \kappa_{rR})L + 2\kappa_{mR}Lz) + c_{q,5}^{lr} \sin((\kappa_{lR} - \kappa_{rR})L - 2\kappa_{mR}Lz) - c_{q,6}^{lr} \sin((\kappa_{lR} - \kappa_{rR})L + 2\kappa_{mR}Lz), \quad (62)$$

and

$$C_q^d = c_{q,1}^d \cos(4\kappa_{mR}L) + c_{q,2}^d \cosh(4\kappa_{mI}L) + c_{q,3}^d \sin(4\kappa_{mR}L) + c_{q,4}^d \sinh(4\kappa_{mI}L) \quad (63)$$

where $c_{q,j}^k$, $c_{q,j}^{lr}$ and $c_{q,j}^d$ are the coefficients.⁷⁶

The closed form solutions may not exist for 2-D irregular shaped samples and also for the samples with temperature dependent dielectric properties. For such cases, the electric field may be decomposed into real and imaginary parts.⁶⁹⁻⁷⁵

Introducing the dimensionless variables,

$$u_x = \frac{E_x}{E_0} \quad \text{and} \quad \nabla^* = r_c \nabla \quad (64)$$

Equation 47 reduces to

$$\nabla^{*2} u_x + \gamma^2 u_x = 0 \quad (65)$$

where u_x is the electric field intensity, $\gamma = (r_c \omega / c) \sqrt{\kappa' + i\kappa''}$ is the propagation constant and r_c is the radius of the cross section of the sample. The incident electric field, E_0 may be obtained from intensity of microwave radiation, I_0 via following relationship;

$$I_0 = \frac{1}{2} c \epsilon_0 E_0^2 \quad (66)$$

Substituting the complex field variable $u_x = v_x + iw_x$ into Eq. 47 would result in system of equations involving real and imaginary parts as given below.^{60,69-75}

$$\nabla^{*2} v_x + \chi_1 v_x - \chi_2 w_x = 0 \quad (67)$$

and

$$\nabla^{*2} w_x + \chi_2 v_x + \chi_1 w_x = 0 \quad (68)$$

with $\chi_1 = (r_c \omega^2 / c^2) \kappa'$ and $\chi_2 = (r_c \omega^2 / c^2) \kappa''$

The boundary conditions for the real and imaginary parts of electric field at the interface of sample and a free space can be obtained by radiation boundary condition (RBC).⁶⁷ RBCs used at the outer surface of the cylinder for lateral radiation (sample incident to microwave at one direction) is given as^{60,69-75}

$$n \cdot \nabla^* v_x = \sum_{n=0}^{\infty} \text{Re}(C_n) \cos n\phi + \sum_{n=0}^{\infty} \text{Re}(D_n) \int_0^{2\pi} v_x(1, \phi') \cos n(\phi - \phi') d\phi' - \sum_{n=0}^{\infty} \text{Im}(D_n) \int_0^{2\pi} w_x(1, \phi') \cos n(\phi - \phi') d\phi' \quad (69)$$

and

$$n \cdot \nabla^* w_x = \sum_{n=0}^{\infty} \text{Im}(C_n) \cos n\phi + \sum_{n=0}^{\infty} \text{Im}(D_n) \int_0^{2\pi} v_x(1, \phi') \cos n(\phi - \phi') d\phi' + \sum_{n=0}^{\infty} \text{Re}(D_n) \int_0^{2\pi} w_x(1, \phi') \cos n(\phi - \phi') d\phi' \quad (70)$$

with the coefficients

$$C_n = \frac{\epsilon_n i^n r_c \omega}{c} \left[J'_n \left(\frac{r_c \omega}{c} \right) - J_n \left(\frac{r_c \omega}{c} \right) \frac{H_n^{(1)'} \left(\frac{r_c \omega}{c} \right)}{H_n^{(1)} \left(\frac{r_c \omega}{c} \right)} \right] \quad (71)$$

and

$$D_n = \frac{r_c \omega \delta_n H_n^{(1)'} \left(\frac{r_c \omega}{c} \right)}{c \pi H_n^{(1)} \left(\frac{r_c \omega}{c} \right)} \quad (72)$$

where

$$\epsilon_n = \begin{cases} 1, & n = 0; \\ 2, & \text{otherwise}, \end{cases} \quad \text{and} \quad \delta_n = \begin{cases} 1/2, & n = 0; \\ 1, & \text{otherwise}, \end{cases} \quad (73)$$

In Eqs. 71 and 72, J_n and $H_n^{(1)}$ are the n th order Bessel and Hankel functions of the first kind respectively and prime indicates the first derivatives.

Similarly, RBCs for lateral irradiation (sample exposed to uniform microwave intensities at all directions) is given as⁷¹⁻⁷⁵

$$n \cdot \nabla^* v_x + c_1 v_x + c_2 w_x = c_3 \quad (74a)$$

and

$$n \cdot \nabla^* w_x + c_1 w_x - c_2 v_x = c_4, \quad (74b)$$

where

$$c_1 = \frac{r_c \omega}{c} \left[\frac{J_1 \left(\frac{r_c \omega}{c} \right) J_0 \left(\frac{r_c \omega}{c} \right) + Y_1 \left(\frac{r_c \omega}{c} \right) Y_0 \left(\frac{r_c \omega}{c} \right)}{J_0^2 \left(\frac{r_c \omega}{c} \right) + Y_0^2 \left(\frac{r_c \omega}{c} \right)} \right], \quad (75)$$

$$c_2 = \frac{2}{\pi [J_0^2 \left(\frac{r_c \omega}{c} \right) + Y_0^2 \left(\frac{r_c \omega}{c} \right)]}, \quad (76)$$

$$c_3 = -\frac{4}{\pi} \frac{Y_0 \left(\frac{r_c \omega}{c} \right)}{J_0^2 \left(\frac{r_c \omega}{c} \right) + Y_0^2 \left(\frac{r_c \omega}{c} \right)}, \quad (77)$$

$$c_4 = -\frac{4}{\pi} \frac{J_0 \left(\frac{r_c \omega}{c} \right)}{J_0^2 \left(\frac{r_c \omega}{c} \right) + Y_0^2 \left(\frac{r_c \omega}{c} \right)}, \quad (78)$$

where Y_0 and Y_1 correspond to zero and first order Bessel functions of the second kind respectively. Equations 67 and 68 along with boundary conditions (Eqs. 69, 70, 74a, 74b) are solved with finite element method.⁷¹⁻⁷⁵

Time-Dependent Analysis of Maxwell's Equations. Equations 67 and 68 along with boundary conditions (Eqs. 69 and 70) are solved with finite element method.⁷¹⁻⁷⁵ For the microwave of TE₁₀ mode, the components of electric and magnetic field intensities are given by,

$$\begin{aligned} E_x = E_z = H_y &= 0 \\ E_y, H_x, H_z &\neq 0 \end{aligned} \quad (79)$$

Using the relation of Eq. (79) in the Maxwell's field equations (Eqs. 38–41), the governing equations can be written as,^{13–16,77–79}

$$\frac{\partial E_y}{\partial z} = \mu \frac{\partial H_x}{\partial t} \quad (80)$$

$$\frac{\partial E_y}{\partial x} = -\mu \frac{\partial H_z}{\partial t} \quad (81)$$

$$-\left(\frac{\partial H_z}{\partial x} - \frac{\partial H_x}{\partial z}\right) = \sigma E_y + \varepsilon^* \frac{\partial E_y}{\partial t} \quad (82)$$

where the permittivity ε^* , magnetic permeability μ and electric conductivity σ are given as

$$\varepsilon^* = \varepsilon_0 \kappa^* \quad (83)$$

$$\mu = \mu_0 \mu_r \quad (84)$$

$$\sigma = 2\pi f \varepsilon^* \tan \delta \quad (85)$$

where μ_r is the relative magnetic permeability

The solution for the three coupled scalar partial differential equations (Eqs. 80–82) with appropriate boundary conditions^{77–79} governing Maxwell's equation inside a rectangular wave guide can be obtained by using the finite difference time-domain (FDTD) method. By this method, the electric and magnetic fields are evaluated at alternate half time steps and are expressed by the total field FDTD equations as^{15,16,77–79}

$$\begin{aligned} E_y^n(i, k) &= \frac{1 - (\sigma(i, k)\Delta t)/(2\varepsilon^*(i, k))}{1 + (\sigma(i, k)\Delta t)/(2\varepsilon^*(i, k))} E_y^{n-1}(i, k) \\ &+ \frac{1}{1 + (\sigma(i, k)\Delta t)/(2\varepsilon^*(i, k))} \frac{\Delta t}{\varepsilon^*(i, k)} \\ &\times \left\{ \frac{-(H_z^{n-1/2}(i + 1/2, k) - H_z^{n-1/2}(i - 1/2, k))}{\Delta x} \right. \\ &\left. + \frac{(H_x^{n-1/2}(i, k + 1/2) - H_x^{n-1/2}(i, k - 1/2))}{\Delta z} \right\} \end{aligned} \quad (86)$$

$$\begin{aligned} H_x^{n+1/2}(i, k + 1/2) &= H_x^{n-1/2}(i, k + 1/2) + \frac{\Delta t}{\mu(i, k + 1/2)} \\ &\times \left\{ \frac{E_y^n(i, k + 1) - E_y^n(i, k)}{\Delta z} \right\} \end{aligned} \quad (87)$$

$$\begin{aligned} H_z^{n+1/2}(i + 1/2, k) &= H_z^{n-1/2}(i + 1/2, k) - \frac{\Delta t}{\mu(i + 1/2, k)} \\ &\times \left\{ \frac{E_y^n(i + 1, k) - E_y^n(i, k)}{\Delta x} \right\} \end{aligned} \quad (88)$$

The stability of the time-stepping algorithm Δt was chosen in order to satisfy the courant stability condition which is defined as

$$\Delta t \leq \frac{\sqrt{(\Delta x)^2 + (\Delta z)^2}}{c} \quad (89)$$

The spatial resolution of each cell is defined as

$$\Delta x, \Delta z \leq \frac{\lambda_g}{10\sqrt{\varepsilon'}} \quad (90)$$

where c and λ_g are the velocity and wavelength of an electromagnetic wave, respectively.

Similarly, the governing equations for multimode, domestic microwave ovens are given as,⁴³

$$\frac{\partial^2 E}{\partial x^2} = \sigma \mu \frac{\partial E}{\partial t} + \varepsilon^* \mu \frac{\partial^2 E}{\partial t^2} \quad (91)$$

$$\frac{\partial^2 H}{\partial x^2} = \sigma \mu \frac{\partial H}{\partial t} + \varepsilon^* \mu \frac{\partial^2 H}{\partial t^2} \quad (92)$$

$$\text{where } E = E_0 e^{j\omega t - \gamma x}, H = H_0 e^{j\omega t - \gamma x} \quad (93)$$

where E_0 and H_0 are the incident electric and magnetic field respectively and γ is the propagation constant. The above equations are derived based on the assumption that in the microwave oven, the microwave field is a planar wave propagating on an infinite cylindrical test section and the total amount of microwave power absorbed within the sample was assumed constant.⁴³

Spatial Analysis of Maxwell's Equations—Test Studies. Ayappa and coworkers⁸⁰ computed the power absorption based on Maxwell's equations for finite slabs and also found certain critical slab thickness as a function of the penetration depth of the microwave radiation. It is seen that the Lambert's law predictions agree well with the power estimation based on Maxwell's equations. Further, they developed a general formulation of power absorption based on Maxwell's equations for a homogeneous, isotropic multilayered medium exposed to plane waves from both face and they found temperature profiles by solving the energy balance equation with the microwave power as a source term using temperature-dependent thermal and dielectric properties. Using effective heat capacity method, microwave thawing of materials such as tylose slabs were analyzed over a finite temperature range and the microwave power was calculated from Maxwell's equations.⁸¹ Using Galerkin finite elements, the microwave power, temperature and liquid volume fractions were obtained for microwave thawing of tylose slabs and it was found that for slabs ≥ 5 cm, thawing progresses predominantly from the surface of the sample.⁸¹

Oliveira and Franca⁸² presented a mathematical model to predict the temperature distribution during microwave heating of solids. The electric field distribution was obtained by solving Maxwell's equations and electric field is further coupled to the transient heat conduction equation. They incorporated the effect of sample rotation to the model to achieve a more uniform temperature distribution during microwave heating of solids. They found that increase in microwave frequency from 900 to 2800 MHz induces higher temperature gradients near the sample surface and at lower frequencies, heating was more significant at the center of the sample.⁸² Later, several works have been reported on power absorptions based on Maxwell's equations.^{83–85} Spatial analysis of Maxwell's equation has also been carried out for food processing. Maxwell's equations for electromagnetic fields and the heat conduction equation were solved to predict temperature distribution in food processing for the pasteurization of prepared meals. It was found that the model was able to identify regions of the highest and lowest temperature for the food samples.⁸³ Similarly for ceramic materials such as Al_2O_3 and SiC, Maxwell's equations were solved along with the

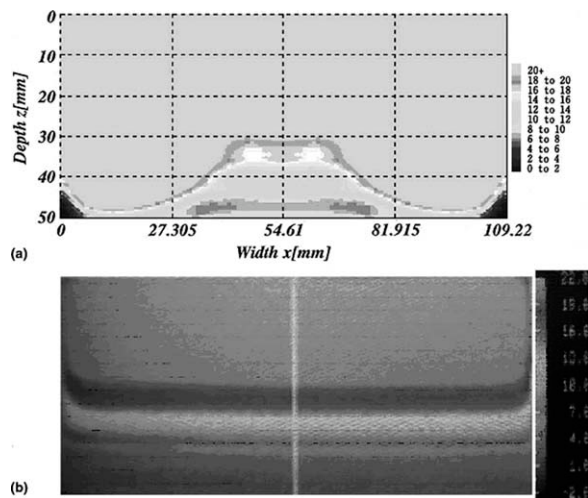


Figure 8. Comparison between (a) predicted results and (b) experimental results of microwave heating of water layer ($P = 1000$ W, $t = 60$ s)⁷⁷ (Reproduced from Ref. 77, with permission from Elsevier).

heat conduction equations and evolution equations for porosity and grain diameter to predict the temperature, power, densification and grain size distributions during microwave sintering. It was found that the time required for sintering, densification rates, and grain growths were identical for both conventional and microwave sintering indicating that the effect of microwaves is purely thermal.⁸⁴

Maxwell's equations for electromagnetic waves were used for the analysis of microwave heating of materials with temperature-dependent dielectric and thermal properties. Galerkin finite element method was used to solve simultaneous Maxwell's equations and energy balance equation for multilayer slabs and it was found that as the sample gets heated, gradual increase in loss tangent occurs due to the decrease in the penetration of microwaves.⁸⁰ Alpert and Jerby⁸⁵ reported 1-D model for the coupled electromagnetic-thermal process and later they extended their work to 2-D systems. Using finite elements, microwave heating of long rods with square and circular cross sections was analyzed. They studied the transient temperature profiles for lossy materials with temperature dependent dielectric properties exposed to plane waves. Ayappa et al.⁶⁷ analyzed the effect of incident wave polarization on the heating rate of the 2D cylinders and squares. They found that TM^z polarization, where the electric field is polarized along the long axis of the 2D samples, caused higher power absorption than that with TE^z polarization, where the electric field is polarized perpendicular to the sample axis.⁶⁷

Time-Dependent Analysis of Maxwell's Equations—Test Studies. Rattanadecho and coworkers^{13–15,43,61,77} had carried out various experimental and numerical studies on microwave heating of materials using TE_{10} mode rectangular waveguide and domestic microwave oven. Maxwell's equations (Eqs. 80–82) along with heat flow equation (Eq. 5) form the basis for modeling of microwave melting of frozen packed beds, microwave heating of wood, liquid layer, and multilayered materials. Melting of frozen packed bed using rectangular waveguide were analyzed numerically and experimentally for both frozen and unfrozen layers and the model predictions were in good agreement with the experimental results.¹³ The results indicate that the direction of melting by

the incident microwave strongly depends on the layer configuration, due to the differences in the dielectric properties between water and ice.¹⁴ The electromagnetic field equations were solved by using FDTD and the subsequent heat transport equation was solved using finite difference method.

The experimental and theoretical studies carried out for liquid layers (water layer and NaCl-water solution layer) showed that the degree of penetration and rate of heat generation within the liquid layer was changed with the variation of microwave power level and electric conductivity values.^{77,78} Figure 8 shows the comparison between numerical and experimental results for microwave heating of water layer at 1000 W power level and for a duration of 60 s.⁷⁷ It is seen that most of the heating takes place inside the water level due to skin-depth heating effect. For microwave heating/drying of wood, three-dimensional (3-D) FDTD scheme was used to determine electromagnetic fields, and it was found that at a microwave frequency of 2.45 GHz, the power distribution as well as temperature distribution within the sample exhibit a wavy trend due to the significant thickness of sample, which is close to the penetration depth. Furthermore, most of the heating occurs at the center of the test sample where the electric field is maximum for TE_{10} mode configuration.⁷⁹ Figure 9 shows the temperature distribution for microwave heating of wood at 2.45 GHz and the results displayed a wavy behavior due to the resonance of electric field.⁷⁹ Similarly, Ma et al.⁸⁶ proposed a combined electromagnetic and thermal (FDTD) model to study the temperature distributions of food products in a microwave oven. They found that the hot spots occurred at the center of the front face and at the corners of the load. The heating pattern predicted by the model was found to agree well with the experimental results.⁸⁶

Microwave heating of multilayered materials finds an important application in the design of the electromagnetic

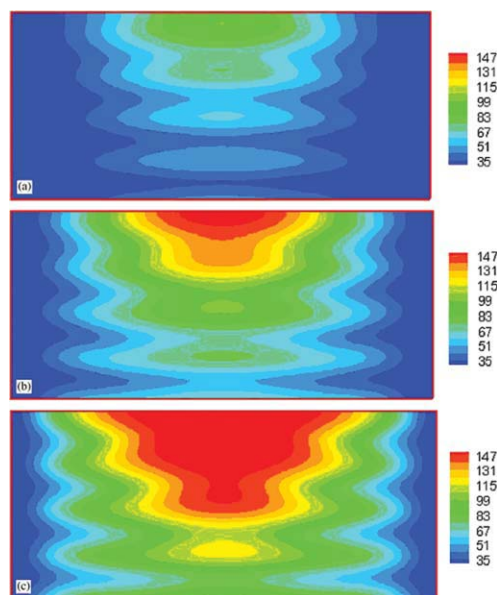


Figure 9. Temperature distribution of microwave heating of wood samples at 2.45 GHz at various heating times (a) 10 s; (b) 20 s; (c) 30 s⁷⁹ (Reproduced from Ref. 79, with permission from Elsevier).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hyperthermia system for the treatment of cancer. Multilayered materials consist of the layer of lower dielectric material (antireflection layer) and higher dielectric material (sample) and when the microwave energy was absorbed, the temperature distributions within the sample were enhanced, if a layer of lower dielectric material was attached in front of the sample. Because of the presence of antireflection layer of suitable thickness, the reflected wave from the surface of the sample was found to be decreased.¹⁶ Note that Eq. 91–93 were used as the governing equations for investigating microwave thawing of frozen layer using a domestic multi-mode microwave oven. It was assumed that the magnitude of the electric field decays exponentially (i.e. infinite medium) from its value at the surface. However significant amount of reflected light might alter the electric field pattern, as Lambert's law may not be valid.⁸⁷ The results showed that within the layered sample, the heating pattern was changed with the change of layered configuration. Further, Figures 10a, b demonstrate that the thawing rate decreases with increasing unfrozen layer thickness and an increase in electric field intensity input leads to an increase in the heating rate as well as the thawing rate.⁴³

Lambert's law vs. Maxwell's equation

Most of the reported works during 1970s and 1980s were based on the Lambert's law for the formulation of the power absorption. But, later during early 1990s, Ayappa and co-workers^{65,67,80} established the theoretical foundation on combined electromagnetic and thermal transport using Maxwell's equations. Lambert's law is based on transmission only, which provides a good approximation for microwave propagation for semi-infinite samples, whereas Maxwell's equation provides the exact solution for microwave propagation within samples. Barringer et al.⁸⁸ performed a comparative analysis of microwave power and temperature profiles for thin slabs between experimentally measured values and predicted values based on Lambert's law, Maxwell's field equations and a combined equation. They found that Lambert's law and the combined equation predicted a much slower heating rate while Maxwell's field equations gave a much more accurate prediction. Oliveira and Franca⁸⁹ compared the power distribution obtained by Maxwell's solution and Lambert's law and they found that the sample size within the Lambert's law limit is higher for cylinder as compared to slabs. Similarly, Kostoglou and Karapantsios⁹⁰ proposed approximate relationship based on Lambert's law for heat source distribution within cylindrical samples. They found that approximate relationship via Lambert's law requires easier analytical manipulation, whereas the solution of the Maxwell equations couples with the heat-transfer equation and that further increases the computational effort many times. Basak⁸⁷ analyzed microwave propagation within typical multilayered systems consisting of low and high dielectric materials based on exponential Lambert's law along with the exact solution of Maxwell's equation and it was found that for low dielectric material, Lambert's exponential law predicts results qualitatively similar to those of exact solution, whereas for high dielectric material, the absorbed power with Lambert's law may be overestimated. Yang and Gunasekaran⁹¹ reported comparative studies on temperature distribution in model food cylinders along with experimental measurements using pulsed and continuous microwave energy. They found that the temperature profile

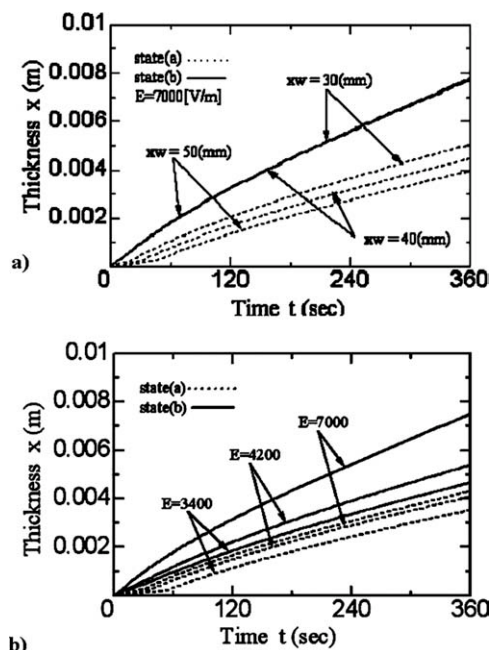


Figure 10. Thawing thickness at various (a) unfrozen layer thickness (b) electric field intensity input⁴³ (Reproduced from Ref. 43, with permission from Elsevier).

and power formulations based on Maxwell's equations were statistically more accurate than those based on Lambert's law.⁹¹ Curet et al.⁹² carried out numerical analysis to solve the Maxwell's equations for calculating microwave power using finite element scheme and compared those results with closed form expressions. The results showed a good agreement between both approaches for low and high dielectric materials for 1D configuration problems whereas for 2D configuration problems, it was found that closed form relationship was more effective for microwave power calculations.⁹²

Resonance in power absorption

Resonance in power absorption occurs during microwave heating as the average power absorption within the sample may have local maxima at the resonant condition. Greater heating effect within a sample is attributed by greater power absorption within a sample and the maxima in power is termed as 'resonance'. Resonance occurs due to the constructive interference between transmitted and reflected waves within the sample⁹³ and a significant amount of research has been devoted on the analysis of resonance and its effect on microwave power absorption within samples.^{76,94–97} Earlier experimental studies reported that the cylindrical samples in a customized oven with unidirectional microwave source exhibit the oscillatory heating phenomenon as a function of sample size. The power absorbed by the samples was due to the resonant absorption of microwaves, which occur due to standing waves produced by the internally reflected microwaves.⁹⁴

Ayappa et al.⁹⁵ investigated the occurrence of resonances during the incidence of the plane electromagnetic waves on infinitely long cylinders and slabs, and they found that the average power absorbed by the sample attain a local maximum at a resonant condition and due to attenuation within the sample, the resonant intensity decreases as the sample size increases. Later, microwave heating of 2D cylinders of

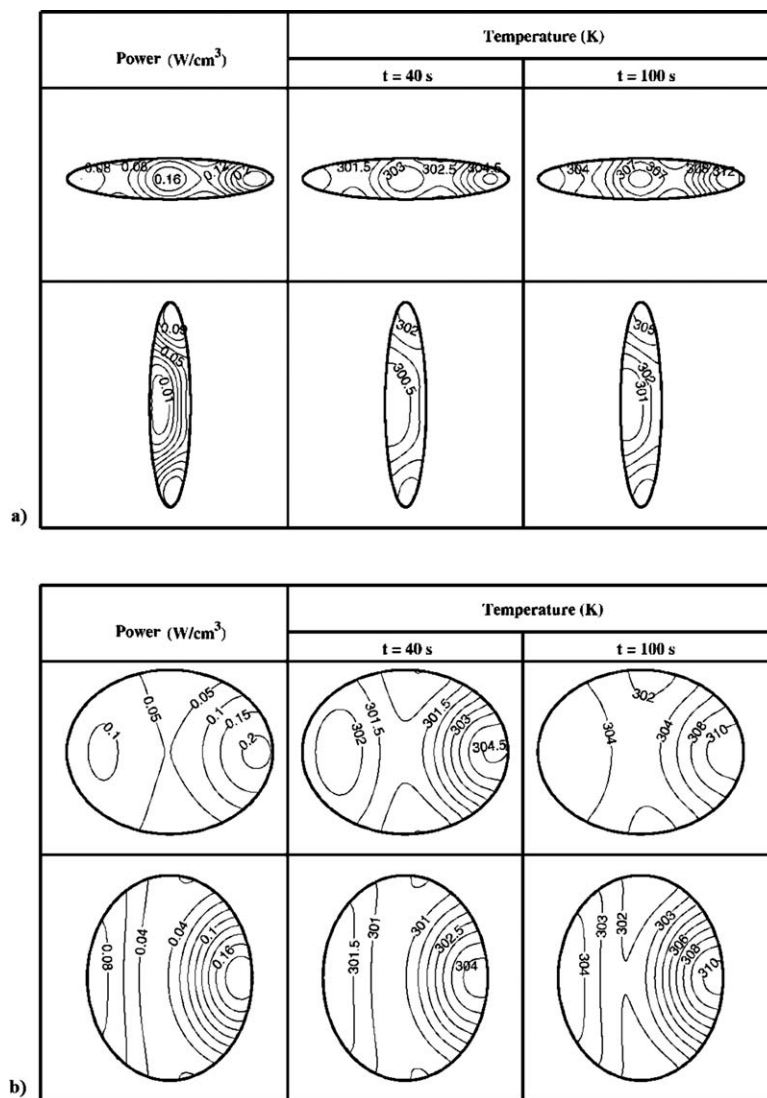


Figure 11. Power and temperature profiles of microwave heating of oil samples of regime II with (a) $a = 0.2$ and (b) $a = 0.8$ for type A and B cross sections⁷⁰ (Reproduced from Ref. 70, with permission from John Wiley and Sons).

various elliptical shapes/cross sections were analyzed for beef and oil samples.⁷⁰ Note that, type A (ellipse with major axis along the horizontal plane) and type B (ellipse with minor axis along the horizontal plane) were the two types of elliptical cross sections considered for several regimes (I, II, and III) of beef samples. Regimes I and II correspond to minima and maxima in average power respectively and regime III represents a large sample. Figures 11a, b represent power and temperature profiles of oil samples corresponding to regime II and for small aspect ratio ($a = 0.2$), larger thermal gradient was observed with type A cross section whereas for large aspect ratio, similar thermal gradients was observed for both types of cross section.⁷⁰ On the whole, the average power absorption in oil samples for all sample dimensions was much smaller than that in beef samples due to small dielectric loss of oil and the average power was invariant with aspect ratios for regime I irrespective of type A/B cross section.⁷⁰

Correlations for material invariant analysis on resonances of microwave power absorption were also studied with closed form solutions of microwave power to predict the locations of resonating peaks as the function of wavelengths,

free space, and penetration depth within the sample.⁹⁶ It has been shown that depending on sample length and dielectric properties of the material, absorbed power distribution can exhibit three distinct behaviors: thin sample regimes ($2L \ll \lambda_m/2\pi$) where uniform power distributions are attained, thick sample regimes ($2L \gg D_p$) where absorbed power distributions are exponential and resonating regime, where the power distributions exhibit spatial oscillations, which exists in between thin and thick sample regimes. Note that, λ_m and D_p are the wavelength and penetration depth within the sample. In a resonating regime, average absorbed power is a nonmonotonic function of sample length showing peaks at resonances, and it has been shown that average power in most of the food materials exhibits resonance if $n < 1.5/\pi$, where $n = \lambda_m/2\pi D_p$.⁹⁶ Note that, n is the ratio of κ_i (imaginary part of κ) and κ_R (real part of κ), where $\kappa = \frac{2\pi}{\lambda_m} + i\frac{1}{D_p}$. The maxima in average power at the odd resonating peaks are gradually suppressed with an increased ratio of distributions of microwave incidence, which finds an important significance for optimal heating with minimal thermal run-away.⁹⁷ The closed form analysis may also be helpful in obtaining the quantitative measure of absorbed power during

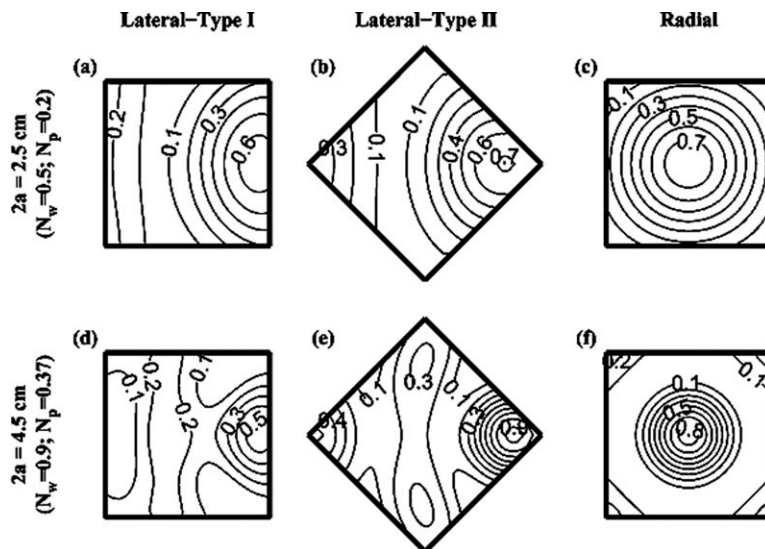


Figure 12. Spatial power contours of bread samples for type I configuration in the presence of lateral irradiation (a and d), type II configuration in the presence of lateral irradiation (b and e) and type I configuration in the presence of radial irradiation (c and f)⁷² (Reproduced from Ref. 72, with permission from IOP Publisher).

material processing and it was observed that the number of resonating peaks and the maxima in average power corresponding to all peaks differ for all materials. It was found that the higher number of resonating peaks occurs for alumina with $n = 0.0072$ and the average power decays almost exponentially with dimensionless sample length ($2L/\lambda_m$) for SiC with $n = 0.4257$.⁷⁶

Nonuniformity on heating rates: hot spots/thermal runaway

One of the most significant challenges for microwave-assisted processing of materials is to control heating rate, which arises due to 'hot spots' and/or 'thermal runaway' within samples. Hot spots are localized areas of high temperature that may develop during the microwave radiation. Hot spots are undesirable for sintering of ceramics which leads to product damage whereas in smelting process hot spots are desirable to quicken the process. Hence it is necessary to predict the condition under which hot spots arise, so that their occurrence can be either avoided or utilized. In order to predict hot spot, a mathematical model for microwave heating based on the forced heat equation with dual reciprocity boundary element method (DRBEM) was developed and it may be concluded that the condition of hot spot could be accurately predicted with the DRBEM. Additionally, it was shown that, for linear thermal absorptivity, the temperature increases to infinity in infinite time (i.e., thermal runaway occurs gradually) whereas for nonlinear thermal absorptivity, the temperature increases to infinity in finite time (i.e., thermal runaway occurs abruptly).⁹⁸ Hill and Marchant⁹⁹ reviewed various mathematical modeling strategies of microwave heating to spread light on the phenomena of nonuniform heating leading to the occurrence of hot spots and they found that there is a critical temperature above which the material experiences a thermal runaway and below which the temperature evolves to the lower branch of the S-shaped curve. Hot spots might occur during microwave heating of thin ceramic cylinder of highly resonant cavity.⁹⁹ Kriegsmann¹⁰⁰ developed a 1-D model which is based on both the

mathematical model and physical mechanism for the formation of hot spots. The model equations were solved numerically, and the results were found to agree qualitatively well with the experiments.

Basak⁷² carried out theoretical analysis for microwave heating of materials with various orientations of square cross sections in the presence of lateral (sample incident at one direction) and radial irradiation (sample exposed to uniform microwave intensities at all directions). Two different configurations type I and type II were used for the theoretical investigation. Type I represents the square cross section which is aligned perfectly with the horizontal plane whereas in type II the square cross section is aligned 45° with the horizontal plane incident with a uniform plane wave. Figures 12 and 13 represent spatial power and temperature distribution of bread samples in the presence of lateral and radial irradiation for various wave number (N_w) and penetration number (N_p).⁷² It was found that type I configuration with lateral and radial irradiation are favored due to less thermal runaway whereas for type II configuration the thermal runaway is larger and hence might be selected for heating near the unexposed corner.⁷² It was also found that for low N_w , the radial irradiation provided larger power or heating rate than that of lateral irradiation. Moreover, the radial irradiation has a higher degree of thermal runaway at the center resulting in large thermal gradients than lateral irradiation especially for large oil samples.⁷¹ Hence, the lateral irradiation was recommended for larger oil samples due to its minimal thermal runaway.⁷¹ Similarly, discrete samples with large air thickness have the tendency to minimize thermal runaway than continuous samples, especially for high lossy substances (beef samples).¹⁰¹ Further, Bhattacharya and Basak⁵⁹ provided a closed form solution of energy balance equation with microwave power absorption, which is a function of spatially distributed electric field. finite Fourier transformation was used to obtain the closed form solution for temperature field. Figure 14 shows the dimensionless temperature distribution and absorbed power distribution for microwave processing of shrimp, bread, potato and

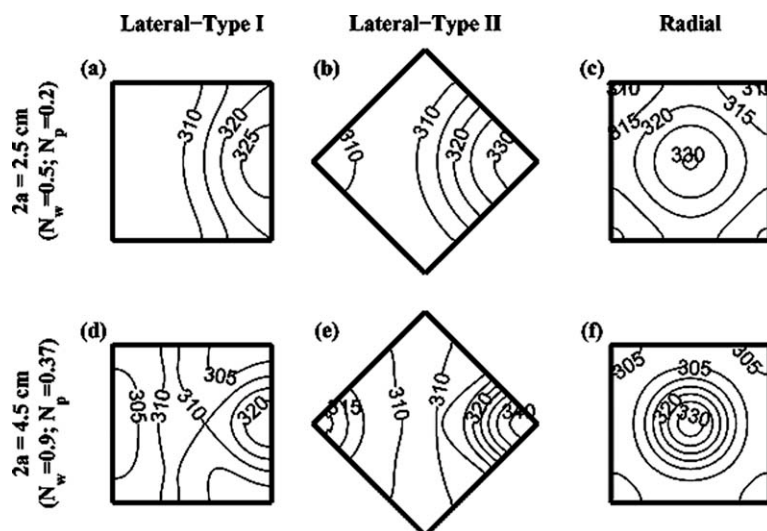


Figure 13. Spatial temperature contours of bread samples for type I configuration in the presence of lateral irradiation (a and d), type II configuration in the presence of lateral irradiation (b and e) and type I configuration in the presence of radial irradiation (c and f)⁷² (Reproduced from Ref. 72, with permission from IOP Publisher).

alumina slabs of length 2.5 cm and heat transfer coefficient $2 \text{ W m}^{-2} \text{ K}^{-1}$.⁵⁹ It can be seen that the temperature distribution of shrimp and potato were in accordance with absorbed power profiles and whereas alumina sample exhibited uniform temperature distributions. Also, for shrimp and potato samples, the internal oscillations were found to die off with time.⁵⁹

Vriezinga¹⁰² has modeled the microwave heating of slabs of water bound with a gel and it was found that the phenomenon of thermal runaway was basically caused by resonance of the electromagnetic waves within the object, combined with heat loss. Thermal runaway can be described using the

average temperature of the nonisothermal slab, regardless of the Biot number. In addition, studies on temperature profiles in a cylindrical model of food samples during pulsed and continuous microwave heating found that the local hot spot formation at the center portion of the sample could be eliminated using pulsed microwave heating instead of continuous one.¹⁰³ An implicit finite-difference model was used to estimate temperature profiles within the sample during microwave heating, and the estimated temperature profiles agreed well with the experimental data.¹⁰³ Similarly, a mathematical model of coupled heat and mass transfer applied to a batch fluidized-bed drying with microwave heating of heat

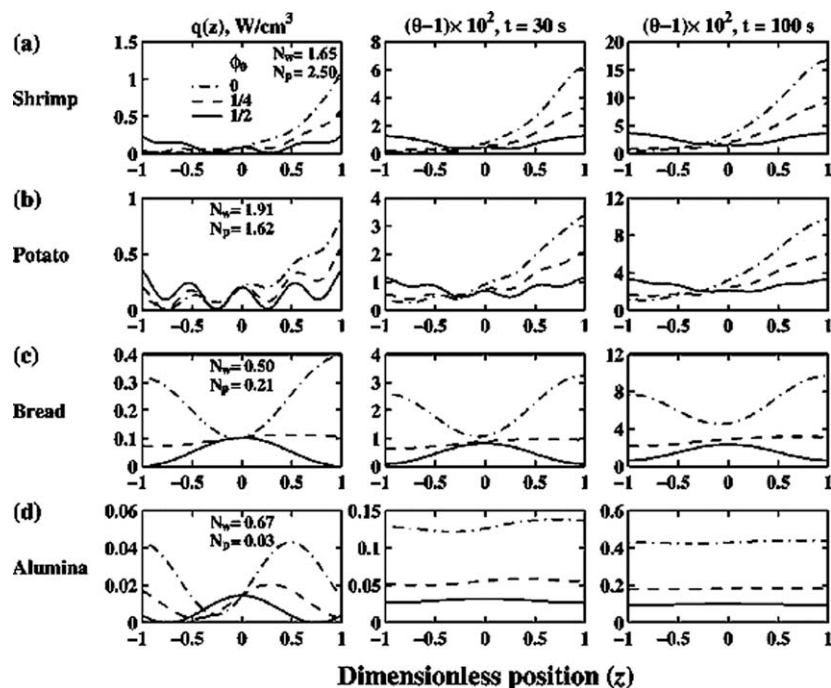


Figure 14. Dimensionless temperature distributions $(\theta - 1) \times 10^2$ at 30 and 100 s and absorbed power distributions are shown for shrimp, potato, bread, and alumina slabs of length 2.5 cm⁵⁹ (Reproduced from Ref. 59, with permission from John Wiley and Sons).

sensitive material (carrot) was developed, and the numerical results showed that different microwave heating patterns can affect the fluidized bed drying significantly. It was found that changing the microwave input pattern from uniform to intermittent mode can prevent material from overheating under the same power density.¹⁰⁴ Besides, supplying more microwave energy at the beginning of drying can increase the utilization of microwave energy at the same time keeping temperature low (less than 70°C) within the particle.¹⁰⁴

Microwave heating of multiphase systems

A large amount of earlier research was primarily devoted on microwave heating of pure substance or layered materials and few studies on microwave heating and processing of multiphase systems, especially emulsions. Microwave heating of multiphase systems may be required in many industrial and domestic applications. Although the multiphase system may refer to many physical systems, in the present context, we have considered systems related to heating with susceptors, heating of emulsions, and heating with phase change (thawing).

Microwave Heating of Materials Attached with Supports. A significant amount of studies had been devoted on microwave heating of materials on the absence of any support.^{60,65,67,68,80,87,95,105–107} However, in reality, samples are processed with supporting plates, especially for cases involving liquid samples, during microwave heating. The presence of supporting plate may alter the heating patterns significantly due to complex interactions of microwaves with assembly of materials. Qualitatively, interaction of microwaves with materials can be classified into three categories such as, transparent, opaque/reflective and absorbing materials.⁹ Table 1 gives the thermal and dielectric properties for water, oil, Al₂O₃ and SiC. The supporting plates such as metals and ceramics (Alumina, SiC) may play a critical role on focusing microwaves within samples. The metals completely reflect microwaves, alumina is transparent for microwaves and SiC absorbs microwaves considerably.^{108–110} One of the main reasons to use the ceramic plate in microwave heating is that the ceramics can withstand high temperature. In addition, the temperature profile within ceramic materials is uniform due to higher thermal conductivity and these materials may be suitable to be used as supporting plates. It was found that, alumina support does not influence heating rates for water and oil samples, whereas with SiC support, uniform heating rates were observed for water and localized heating as well as runaway effects were observed for oil samples.¹⁰⁹ Figure 15 represents the average power contours in the N_w - N_p domain, where N_w and N_p are wave number ($N_w = 2L/\lambda_m$) and penetration number ($N_p = 2L/D_p$) respectively.¹⁰⁸ It was found that the oscillations in average power were observed for a smaller N_p regime and with increase in N_{w0} , the oscillations were suppressed when the slabs were

exposed to free space. Also, for samples with metallic support the oscillations were predominant with smaller N_{w0} regime and the maximum in spatial power occurs for $N_w = 0.25$.¹⁰⁸ Although metallic plates do not allow microwaves to penetrate through, significant reflection may cause greater intensities of stationary waves within the sample.¹⁰⁸ Moreover, ceramic-metallic composite plate may be used based on the dielectric properties of the sample to carry out faster, efficient and/or selective thermal processing. Enhanced heating rates were observed for ceramic-metallic composite support than single metallic support.¹¹⁰ Figure 16 shows a schematic representation on the optimal heating strategies for water and oil samples with ceramic, metallic and combination of ceramic-metallic supports.^{109,110} Further studies found that pulsed microwave incidence was more effective for high dielectric loss samples (natural rubber) without ceramic support compared to continuous microwave incidence. In addition, large thickness of low dielectric loss samples such as Nylon 66 with ceramic support require pulse microwave incidence due to higher thermal runaway especially for samples with large thickness.¹¹¹

Further investigations for other materials such as oil and beef samples reported that the supporting plate (ceramic and/or metallic) may drastically alter the heating effects with a range of dielectric properties.^{69,112–115} It was observed that beef samples would exhibit greater thermal runaway especially with SiC plate in the presence of both sides distributed microwave incidence, whereas the oil samples would exhibit smaller thermal runaway effects with both sides equidistributed microwave incidence irrespective of any ceramic plates.^{69,112} It was observed the average power absorption was enhanced for samples (beef-air and beef-oil) in presence of Al₂O₃ support whereas the average power was smaller with SiC support for porous dielectric materials such as beef-air (b/a) and beef-oil (b/o). Three test cases for porosities (ϕ) 0.3, 0.45 and 0.6 were considered and it was found that runaway heating was observed at the face which was not attached with support for b/a samples and the intensity of thermal runaway increases with porosity whereas lower thermal runaway was observed for w/o samples at all porosity values.¹¹⁴ In addition, metallic support was recommended as optimal heating strategy for higher porosities ($\phi \geq 0.45$) whereas alumina-metallic composite support might be suitable for smaller porosities ($\phi \leq 0.45$) of b/a samples.¹¹⁵ Similarly, microwave heating of oil-water emulsion were also carried out in presence of ceramic and metallic supports and it was found that SiC support was favored over alumina support due to the lesser thermal runaway for emulsion slabs.¹¹⁶ Further, extensive studies have been carried out to investigate the role of metallic annulus on microwave heating of emulsion samples confined within 2D cylinders due to lateral and radial irradiations and provided a optimal heating strategy for any emulsion sample.⁷⁵

Microwave Heating of Emulsion Systems. An emulsion is a two phase oil/water system where one of the phases is dispersed as droplets in the other. The phase which is present in the form of droplets is referred to as the 'dispersed phase' and the phase which forms the matrix in which these droplets are suspended is called the continuous phase. Emulsions are unstable and thus they do not form spontaneously. Emulsions tend to revert to the stable state of the phases over time and hence surface active substances (surfactants) were used to increase the kinetic stability of emulsions greatly so

Table 1. Thermal and Dielectric Properties of Water, Oil, Alumina, and SiC¹¹⁰

Material Properties	Water	Oil	Al ₂ O ₃	SiC
Heat capacity, C_p (J kg ⁻¹ K ⁻¹)	4190	2000	1046	3300
Thermal conductivity, k (W m ⁻¹ K ⁻¹)	0.609	0.168	26	40
Density, ρ (kg m ⁻³)	1000	900	3750	3100
Dielectric constant (2450 MHz), κ'	78.1	2.8	10.8	26.66
Dielectric loss (2450 MHz), κ''	10.44	0.15	0.1566	27.99

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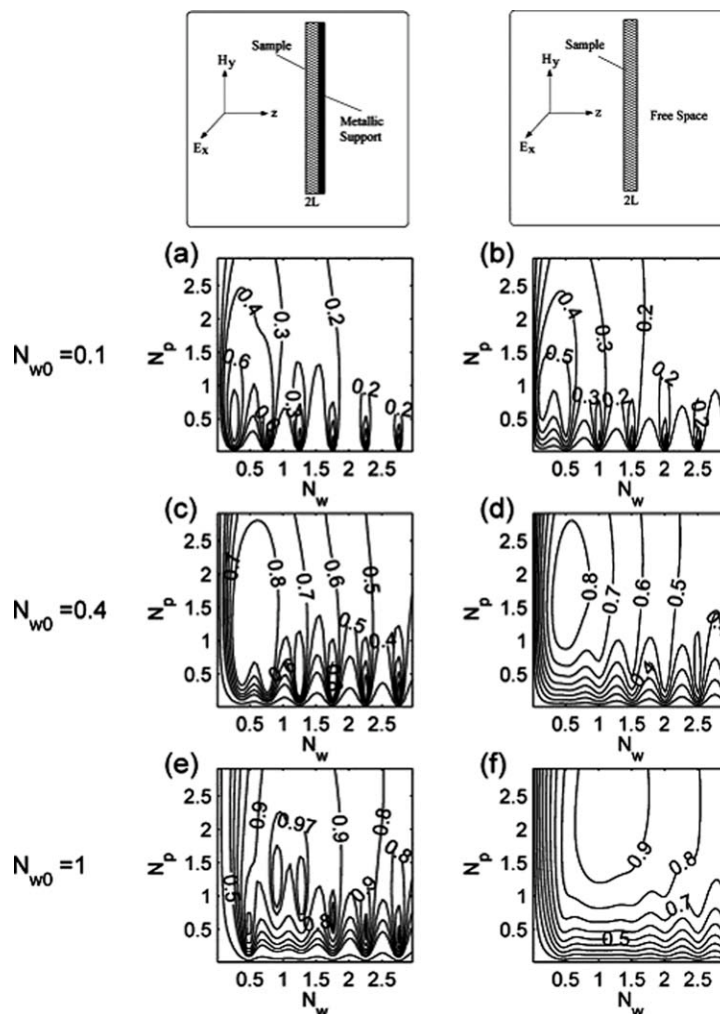


Figure 15. Average power (q_{av}) contours in the N_w - N_p for different N_{w0} values with cases a, c, and e correspond to slabs with metallic support, and cases b, d, and f correspond to slabs exposed to free space¹⁰⁸ (Reproduced from Ref. 108, with permission from ACS Publication).

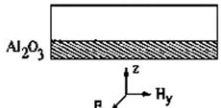
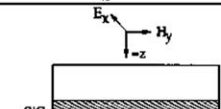
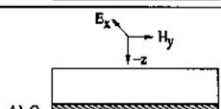
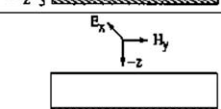
that, once formed, the emulsion does not change significantly.¹¹⁷ A detailed experimental study on microwave heating of oil–water emulsion systems was carried out for various oil–water fractions with fixed beaker radii in a microwave oven, and it was found that resonance (maxima in average power) occurs only for fixed sample dimensions.¹¹⁸ Later, Erle et al.¹¹⁹ studied dielectric properties of oil-in-water (o/w) and water-in-oil (w/o) emulsions at a frequency of 2.45 GHz and they proposed correlations for the effective dielectric properties of oil–water emulsions which showed well agreement with experimental results. Morozov and Morozov¹²⁰ carried out mathematical modeling on microwave heating of oil water emulsion and they found that the temperature in the center of a oil drop might exceed temperature of the surrounding medium.

Modeling of emulsion polymerization of styrene activated by simultaneous microwave irradiation and conventional heating was proposed to determine polymerization rate and molecular weight via the simulation packages Predici®¹²¹ and EMULPOLY®.¹²² The results showed that the model predictions agreed well with the experimental data of various conditions. Similarly, Holtze and Tauer¹²³ proposed a “surviving radicals” model for microwave effect on miniemulsion polymerization of styrene. Their analysis established that short

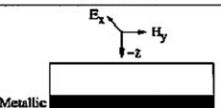
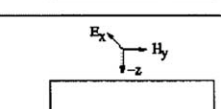
pulses of high temperature generate many radicals which may nucleate miniemulsion droplets containing a monomer (styrene) and thus the monomer get polymerized.¹²³

The effective dielectric properties of an emulsion are strong functions of the continuous medium, and hence they were highly nontrivial to predict efficient microwave heating of emulsions, either oil-in-water (o/w) or water-in-oil (w/o) emulsions.¹⁰⁶ Heating strategies involving one side microwave incidence and both-side microwave incidence were studied to achieve greater rates in thermal processing of 1-D emulsion samples in the presence of resonances. Two dominant resonance modes R_1 and R_2 were considered and the average power at R_1 is larger than that at R_2 . During one side incidence, it is observed that processing rates are greater at the R_2 mode for both o/w and w/o emulsions, whereas for both side incidences, the R_1 mode is favored for o/w emulsion and the R_2 mode is advantageous for w/o emulsion.¹⁰⁶

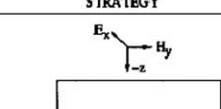
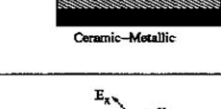
Investigation on microwave heating of oil–water emulsion was also carried out in the presence of various supports such as ceramic, metallic and composite or ceramic/metallic plates.^{74,116,124} Detailed analysis on the role of ceramic plates illustrate that alumina plate causes greater power absorption for both o/w and w/o emulsion slabs with controlled thermal runaway, whereas SiC support may be

MATERIALS	STRATEGY	CONCLUSIVE REMARKS
WATER		<ul style="list-style-type: none"> ● SUPPORT IS AT THE EXPOSED FACE ● SUPPORT DOES NOT INFLUENCE HEATING RATES
		<ul style="list-style-type: none"> ● SUPPORT IS AT THE UNEXPOSED FACE ● LOWER BUT UNIFORM HEATING RATES ARE OBSERVED
OIL		<ul style="list-style-type: none"> ● SUPPORT IS AT THE UNEXPOSED FACE ● SUPPORT DOES NOT INFLUENCE HEATING RATES
		<ul style="list-style-type: none"> ● SUPPORT IS AT THE UNEXPOSED FACE ● LOCALIZED HEATING AND RUN-AWAY EFFECTS ARE OBSERVED

a)

MATERIALS	STRATEGY	CONCLUSIVE REMARKS
WATER		<ul style="list-style-type: none"> ● ENHANCED HEATING RATES ARE OBSERVED FOR SMALLER SAMPLE THICKNESSES
OIL		<ul style="list-style-type: none"> ● ENHANCED HEATING RATES ARE OBSERVED FOR HIGHER SAMPLE THICKNESSES (>1 CM)

b)

MATERIALS	STRATEGY	CONCLUSIVE REMARKS
WATER		<ul style="list-style-type: none"> ● ENHANCED HEATING RATES ARE OBSERVED FOR Al_2O_3-METALLIC SUPPORT
OIL		<ul style="list-style-type: none"> ● ENHANCED HEATING RATES ARE OBSERVED FOR SiC-METALLIC SUPPORT

c)

Figure 16. The optimal heating strategies for water and oil samples for (a) ceramic support¹⁰⁹ (b) metallic support and (c) composites (ceramic-metallic) support.¹¹⁰

The dark shaded regime denotes the metallic support and the light shaded regime denotes ceramic support. (Reproduced from Refs. 109 and 110, with permission from American Institute of Physics and Elsevier).

avored for o/w emulsion samples due to lesser thermal run-away.¹¹⁶ On the other hand, microwave power absorption was significantly enhanced for both o/w and w/o emulsion slabs supported on metallic and ceramic-metallic composite plates during various resonance modes (R_1 and R_2). Based on detailed spatial distributions of power and temperature, SiC-metallic composite support may be recommended as an optimal heating strategy for o/w samples with higher oil fractions ($\phi \geq 0.45$) whereas metallic and alumina-metallic composite supports may be favored for samples with smaller oil fractions ($\phi = 0.3$) during R_1 mode. For w/o samples, SiC-metallic composite support may be suitable heating strategy with all ranges of water fractions during R_1 mode. During R_2 mode, metallic and alumina-metallic composite supports are efficient for both o/w and w/o emulsion sam-

ples.^{124,125} Similarly, detailed theoretical analysis was carried out to assess the role of lateral and radial irradiations on the microwave heating of the 2D cylinder for both o/w and w/o emulsion samples. For both of lateral and radial irradiations, the effective microwave incidence from the source is assumed to be identical. Figure 17 depicts the power and temperature contours for w/o emulsion cylinder ($\phi = 0.2$) of various regimes due to lateral and radial irradiations.¹²⁵ It was found that high heating rate was achieved for regime I due to radial irradiation which resulted in uniform heating. Also, the samples with smaller diameter were found to have larger average power with radial irradiation for both o/w and w/o emulsion samples.¹²⁵ Further, an analysis with the metallic annulus on microwave processing of oil-water emulsions due to lateral and/or radial irradiation demonstrates

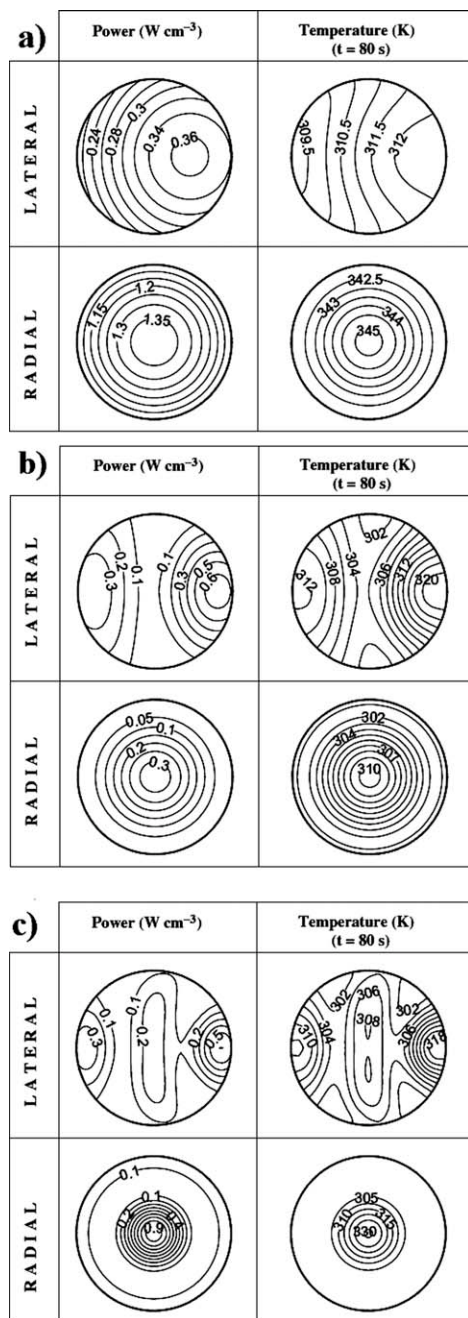


Figure 17. Power and temperature contours (at $t = 80$ s) for w/o emulsion cylinders ($\phi = 0.2$) with (a) $d_c = 1.22$ cm; (b) $d_c = 3.71$ cm; (c) $d_c = 6.28$ cm due to lateral and radial irradiations¹²⁵ (Reproduced from Ref. 125, with permission from Elsevier).

that average power absorptions exhibit greater intensification for o/w emulsions of most sample diameters than that of w/o emulsions. However, for samples with smaller diameters (for both o/w and w/o samples) radial irradiation is favored, whereas for larger size samples, lateral irradiation may be the optimal heating strategies.⁷⁵

Microwave-Assisted Thawing. A few earlier researches on microwave-assisted thawing have been briefly reviewed here. During thawing or melting, heating can be accompanied by phase change, and the sample domain would consist

of liquid, solid and mushy (intermediate state in which the transition from solid to liquid occurs for multicomponent substances) regions. Basak and Ayappa⁸¹ analyzed microwave thawing of tylose slabs using effective heat capacity method, elucidating models for phase change in substances, which melt over a range of temperatures. The thawing mechanism was analyzed using Galerkin finite element method and the role of various parameters such as the microwave power absorption (especially at resonance), liquid volume fractions, temperature and slab dimensions on the thawing process were determined as well. It was found that thawing progresses predominantly from the surface of the sample for slabs greater than or equal to 5 cm. On-off control on the microwave power has also been used to control the temperature rise in the liquid regions and microwave power savings on thawing process were shown in detail.⁸¹ Later, Basak and coworker⁶⁰ extended their work to 2D systems using finite element analysis and studied the influence of internal convection during microwave thawing of cylinders. It was found that for small sample diameters ($D/D_p \ll 1$), convection plays a small role, and thawing was found to be independent of the direction of the microwaves. Note that, D is the sample diameter and D_p is liquid-phase penetration depth.⁶⁰ Figure 18 shows the power and temperature contours during microwave thawing for $D = 2$ cm cylinder when microwaves are incident from the bottom.⁶⁰ The results showed that during final stages of thawing, thermal stratification occurs due to the absence of convection.⁶⁰

Further, Basak and Ayappa⁶⁸ studied the role of length scales on microwave thawing dynamics in 2D cylinders and they found that D/D_p and D/λ_m are the two length scales that control the thawing dynamics where D , D_p and λ_m are the cylinder diameter, penetration depth, and wavelength of

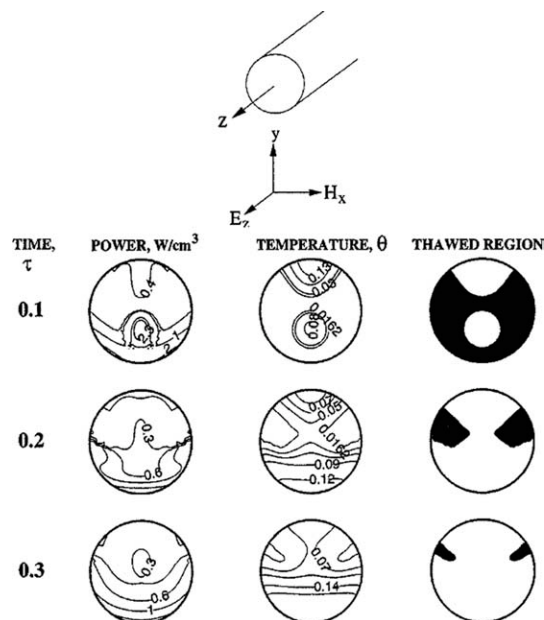


Figure 18. Power and temperature contours with the thawed region in the absence of convection, during microwave thawing for a $D = 2$ cm cylinder exposed to microwaves from the bottom.⁶⁰

($D/D_p = 3.73$, $D/\lambda_m = 1.58$; $Pr = 0.5$; $G = 9$; $Bi = 0.02$; $St = 6.8$) (Reproduced from Ref. 60, with permission from John Wiley and Sons).

radiation in the sample medium, respectively. For very low D/D_p , D/λ_m ($\ll 1$) values, power absorption was uniform and thawing occurs simultaneously across the sample, whereas for $D/D_p \gg 1$, thawing was seen to occur from the incident face, as the power decays exponentially into the sample.⁶⁸ It was also found that for one side and both side incidence cases, greater microwave power deposition was attributed by greater intensity of resonances occurring within a secondary thawed regime which appeared at later stages for intermediate sample thicknesses.¹⁰⁵ Based on spatial resonance pattern, microwave incidence from one face or both faces were preferred for thawing of slabs.¹⁰⁵

Chamchong and Datta^{41,42} carried out theoretical analysis on thawing of foods in a microwave oven using Lambert's law and they found that the thawing was faster with the decrease in the load aspect ratio and the thawing time was found to increase linearly with volume of food samples. Lee and Marchant^{126,127} studied microwave thawing of semi-infinite 1-D slab and cylinder using an approximate analytical model based on Galerkin method. The microwave radiation within system (slab and cylinder) was governed by the Maxwell's equations and the absorption and diffusion of heat was governed by forced heat equation. It was shown that the model produces accurate results in the limits of no heat-loss (insulated) and large heat-loss (fixed temperature) at the leading edge of the slab when compared with the full numerical solution for a number of different parameter choices. The model was coupled with a feedback control process in order to examine and minimize slab melting times whilst avoiding thermal runaway and thus improving the efficiency of the thawing process.^{126,127}

Rattanadecho⁴³ combined electromagnetic and thermal model to carry out the microwave thawing of layered samples for various layered configuration and the simulation predictions were in good agreement with the experimental results. It was found that the thawing rate decreases with the increase in unfrozen layer thickness and increases with the increase in electric field intensity input. Further, Akkari et al.¹²⁸ proposed a gray-box model based on Lambert's law for microwave thawing of tylose using a 2D finite elements approach and they found that the temperature increase at the center of the sample and with increase in time. Campanone and Zaritzky¹²⁹ developed a 3D model to analyze the behavior of food microwave thawing. The model was used to solve coupled mass and energy balances of thermal, mass transport, and electromagnetic properties varying with temperature. They also found that the simulated thawing times were lower for the microwave process in comparison with the conventional method for different product sizes.

Microwave Heating of Porous Media. Porous materials containing moisture can be removed with the help of microwave heating which is caused by the pressure driven flow due to internal evaporation. Constant and coworkers¹³⁰ presented a model of simultaneous heat and mass transfer for microwave drying of capillary porous material. Saturated and unsaturated zones were explained in the model and the numerical results agreed well with the experimental observations with respect to drying kinetics and transfer mechanisms.¹³⁰ Ni and coworkers¹³¹ developed a multiphase porous media model to predict moisture movement in wet biomaterials during microwave heating. They found that the heating rate and moisture loss were higher for high moisture material than compared to low moisture material which was

due to liquid water eluding from the surface without undergoing phase change.¹³¹ Later, Datta and Ni¹³² combined infrared and hot-air-assisted microwave heating to control surface moisture and temperature distributions in the food.

Chen et al.¹³³ coupled heat and mass transfer model to investigate the effects of microwave heating patterns on batch fluidized bed drying of porous material (apple). Three different microwave heating patterns (uniform, sinusoidal and rectangular) were used while keeping the electric field strength constant. It was found that the intermittent heating with rectangular pattern has the shorter drying time but has the highest energy consumption as well.¹³³ Basak and coworkers¹¹⁴ carried out theoretical analysis on microwave heating of various porous food materials. The role of various supports such as ceramic¹¹⁴, metallic, and composite supports¹¹⁵ on efficient heating of porous materials were investigated in presence of resonances. Jindarat and coworkers¹³⁴ analyzed energy consumption for microwave drying of porous material using a rectangular waveguide. They considered two porous packed bed systems, F-C bed (fine bed attached over coarse bed) and C-F bed (coarse bed attached over fine bed). It was found that the specific energy consumption decreased with increasing energy efficiency during the drying process. F-C bed with layered thickness provide higher drying rate and energy efficiency than other porous packed bed.¹³⁴ Application of microwave heating has been extensively investigated for unsaturated and saturated porous medium.

Case 1: Microwave Heating of Unsaturated Porous Medium. Rattanadecho et al.^{61,135,136} carried out experimental and theoretical analysis of drying of capillary porous packed bed of glass by microwaves using a rectangular waveguide. Their analysis was based on the strong coupling between the heating model and electromagnetic model with effective dielectric properties of the unsaturated porous bed. They found that the degree of penetration and the rate of heat generated within the sample depend on the variation of microwave power level and glass size. Also, the porous packed bed consists of small bead size lead to faster drying time due to the exertion of high capillary forces. Dincov and coworkers¹³⁷ presented a computational approach to explain microwave heating of porous material (potato). They combined finite difference time domain and finite volume methods to solve electromagnetic field equations and heat and mass transfer equations. They found that most of the moisture was vaporized before leaving the sample due to internal heat generation.

Sungsoontorn et al.⁶² proposed a 1-D model for heat and mass transfer and pressure buildup in unsaturated porous media (glass beads, water and air) using microwave energy. They found that the moisture transport near the heated edge of the sample was higher for high frequency than for lower frequencies. At high frequencies, more energy was absorbed which causes high rate of moisture transfer.⁶² Later, Suwanapum and Rattanadecho¹³⁸ presented a 2-D model for microwave heating of unsaturated porous materials (glass beads, water and air) and they showed that the particle size and thickness of porous packed bed play a major role to determine the heat and mass transfer during multiphase flow. Thick packed bed consists of more water than thin packed bed and hence it requires more thermal energy to evaporate moisture.¹³⁸ It was shown that the water saturation distribution and pressure buildup distribution due to temperature distribution during microwave heating of unsaturated porous

packed bed. Hot spot zone occur near the mid-plane of the sample which lead to the migration of moisture from hot spot zones to cold spot zones due to capillary flow and vapor diffusion.¹³⁸

Case 2: Microwave Heating of Saturated Porous Medium. Microwave heating of liquid layer or fluid-saturated porous packed bed was carried out numerically and experimentally by Rattanadecho and coworkers⁷⁷ and they demonstrated the effects of microwave power level and liquid dielectric properties on degree of penetration and heat generated within the liquid layer. Further, experimental investigations on microwave heating of dielectric materials showed that the samples of smaller volumes exhibited high heating rates.¹⁸ Numerical analysis on microwave heating of a porous medium with uniform and nonuniform (variable) porosity showed that heating rate was slower with nonuniform case than with uniform case.¹³⁹ It was found that nonuniform porosity provide lower temperature due to the presence of more water content near wall which affects the dielectric properties of the porous packed bed. Klinbun and coworkers¹⁴⁰ presented a numerical and experimental analysis on microwave heating of saturated packed bed using rectangular waveguide and they found that the sample placed at middle of the waveguide provided uniform heating. Also, glass bead size affect the fluid flow pattern within the packed bed and higher energy absorbed using small beads than large beads.¹⁴⁰

Thermal Application of Microwaves

Food processing

Food processing is one of the most successful and largest applications of microwaves since the presence of moisture in the food which can couple with microwaves easily facilitates heating. Microwaves are largely used for cooking, drying, sterilizing, thawing, tempering, blanching, baking and extraction of food products.

Factors Affecting Microwave Heating of Food Materials. During microwave heating of food, many variables such as dielectric properties, size, geometry and arrangement of food materials affect the heating performance. The most significant among them is the permittivity of the food. Knowledge of the dielectric properties is important in the selection of proper packaging materials and in the design of the microwave heating equipment. Permittivity measurement showed that the dielectric properties (ϵ' and ϵ'') depend on the composition of the food material, the temperature, and the frequency.¹⁴¹ Studies on microwave heating on macaroni and cheese food products showed that the dielectric constant was found to decrease with increasing temperature (5 to 30°C) at high microwave frequencies (915 and 1800 MHz).¹⁴² Dielectric properties of various food materials at various frequencies were reported by Sosa-Morales et al.¹⁴³ Depending on the values of both the dielectric constant and the loss factor, microwave heating can be used to improve the food quality.

Heating uniformity can be improved by the arrangement and geometry of the food components and the type of tray used.¹⁴⁴ Similarly, other factors such as size and shape influence the microwave heating of food materials. Uniformity in temperature distribution was found to be better in the case of hexagonal prism-shaped products than brick and cylinder-shaped products. Moreover, the time required to reach maximum temperature (80°C) was longer in hexagonal prism-

shaped products than cylinder and brick shaped products.¹⁴⁵ Temperature uniformity of food products can also be increased by providing carousel or rotating turn tables.¹⁴⁶ Apart from these, electric field strength and microwave heating pattern will affect the microwave heating of food products.¹³³

Microwave-assisted Sterilization and Pasteurization. Microwaves were used as an alternative for pasteurization of orange juice to inactivate pectin methylesterase (an undesirable enzyme) in orange juice. It was found that microwave heating was significantly faster than the conventional thermal heating mode and provided some contributory nonthermal effects.¹⁴⁷ Specific spoilage microorganisms in apple juice could be destroyed faster under continuous flow microwave heating than under conventional heating conditions.¹⁴⁸ Heddleson and Doores¹⁴⁹ investigated the variables influencing temperature and bacterial destruction in foods with microwave heating and they reported that the microbes were inactivated by microwaves solely due to thermal effects. Later, microwave-assisted sterilization of solid foods was performed by several researchers and it was found that the optimal heating can be achieved by choosing suitable combinations of factors such as geometry (shape and size) and dielectric properties (composition).¹⁵⁰ Studies on heat disinfestations of dried fruits such as date fruits showed that the microwave heating was better than intensive conventional heating, since it retained the quality of the food products.¹⁵¹

Microwave-assisted Cooking of Foodstuffs. Microwave heating found successful applications in cooking purposes such as cooking of bacon, baking of foods, and heating of baked dough products. The use of microwave baking technique improved the heating uniformity inside the loaf and enabled good crust formation.^{152,153} Similarly, use of susceptor package in microwave heating might improve the crispness of the food samples.¹⁵⁴ Microwave frying of potato slices using frying oil (mixture of palmolein and soybean oil) and sunflower oil proved to be an alternative for conventional frying due to its less degradation of oil. Potato slices were fried in both oils by microwave (550 W) for a duration of 20 min and the frying was repeated for 15 times with the same oil. Results obtained from chemical tests showed that the frying oil had lower polar compounds and more saturated fatty acids than sunflower oil.¹⁵⁵ The frying time of potato slices for French fries can be reduced with the help of microwave prethawing. The frozen potato strips were prethawed using microwaves which results in the significant reduction of acrylamide level in French fries.¹⁵⁶

Microwave Drying of Food Materials. Microwave-assisted heating combined with conventional heating can be used as a dehydration technique for drying of fruits and vegetables. Microwave heating causes a substantial reduction in drying time; by a factor of two for apple and a factor of four for mushroom. The rehydration capacity of dried apples and mushrooms was 20–25% better with TM mode applicator drying than with multimode cavity drying.³¹ Theoretical studies on microwave freeze drying of skimmed milk showed that the drying time will reduce upto 33% with the help of dielectric materials (SiC), than that of microwave freeze-drying without the use of dielectric materials.¹⁵⁷ Quality damages of tuna, oyster and mackerel due to freezing and thawing can be reduced by microwave vacuum drying. Samples dehydrated at 4 kPa and temperature less than 25°C

Table 2. Applications of Microwave Heating of Food

Processes	References
Drying of sliced potatoes	159
Drying of grapes	161
Drying of carrot	162, 163
Drying of garlic cloves	164
Drying of olive pomace	165
Drying of kiwi fruits	166
Drying and dehydration of strawberries	167
Drying of parsley	168
Drying of spinach	169
Drying of sliced mushroom	170
MW finish drying of banana	171
Osmotic dehydration of potato and apple	160
Freeze drying of beef cubes	172
Freeze drying of instant vegetable soup	173
Spouted drying of diced apples	160, 174
Spouted drying of sliced blueberries	160
Pasteurization of pickled asparagus	175
Pasteurization of apple cider	176
Pasteurization of milk	177
Pasteurization and sterilization of cheese sauce and whey protein products	178
Blanching and dehydration of potato cubes	179

showed that partial dehydration by microwave vacuum drying reduced the freezing time of food samples. Removal of some water reduced the size of ice crystal and the drip loss in food samples.¹⁵⁸ Drying rates of sliced potatoes by microwave heating were not affected by slice thickness, but were found to increase with the microwave power/mass ratio.¹⁵⁹ Zhang et al.¹⁶⁰ reviewed various microwave-assisted drying methods such as microwave-assisted air drying, microwave-assisted vacuum drying, microwave-enhanced spouted bed drying and microwave-assisted freeze drying for a wide range of fruits and vegetables. They reported that combining microwave with other drying methods reduces drying time as well as improves product quality.¹⁶⁰ Table 2 gives the application of microwave heating of foodstuffs.

Ceramic processing

Next to food processing, ceramic processing is an area where microwaves have been widely used. Ceramic processes generally require high temperature and hence use of microwave heating has gained importance for the last two decades. Sintering is one of the most common microwave-assisted ceramic processing in which ceramics are compacted under high pressure, followed by the high temperature sintering in the furnace.¹² Low loss ceramics can be sintered using a hybrid microwave system, with the help of a partially oxidized SiC powder bed which acts as a susceptor (preheater). Microwave sintering was found to occur at lower temperatures than that of conventional sintering.¹⁸⁰ Menezes et al.^{181,182} performed hybrid fast sintering for samples such as porcelain bodies and alumina-zirconia nanocomposites. They found that the control of the heating cycle was the main factor in achieving hybrid microwave fast sintering in which heating cycles lower than 60 minutes were used for the sintering of the porcelain bodies¹⁸¹ and sintering cycles of 35 minutes was used for alumina-zirconia samples.¹⁸²

The mechanical properties of the sintered ceramics can be improved by the microwave-assisted heating, and thermal residual stress distribution characteristics were investigated to evaluate the homogeneity. Thermal residual stresses during the sintering process are caused by the nonuniform temperature distribution in the material or the different expansion/

contraction mismatch between the constituent phases. Figures 19a, b show the comparison of thermal residual stress distributions and Vickers Hardness distribution of microwave and conventionally sintered samples.¹⁸³ The thermal residual stress investigation shows that the microwaves can sinter ceramics in entire volume, resulting in improved mechanical properties. The micro hardness test on microwave-sintered specimen finds superior mechanical properties compared to conventionally sintered specimen.¹⁸³ Similarly, microwave sintering of calcium phosphate ceramics (hydroxyapatite and tri-calcium phosphate) were carried out using a 3 kW microwave system operated at a frequency of 2.45 GHz. It was found that the samples sintered by microwave at 1250°C for 30 minutes had high density and homogeneous microstructure for all compositions.¹⁸⁴ Microwave sintering of Al₂O₃ slabs with the same incident power showed that the samples with higher heating rate took longer time to sinter. The heating rate was found to be a strong function of the slab thickness due to resonance effects.⁸⁴ Microwave sintering of various ceramics such as alumina, zirconia (3Y-TZP) and Ni-Zn ferrites were achieved successfully with improved mechanical properties.^{3,5} The magnetic properties measurements for microwave sintered specimens showed higher magnetization values and the dielectric properties measurements showed lower dielectric constant values.⁶

Microwave heating of ceramic laminates composed of multiple layers were modeled and analyzed using an asymptote theory for diverse dielectric properties.¹⁸⁵ Using the same theory, microwave heating of ceramic composites consisting of many small ceramic particles embedded in a ceramic cement were also modeled and analyzed. This model found a strong dependence of the steady state temperature of the composite on the radii of the embedded particles, and the analysis agreed well with the experimental results.¹⁸⁶ Other processing of ceramics such as synthesis of SiC, biphasic calcium phosphate ceramics, and transparent alumina were achieved at lower sintering temperature and shorter sintering time with microwaves.^{187,188} Microwave hybrid heating principle was used for joining alumina-(30%) zirconia ceramic composites using sodium silicate glass as the bonding interlayer. The molten layer of glass spreads over the surface of the ceramics thus facilitating the built-up of the interface.¹⁸⁹

Permittivity measurements made on SiC shows that with an increase in the temperature, the dielectric constant increases linearly, whereas the dielectric loss was found to increase exponentially. Because of the exponential increase in dielectric loss, thermal runaway occurs when the temperature increased beyond 1400 °C.¹⁹⁰ When SiC and ZrO₂ are exposed to microwave simultaneously, SiC couples better with microwaves at room temperature than ZrO₂ due to high dielectric loss properties. The condition remains same upto 500 °C, but beyond a certain critical temperature the dielectric loss of ZrO₂ increases rapidly with increasing temperature. At a certain temperature, the loss factor of ZrO₂ exceeds that of SiC and ZrO₂ absorbs most of the microwave radiation due to self-limiting absorption.^{2,10} Thus, high dielectric loss ceramic materials such as SiC, CuO and Fe₃O₄ can be heated rapidly using microwaves. Other ceramic materials such as Al₂O₃, ZrO₂, Si₃N₄ and AlN do not couple with 2.45 GHz microwave at room temperature. Hence, by means of hybrid heating method, poorly absorbing ceramic materials were initially heated to a critical temperature above which they can couple with microwaves easily.¹⁰

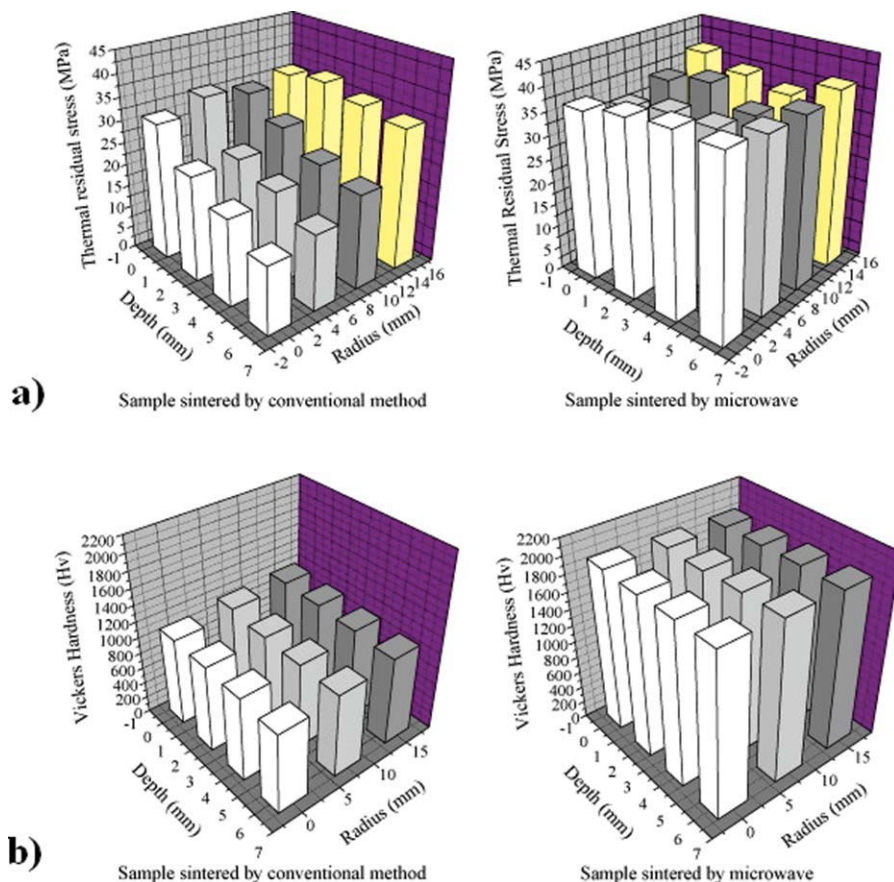


Figure 19. Comparison of microwave and conventionally sintered samples for (a) thermal residual stress distributions and (b) Vickers hardness (HV) distributions¹⁸³ (Reproduced from Ref. 183, with permission from Elsevier).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Chemical reacting system

Microwave irradiation was applied as an alternative heating source for various chemical reacting systems. The effect of microwave irradiation on a chemical reaction is very complex in nature and that involves thermal (e.g. hot spots, superheating) and athermal (e.g. molecular mobility, field stabilization) effects, and in order to obtain the desired results, the advantages of both thermal and athermal effects are utilized.¹⁹¹ The energy utilized in a microwave-heated experiment depends on the absorbance characteristics of the reaction mixture. Significant amount of microwave energy need to be used for low-absorbing reaction mixture, whereas strongly absorbing reaction media were easier to heat and thus the heating process consumes less energy. Microwave heating reduces the generation of hazardous substances in chemical products when reactants processed under solvent-free conditions or using greener solvents (environment friendly solvents) such as water, ionic liquids, and poly(ethylene glycol).¹⁹²

Microwave-assisted Organic and Inorganic Chemical Reactions. Microwave dielectric heating has been extended for the synthesis of a wide range of organic and inorganic chemicals. The Mathews reaction is a dry hydrolysis procedure of preparing carboxylic acids from nitriles or amides with phthalic acid or anhydride, in the absence of solvents. The Mathews reaction was attained within short reaction times with microwave heating and a yield and selectivity of

99% were attained.¹⁹³ Microwave assisted Diels-Alder reaction and benzamide hydrolysis under sealed-vessel conditions were significantly more energy-efficient than conventional heating in open vessels.¹⁹⁴ Microwave-assisted reactions such as Finkelstein reactions (halide exchange), Williamson ether syntheses, Diels-Alder reactions and other common organic transformations were achieved with good chemical yield.¹⁹⁵ Microwave heating was also able to accomplish freeze-drying of mannitol with the help of sintered SiC. The use of dielectric material effectively enhanced the freeze drying rate by more than 20%.¹⁹⁶ Similarly, reaction rates in ethanol and butanol for alcoholysis of poly(L-lactic acid) were found to be larger under microwave irradiation than under conventional heating due to the reaction frequency factor.¹⁹⁷

Microwave-assisted Catalytic Reactions. Catalyst studies involving catalyst preparation, catalyst characterization, and catalytic reaction show that the benefits are more with microwave heating over conventional heating.¹⁹⁸ Microwave heating has the advantages of rapid drying for drying of catalysts and the dried materials are physically stronger than conventional heating. The distribution of metal (nickel) on the alumina support was much more uniform in the microwave dried catalysts than conventional drying.¹⁹⁹ Microwave heating was applied to catalytic reforming reaction of methane with carbon dioxide over platinum catalysts, and it was found that CO₂ and CH₄ conversions and the product

selectivity (H_2/CO) were generally higher under microwave heating than under conventional heating at the same temperature.²⁰⁰ Catalytic reactions such as decomposition of hydrogen sulphide, reduction of sulfur dioxide with methane and hydrodesulfurization of thiophene were achieved with the aid of microwaves.²⁰¹ In addition to the enhancement of reaction rate, an apparent equilibrium shift was observed for both endothermic and exothermic reactions, which were attributed to the formation of spatial hot spots in the catalyst bed.²⁰¹ Similarly, selective heating of catalyst particles also lead to the increase in reaction rate for heterogeneous catalytic reactions.²⁰²

Fernandez et al.²⁰³ carried out microwave-assisted pyrolysis of glycerol to produce synthesis gas using carbonaceous catalysts (bitumen coal and coconut shell). Higher gas fraction with an elevated content of synthesis gas was obtained at low temperatures (400°C). Other catalytic studies such as catalytic reforming of methanol,²⁰⁴ isomerization of *m*-xylene, hydrolysis of hexanenitrile, oxidation of cyclohexene, esterification of stearic acid,²⁰⁵ degradation of phenol wastewater using activated carbon as catalyst²⁰⁶ and catalytic decomposition of methane²⁰⁷ shows that microwave-assisted heating is better than conventional heating in terms of less processing time, reduced energy consumption with higher yields, generation of minimal waste and high selectivity of products.

Polymer processing

Microwave heating has found many applications in polymer processing. Microwave energy was used to enhance diffusion rates in solid-state polycondensation of polyethylene terephthalate (PET) and Nylon 66. The diffusion enhancement was not due to the heating of polymers but by the excitation of rotational states of small molecules through microwaves.²⁰⁸ A significant amount of research has been carried out on microwave-assisted polymerizations. He et al.²⁰⁹ studied the soapless emulsion polymerization of *n*-butyl methacrylate through microwave heating with potassium persulfate as an initiator. They found that the microwave polymerization had a much higher rate and the particle size distribution was broader, compared to that of conventional polymerization.²⁰⁹ Polymerization reactions such as emulsion polymerization of styrene and methyl methacrylate were achieved with high power pulsed microwave irradiation^{7,8} and also, with single-mode microwave synthesizer.²¹⁰ Microwave heating showed enhanced polymerization rate compared to conventional heating.^{7,8} Microwave-assisted emulsion polymerization of styrene showed an incremental increase in molecular weight with conversion and the resulting products were colloiddally stable.²¹⁰ Similarly, emulsion polymerization of methyl methacrylate with the help of microwaves yielded smaller polymer particles at faster rates.²¹¹

Microwave-assisted oxidative degradation of polystyrene in dichlorobenzene in the presence of benzoyl peroxide was carried out for different cycle heating periods ranging from 20 to 45 seconds. The microwave-assisted process was found to be more efficient than conventional thermal process and the activation energy obtained for the microwave-assisted oxidative degradation of polystyrene was 46.4 kJ/mol, which is lower than that for conventional process.²¹² Similarly, studies on thermal and microwave-assisted oxidative degradation of poly(ethylene oxide) with potassium persulfate as oxidizing agent indicated that lower activation energy was achieved with microwave-assisted heating (43.1 kJ/mol)

compared to that of thermal degradation (105.5 kJ/mol).²¹³ Temperature profile measurement during dehydrochlorination of poly(vinyl chloride) using microwave irradiation showed that the thermal runaway was influenced mainly by the strength of incident microwave power by the preheating temperature of polyvinyl chloride (PVC) before irradiation.²¹⁴ Pyrolysis of waste polystyrene by microwave irradiation was carried out in the range of 1100–1200°C and it was found that polystyrene was converted into 80% liquid, 15% gas and 5% char residue.²¹⁵ Similarly, oxidation of poly(alkyl acrylates) such as poly(methyl acrylate), poly(ethyl acrylate) and poly(butyl acrylate) were successfully carried out with the help of microwaves in the presence of various oxidizers.²¹⁶ Other applications of microwaves in polymer synthesis include free radical polymerizations of monomers like styrene or methyl methacrylate, step-growth polymerizations of polyamides, polyimides, polyethers and polyesters, and the ring-opening polymerizations of ϵ -caprolactams and ϵ -caprolactones.^{217,218}

Environmental applications

With increasing industrialization, the demand for treating industrial wastes has grown up and the requirement for new technologies to reduce the amount of pollutants and waste is necessary. Microwave energy was applied to treat sewage and industrial waste water,²¹⁹ plastic wastes,^{220,221} nuclear wastes,²²² hospital wastes²²³ and for decontamination of soil.^{224,225}

Microwave-assisted Waste Water Treatment. Sewage sludge from urban and industrial wastewater treatment plants was processed by pyrolysis, which is less polluting than incineration, since it concentrates the heavy metals as a solid carbonaceous residue. The pyrolysis of sewage sludge can be done using a microwave furnace in which the sludge was mixed with a small amount of microwave absorber (such as char) to achieve high temperatures (up to 900°C) so that the pyrolysis would take place rather than drying. The microwave treatment of sewage was found to save considerable time and energy than conventional heating, and a volume reduction of more than 80% was achieved.²¹⁹ Similarly, microwave heating along with bio-additives such as chitosan were used to effectively stabilize copper and other heavy metal ions in industrial waste sludge.²²⁶ Treatment of pharmaceutical waste water requires meeting certain effluent standards, which was met by advanced oxidation processes. Among these, microwave enhanced Fenton's oxidation or Fenton-like (FL) reaction appears to be the most promising treatment technology and a reduction in COD of 57.3% (initial COD loading of 49,912 ppm) along with enhancement of BOD_5/COD from 0.165 to 0.47 was achieved. Note that, COD and BOD represent Chemical Oxygen Demand and Biological Oxygen Demand, respectively. Thus microwave enhanced FL process displayed superior treatment efficiency than traditional FL reagent process by improving the degradation efficiency and the settling quality of sludge.²²⁷ Lam et al.^{228,229} showed that the used-car-engine oil can be recycled by pyrolysis using microwave heating at a reaction temperature of 600°C. The recovered liquid oils were composed of light paraffins and aromatic hydrocarbons and it was found that a significant reduction in the metal contaminants also occurs.^{228,229}

Microwave-assisted Solid Waste Treatment. Plastic waste such as aluminium/plastic laminates can be thermally degraded with the help of microwave induced pyrolysis.

Plastics which are highly transparent to microwaves were mixed with carbon prior to or during heating and the energy absorbed from the microwaves was transferred to plastics by conduction. The waste generated due to degradation consists of linear hydrocarbons (alkanes, alkenes and dialkenes) in the form of oils/waxes (81–93%). It may be noted that, 100% recovery of aluminium from laminate was achieved by this method.²²⁰ In treating hospital wastes, the wastes were first ground followed by preheating and heating using steam (temperature upto 140°C and pressure upto 5×10^5 Pa) for sterilization and they were treated with microwave upto 135°C for 10–15 minutes and the treated wastes were sent for disposal. On comparing with electron beam treatment, microwave treatment was safer and economically viable for a throughput of less than 200 kg/hr.²²³

Microwave-assisted Soil Remediation. Microwaves were used for thermal decontamination of soil. Microwave radiation penetrates the soil, heats water, and contaminants to a temperature not exceeding 100°C. The developing vapors were withdrawn from the soil. The process was rapid as compared to other methods in removing volatile and semivolatile components and more effective in the case of polar compounds.²²⁴ Experimental and theoretical studies on microwave induced steam distillation using an opened microwave applicator showed that it was an effective method to remove volatile organic compounds from soil.^{230,231} Similarly, decontamination of soil containing persistent organic pollutants was successfully performed by microwave-assisted FL reagents and the results showed that 4-chloronaphthol, 2,4-dichlorophenoxyacetic acid and *p*-nonylphenol had been degraded completely and degradation of 2,4-dibromophenol was achieved to a large extent.²²⁵ Thus in treating vast amount of wastes, microwave heating has many advantages such as rapid and selective heating, significant waste volume reduction, enhanced chemical reactivity, ease of control, immobilization of hazardous components, ability to treat wastes in situ, improved safety, and overall cost effectiveness/savings.¹¹

Glass and mineral processing

Microwave heating has found applications in glass processing such as preparation of silica glasses, phosphate glasses,²³² optical glasses, glass-ceramics²³³ and glasses reinforced with metals, due to its ability to melt glasses in a short duration and due to its ability to achieve high heating rates.^{234,235} Microwaves were also applied for coating glasses with metals, carbon, metal-oxides, and organic paints.²³⁴ The heating rate of phosphate glass processing can be improved by adding water to the raw mixtures. The hydroxyl group was thus increased by adding water and hence existence of H_3PO_4 in water mixtures promote microwave heating.²³² Microwave processing of hard glass-ceramic (MgO-Al₂O₃-TiO₂ system) coating on nickel based super alloy substrate exhibited lower surface roughness value and exhibited higher hardness (~6 GPa) compared to that of conventionally processed coating.²³⁶ Apart from high heating rate and shorter melting times, microwave processing has the advantages of yielding good product quality. Greater melt uniformity and decreased power consumption were achieved by microwaves due to convection induced by the larger thermal gradients.^{233,237} Other glass processing operations such as surface modification by ion exchange can also be improved by microwaves. Microwave energy was used as a heat source for ion exchange reactions, resulting in the

enhanced rate of exchange and hence a thicker ion exchange layer.⁹ It was also used for the nucleation and crystallization in glasses to form glass-ceramics which gives the advantages of increased process uniformity and selective heating, as the dielectric losses were higher in the glassy phase than polycrystalline phase.⁹

Microwave heating has been investigated for use in the extraction of metals and other useful compounds from minerals. Dehydration of borax compounds such as borax pentahydrate and decahydrate minerals were carried out in a 650 W, 2.45 GHz microwave oven. It was found that 97.5% Na₂B₄O₇ anhydrous borax products were achieved with the help of microwave heating.²³⁸ In the gold mining industry, microwave heating is used to recover gold from the activated carbon. The regeneration of activated carbon after removing gold cyanide molecule was done with the help of microwave heating.²³⁹ Deng et al.²⁴⁰ demonstrated the use of microwave radiation to prepare activated carbon from cotton stalk using different activation agents (KOH and K₂CO₃). Microwave heating shortened the processing time and reduced the consumption of KOH.²⁴⁰ The desorption of methanol from silicalite zeolite in a cylindrical column was achieved in the presence of microwaves. The desorption process can be accomplished quickly with the help of using high microwave power or high flow rates.²⁴¹ Other industrial applications include microwave heating of a high volatile bituminous coal for rapid coke making²⁴⁰ and pyrolysis of oil shale to enhance oil yield and oil quality by yielding oil containing less sulfur and nitrogen.²⁴² Use of microwave energy in mineral processing brings considerable benefits by reducing energy consumption and environmental pollution.¹⁰

Biomedical applications

Microwave heating applications have been extended to biomedical and biosciences applications. Early in the 1930s, microwaves were initially used for therapeutic purposes such as diathermy where the tissue beneath the skin was heated electromagnetically without excessive heating of the skin.²⁴³ Microwave absorption in tissue occurs because of a broad absorption band due to water molecule resonance that covers the entire microwave region. Tissue with high water content was significantly more absorbent than low-water type tissue. The microwave heating process was not only due to free water molecules in the tissue, but also due to water molecules bound to the structure of large biomolecules.²⁴⁴ Later, microwaves were applied for detection and treatment of cancer in which microwave thermography was used to detect cancer by inducing significant temperature differential between tumor and the surrounding tissue. Microwave power levels required to detect were small, resulting in minimal heating of healthy tissue.²⁴⁵ Similarly, hyperthermia treatment of cancer using microwaves exposes the body tissue to high temperatures for a period of time, with minimal injury to the surrounding healthy tissue.^{10,246}

Microwave ablation is another application of microwaves which could be used for the treatment of liver cancer.^{247–250} Microwave energy is emitted by the Microwave Coaxial Antenna (MCA) which generates heat in the local cancerous tissue without affecting the surrounding tissue.²⁴⁷ Wessapan et al.²⁴⁸ carried out numerical studies on the temperature distribution and specific absorption rate of microwaves in human body which was exposed to different frequencies. It was found that at 2.45 GHz, the maximum temperature was found at the skin whereas at 915 MHz, the maximum

temperature was found at the fat. Meanwhile, maximum specific absorption rate was found at the skin at both the frequencies. They also found that when a dielectric shield was kept in front of human model, the temperature increase, and the specific absorption rate were significantly affected with respect to the operating frequency.²⁴⁹ The specific absorption rate and temperature increase were found to be lesser at high frequencies (1300 and 2450 MHz) than compared to low frequencies (300 MHz).²⁴⁹ Further, studies on using single and double slot MCA for microwave ablation were carried out and the results showed that the specific absorption rate distribution and temperature increase was found to be higher for single slot MCA than that of double slot MCA.²⁵⁰ In the same manner, microwave surgery which consists of a microwave tissue coagulator is used to control hemorrhage during hepatic resection. This surgical tool radiates a 2.45 GHz microwave from a monopolar antenna within the tissue, and the heat generated was limited to within the electromagnetic field generated around the antenna, leading to coagulation of protein in that field. In addition, microwave surgery has found use in the gastrointestinal tract endoscopic surgery, laparoscopic surgery, and percutaneous surgery.²⁴⁴

Biomaterial applications

Microwave heating has found considerable applications in processing bioproducts such as preparation of biodiesel.^{251–253} Biodiesel is generally made from vegetable oils or animal fats by transesterification with methanol using an acid or base catalyst. Microwave heating was used to accelerate synthetic organic transformations. Leadbeater and Stenice^{251,252} performed on batch scales upto 3 kg of oil at a time using vegetable oil and methanol or ethanol in a 1:6 oil/alcohol molar ratio. They found that the microwave heating was more efficient than conventional heating due to high reaction rate seen in microwave-promoted chemistry, thus reducing the time for the biodiesel production process. Biodiesel can be prepared even in a continuous mode in which reaction was carried out with new or used vegetable oil with methanol of 1:6 oil/alcohol molar ratios. The reaction was performed under atmospheric conditions and at a flow rate of 7.2 L/min. The energy consumption calculations suggest that the continuous-flow microwave methodology (26 kJ/L energy consumed) for the transesterification reaction was more energy-efficient than using a conventional heated apparatus (94 kJ/L energy consumed).²⁵³ Azcan and Danisman^{254,255} demonstrated that cottonseed oil and rapeseed oil can be converted to biodiesel by microwave-assisted transesterification reaction. The results showed that the microwave heating reduced the reaction time significantly and increased the biodiesel yield (90%–92%) and enhanced the purity (96%–99%).^{254,255} Bio-oil and biogas can be obtained by the pyrolysis of wood in the presence of moisture without using carbon-rich dopants. The threshold power density of 5×10^8 was required for yield of bio-oil and biogas below which microwave pyrolysis does not occur.²⁵⁶ Similar to biodiesel, microwave heating was also applied for the synthesis of peptides, peptoids, oligopeptides, and carbohydrates, and the results showed that the peptides can be prepared in higher yield and purity using microwave irradiation compared to conventional processing.²⁵⁷

Athermal applications of microwaves

Microwaves have been used to enhance certain processes due to the athermal effects of microwave and not due to its

conversion to heat. Athermal microwave effects on chemical reacting systems essentially result from the direct interaction of the electric field with specific molecules in the reaction medium. The presence of electric field might lead to orientation effects of dipolar molecules and hence a change in activation energy was observed.²⁵⁸ Likewise, for polar reaction mechanisms, the polarity is increased from ground state to transition state which result in an enhancement of reactivity by lowering the activation energy.^{258,259} Thus the reaction rate at a given temperature was found to be changed because of microwaves and since the temperature did not change, the effect was clearly athermal.²⁶⁰ The kinetic constant for hydrolytic decomposition of phenyl acetate in presence of microwave and nonmicrowave environment at same temperature conditions (25 and 35°C) was compared. It was found that at 25°C, a substantial increase in reaction rate was observed in the microwave environment than in nonradiated environment.²⁶¹ But at 35°C, the kinetic constant was found to increase 16 fold from a nonradiated environment to an environment radiated with a microwave of 50 mW. As a result, the activation energy was reduced, illustrating the athermal effect of microwave.²⁶⁰ Similarly, high reaction rate was observed for microwave-assisted reactions than conventional process for various catalytic reactions such as catalytic reforming of methane with carbon dioxide,²⁰⁰ decomposition of hydrogen sulphide and hydrodesulfurization of thiopene.²⁰¹ In addition, the yield and the product selectivity (H_2/CO) of catalytic reforming of methane measured at the same temperature were generally higher under microwave conditions than those obtained in conventional mode.²⁰⁰

Epoxidation of styrene to styrene oxide using perlauroic acid as oxidizing agent was carried out in the presence of microwaves. It was found that microwave irradiation enhanced the collision of molecules and hence an increase in the frequency factor and the entropy of the system was observed. The rate constants were found to change as a result of change in the frequency factor.²⁶² It was reported that enhanced diffusion rates were observed for solid state polycondensation of PET and Nylon 66, due to the excitation of rotational states of small molecules through microwaves.²⁰⁸ Similarly, enhanced polymerization rates were observed for microwave-assisted emulsion polymerization of styrene, methyl methacrylate^{7,8} and *n*-butyl methacrylate.²⁰⁹ In another report, an increase in the rate constant for the ring-opening polymerization of caprolactone by microwaves was found to be induced not only by thermal conditions but also by the athermal microwave effect.²⁶³

Microwaves were used for the inactivation of pectin methylesterase in orange juice¹⁴⁷ and the destruction of spoilage microorganisms in apple juice.¹⁴⁸ It was observed that at 50–65°C the death rates of microorganisms exposed to microwaves were higher than those obtained in conventional heat sterilization at the same temperature. The reason was proposed to be the ability of the microwaves to change the secondary and tertiary structure of proteins of microorganisms by causing ions to accelerate and collide with other molecule or by causing dipoles to rotate and line up rapidly with alternating electric field.²⁶⁴

The athermal effects of microwaves on the membrane of human erythrocytes were studied by measuring hemoglobin loss at different microwave irradiation times and at different power densities. A significant increase of hemoglobin loss by exposed erythrocytes was observed due to microwaves.²⁶⁵

Microwave can also be used as promoting agents in inducing genetic changes in biosystem. It was shown that microwaves were able to induce gene mutation in bacteria when protein, RNA and DNA of bacteria absorb radiation at a frequency of 65–75 GHz.²⁶⁴

Luminescent organisms produce light as a result of their normal metabolic processes and they are commonly used as a rapid screen to estimate the toxicity of chemical compounds. The luminous intensity of micro organisms was found to be reduced by the application of microwaves and the reason for the depression of bioluminescence was proposed to be due to the change in specific enzyme systems of micro organisms by microwaves.²⁵⁹ Athermal microwave effects were used to digest waste activated sludge samples at a temperature range of 50–96°C. During the digestion of waste activated sludge by microwaves an increased biogas production was observed. This indicated that additional cell and floc disruptions occurred at temperatures lower than normal destruction temperature of bacteria by the microwave, due to its athermal effects.²⁶⁶

Sintering of ceramics was reported to be enhanced by microwave due to the alteration of diffusion coefficient or due to the evolution of microstructure.²⁶⁷ Brosnan et al.³ carried out microwave sintering of alumina at a frequency of 2.45 GHz and compared the sintering results with those of conventional sintering. It was found that the activation energy was reduced for microwave sintered samples (85 kJ/mol) compared to the conventionally sintered samples (520 kJ/mol).³ Moreover, sintering of ceramics by microwaves was used to improve other mechanical properties such as densification, enhancement of grain growth, and diffusion rates^{5,44} and as a result, finer microstructures and higher magnetization values were achieved.⁶ Similarly, microwave sintering of PM copper steel metal provided more uniform microstructure with minimum porosity as compared to conventional sintering. In addition, high sintered densities were observed.³⁷ Microwaves were also used to enhance the shrinkage during sintering of metal powder compacts such as iron, cobalt, nickel, copper and stainless steel. Shrinkage of a sample is defined as the ratio of change in compact length to the initial compact length. The shrinkage parameter of metal compacts based on cobalt, nickel, copper and stainless steel were found to be higher for microwave sintering than that for conventional (electric furnace) sintering. It was reported that the microwave radiation did not change the activation energy and sintering mechanism but it enhanced the shrinkage.²⁶⁸ The enhanced shrinkage may be due to athermal effects although the exact mechanism is not clear. The rheological characteristics of coal slurries containing high ash content (38% and 32%) were carried out using microwave at various exposure times (0.5–2 min). The viscosity of microwave treated coal was always found to be lower than that of untreated coal which might be due to the change in surface characteristics of microwave treated coals.²⁶⁹

There is a scope to enhance various reactions, effectively treat wastewater systems, suppress bacteria at low temperatures and to improve the mechanical properties of sintered ceramics and metal powders by the microwave athermal effects. The athermal effects of microwave can be prevented during thermal applications, by using a reaction vessel made out of silicon carbide (SiC). Because of high microwave absorptivity of SiC, any material or reaction mixture contained within the vessel can be effectively shielded from the electromagnetic field.²⁷⁰

Concluding Remarks and Future Scope

The use of microwave heating in material processing has been reviewed with a significant number of theoretical and experimental results and applications. It can be inferred from the above discussions that the microwave heating is a promising alternative for conventional heating due to its high heating rates and significant cost and energy savings. There are two important factors for using microwave processing of materials and these are the knowledge of dielectric properties and penetration or skin depth. Dielectric properties of the materials subjected to microwave irradiation need to be investigated over a range of temperature and frequency and hence with the knowledge of dielectric properties, high dielectric loss materials may be effectively coupled with microwaves whereas low dielectric loss materials are combined with microwave susceptors to form hybrid microwave heating.

Microwaves generated with single-mode cavities are sensitive to product position or geometry whereas microwaves generated with multimode cavities overcome these disadvantages. The uniformity of the microwave field in a domestic microwave oven can be improved by providing either rotating turn table or mode stirrers. Similarly, with suitable design aspects such as increasing the cavity size or operating at high frequency, uniformity of microwave field can be achieved.

Modeling of microwave heating based on Lambert's law and Maxwell's electromagnetic field equations have been reviewed along with their applications. The system of equations (Maxwell's field equation and energy balance equation) along with the appropriate boundary conditions can be solved either by finite difference or finite element method. The solution obtained from Maxwell's equation can be used to predict the temperature distribution and power absorption at various frequencies. Spatial and time dependent analysis of Maxwell's equations has been used to determine microwave power and temperature distribution for various food and ceramic materials. In ceramic processing, these models can be used to predict densification and grain size distribution. In addition, resonance in power absorption due to microwave heating has been analyzed as a function of sample length and dielectric property of the material.

In the past two decades, microwave heating has found tremendous applications in various areas such as food processing, ceramics, glass, minerals, polymer, chemical reacting systems, environmental engineering, biomedical and biosciences. Microwave heating is widely used in the food processing such as cooking, drying, sterilizing, pasteurizing, thawing, tempering, baking and blanching of food products. Microwave sintering of ceramics and metal powder showed better heating results and mechanical properties than conventional sintering. Similarly, an increase in the reaction rate and polymerization rate were observed during microwave heating of chemical reactants and polymers respectively. Thus, microwave heating is proved to be a better alternative than conventional heating due to its high heating rates, reduced processing time, and reduced cost and energy savings. Similarly, athermal effects of microwave were found to enhance various chemical reactions, treat waste water systems and destroy micro organisms at low temperatures. The athermal effects of microwave can be suppressed during thermal applications by using a reaction vessel made out of silicon carbide or other high microwave absorbing materials.

We believe that there is a significant scope for research in the following areas:

1. One of the major concerns in the microwave heating is the formation of hot spots or thermal runaway. Although, several models have been discussed to predict and minimize the hot spots, efforts need to be taken for experimental investigation.

2. Variable frequency microwave also find promising advantages of eliminating multiple hot spots or arcing problems by providing time averaged heating. The advantages can be realized better if the variable frequency microwaves can be made economical.

3. Despite its many advantages, microwave processing might not be a complete substitute for conventional processing in all situations. Rather, in certain cases, it can be used as a hybrid heating in which microwave heating can be combined with conventional methods. Hybrid microwave systems can provide heat to materials which cannot couple with microwaves. Susceptor materials for hybrid microwave heating need to be selected in such a manner as to provide constant heating at all temperature conditions. In spite of various improvements in the microwave processing of materials, this field is far from exhausted and more research needs to be carried out for a better understanding of the process and its application in industry.

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