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MICROWAVE-ASSISTED HOTSPOTS: PROPERTIES AND DIVERSE APPLICATIONS

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Abstract

Non-uniform heating during microwave-assisted synthesis leads to the formation of hotspots. Experimental and numerical simulations have been applied to study the formation, location and size of hotspots. Hot-spot formation also depends on various other factors such as intensity of field, solvent used and property of the material. Major applications of hotspots are discussed and reviewed.

1.1. Introduction

Localized microwave overheating volume and non-uniform temperature distribution, with respect to the rest of the sample's volume is called a "hot spot". This is basically due to absorption differences based on dielectric dissipation.

Microwave penetrates a material until moisture is located and heats up the material volumetrically. Thus a rapid and convenient heating method is offered by microwave application. This unique heating capability has resulted in considerable interest in heating and drying related commercial situations. However, the major drawback associated with microwave heating is the non-uniform temperature distribution, resulting in hot and cold spots in the heated product [1]. This non-uniformity of temperature is due to interference of electromagnetic waves inside the microwave cavity resulting in hot and cold spots and variation in dielectric, physical, and thermal properties of sample material during heating. Pulse or intermittent microwave heating is preferred over continuous heating when uniform temperature distribution is important [2]. This review paper leads researchers and scholars to the field of microwave and makes them familiar with the heating processing of microwave in detail, not only mathematical models but experimental data are listed to relate the technical and theoretical understandings.

Hotspot formations in Microwave: Despite the reflection effect and heating effect, microwave-induced electric discharges could also occur in the forms of corona, arc, spark or some weak discharges when metals with sharp edges, tips and submicroscopic irregularities are subjected to a microwave field. Since the charges on the metal surface accumulate at these macro-, micro- or submicroscopic irregularities will jump out of the material when they accumulate enough kinetic energy, resulting in the ionization and breakdown of the surrounding medium. As a direct consequence, considerable heat is produced during the discharge process, leading to the formation of high temperature local hotspot since the discharge process is transient and concentrated. At a microscopic level, these hotspots are actually plasmas [3].

The microwave absorption capacity of a certain material largely depends on its dielectric dissipation. Composite materials can be selectively heated and non-uniform temperature distribution may occur during microwave heating due to these absorption differences. This temperature gradient is often referred to as the hot-spot effect and is regarded as the source of the so-called non-thermal effects of microwave heating. It is also linked to improved chemical reaction rates, reduction of reaction time, or catalytic effects in microwave chemistry.

The previous and ongoing studies have proven that the hotspot effect is associated with considerable energy conversion (from microwave energy to heat) [4-7]. As is well acknowledged, the plasma that contains highly active species such as electrons, ions and radicals can significantly enhance the reaction rate. Plasma usually plays a catalytic role even though there is no catalyst in the reaction. Microwave-induced discharge is one important techniques used to obtain a non-equilibrium plasma, even under atmospheric pressure, at which the electron temperature is approximately 4000–6000K, while the heavy particle temperature is around 2000 K[8].

Microwave Heating Processing (MHP) is non-uniform, the electromagnetic waves reflection resulting in formation of the standing waves. This phenomenon is called as resonance and it leads to local overheating, also known as heat spot [9, 10]. However, the hot spots in materials may be controlled with the distributed microwave incidence in a closed system, besides controlling the proper thickness.

The hotspot concept was first used in the era of superconducting cryotron devices, when Bremer and Newhouse [11], Broom and Rhoderick [12], Cherry and Gittleman [13] and Garbuny and Gottlieb [14] studied the spread of large hotspots in ordinary thin films. Most of this early work has been summarized by Newhouse [15]. Later, the formation of a resistive spatial region around thinfilm constrictions was suggested by Wyatt [16], who proposed that the size of the resulting S-N-S type of junction played a role in determining the strength of the AC Josephson effect in such bridges.

Firstly, an increase the temperature selectively in the more polar parts causes non-homogeneous heating. Generally, the hot spot exists at non-equilibrium conditions during microwave heating [17]. Internal evaporation around the hot spot is promoted by the rotations of polar molecules. Once the interface between liquid and air appears due to quick thermal response of microwave heating, the microwave absorbance energy is concentrated at the interface. Water molecules at the interface vibrate more actively because the bond at the interface becomes weaker than that of the bulk. Finally, after bubble nucleations, bubbles are rapidly growth. As a result, the energy is stored as fine bubbles. For magnetite particle, heat generation within the particle due to microwave absorption should be considered, and the bubble size is significantly influenced by the power. However, heat is released to the air from the wall of the container via convective heat transfer. At lower power, longer irradiation time is required than of the higher one to reach the designated temperature. Accordingly, when heat generation within the particle is negligible, bubble size became smaller at lower power. Water molecule has natural molecular vibrations and forced vibrations under microwave treatment. However, there are distributions of electromagnetic field inside the liquid. Accordingly, some of the clathrates become larger bubble during the irradiation, and the others speedily become smaller. Theoretically, a temperature of 5000 K and a pressure of 100 MPa are generated within the nano-bubble [18]. This hot spot [17], which is created at the thermal non-equilibrium conditions, quickly spreads to the surrounding liquid. Energy stored as clathrates or fine bubbles is then released when they collapse. Consequently, repetitive process of bubble formation and collapse become important factors for microwave heating.

1.2 Results

1.2.1 Zhang et al. [19] reported microwave dielectric heating of the gas phase decomposition of H_2S catalysed by metal sulfides on a γ-Al_2O_3 support results in significant apparent shifts in the equilibrium constant, which have been attributed to the development of hot-spots in the catalytic beds. The catalytic conversion of H_2S into hydrogen and sulfur, which is commercially important for the coal and petrochemical industry [20, 21] using parallel microwave and conventional heating conditions, was performed.

The reactions were performed under continuous flow conditions using quartz reactors. The temperature in the microwave cavity was monitored using an optical fibre thermometer. The microwaves were generated at 2.45 GHz using an generator (0–200 W) and relayed by means of a co-axial cable to a tunable cylindrical microwave cavity placed around the reactor. The catalysts used for the study were either an impregnated catalyst based on molybdenum oxide on a γ-alumina support, which was sulfided by a pre-treatment using an H_2S–H_2 flow at atmospheric pressure for 2 h, or a mechanically mixed sample of MoS_2 and γ-alumina. The reaction products were analyzed using a quadrupole mass spectrometer.

It is noteworthy to know that for such endothermic reaction the conversion efficiencies are relatively low and that for the conventional thermal reaction the experimental observed percentage conversions are in good agreement with the equilibrium data. For the impregnated catalyst the percentage conversion at a temperature of 800°C has risen from ca. 6.5% with conventional heating to 12% when microwaves are used. The effect is even greater for the mechanically produced catalyst, where the conversion efficiency has risen to21% under microwave heating at 800°C. It was concluded that due to any a thermal microwave effect, but rather that the selective features of microwave dielectric heating have induced an anisotropic temperature profile on the catalytic bed which is giving rise to ‘apparent’ shifts in the equilibrium constant for the reaction. The preferential heating effects associated with microwave dielectric heating can give rise to hot-spots which result not only in rate enhancements, but also in apparent shifts in the equilibrium constant. These hot-spots probably are larger than 90 mm and may be as large as 1000 mm and have temperatures 100-200 K above that of the remainder of the bulk indicated by the help of X-ray diffraction and electron microscopy. The hot-spots also induce a considerable re-organisation of the catalyst under microwave conditions.

1.2.2 Xu et al. [22] confirmed the significant evidence of lowering of the apparent activation energy rather than solely the “hot-spots” hypothesis, a new exact reason for microwave-accelerated heterogeneous gas-phase catalytic reactions.

Microwave heating is liable to cause non-uniform temperature distribution. The hot spots (huge temperature gradient at a given location) and thermal runaway (the uncontrollable temperature rise due to strong dielectric loss and temperature-positive feedback of the material) caused by microwave non-uniform heating may occur when a high-power microwave is applied on the processed materials. In some instances, it even leads to the damage of material or even an explosion. There have been large numbers of studies about improving the uniformity of microwave heating. The research carried out by Funawatashi and Suzuki came to the conclusion that non-uniform heating was due to the standing wave and the rapid decay of the microwave. Based on the analysis, they proposed that metallic stirrers and turning tables employed in microwave ovens can reduce the degree of non-uniform microwave heating [23]. Another research article by Pedreño-Molina et al. focused on the optimal strategy of movement of the sample placed in the microwave applicator to ensure better uniform heating [24, 25].

Additionally, a mode stirrer was implied to change the electric field distributions and the mode of the electromagnetic field in multi-mode cavities, achieving more uniform electric field distribution [26-28]. Another study by Bows proposed phase shifting as a novel method of microwave heating, and indicated that uniform heating can be promoted when samples are heated in various phase differences by changing the position of samples inside particular microwave applicators [29].

1.2.3 Kane et al. [30] reported Microwave Interrogation of an Air Plasma Plume as a Model System for Hot Spots in Explosives. The evolution of hot spots within explosives is critical to understand for predicting how detonation waves form and propagate. However, it is challenging to observe hot spots directly because they are small (~micron diameter), form quickly (much less than a microsecond), and many explosives of interest are optically opaque. Microwaves are well suited to characterize hot spots because they readily penetrate most explosives. They also have sufficient temporal and spatial resolution to measure the coalescence of an ensemble of hot spots inside explosives with the finite element code HFSS, using the simplifying assumption that the plasma acts as a metallic conductor. The simulation predicts reflection from a conductive ellipsoid with 1:5 diameter:length aspect ratio when the diameter approaches 1 mm. Phase changes in the reflected signal appear to correlate with a moving conductive surface at velocities 1160 m/s and 325 m/s. The1160 m/s velocity may correspond to the average velocity of an ionization plume surface, as it is comparable in magnitude to optically-observed plasma velocities from laser pulses measured by others. The 325 ms^{-1} velocity may correspond to a reflection from an air shock. Together these results demonstrate promise for MI to characterize more complex hot spot behavior in solid explosives. Ninety four GHz microwaves were employed to characterize the evolution of individual plasma plumes formed by laser ionization of air. Microwave Interferometry was used to obtain plume diameter as a function of time. Although the plasma plumes are larger than individual hotspots in explosives, they expand rapidly and predictably, and their structure can be optically imaged. They are therefore useful model systems to establish the spatial and temporal limits of microwave interferometry (MI) for understanding more complex hot spot behavior in solid explosives.

1.2.4 Kumar et al. [31] developed a theoretical model for intermittent microwave convective drying to investigate temperature redistribution. This non-uniform temperature distribution challenged us to reduce this non uniformity to minimize the drawbacks. The objectives of this study were to develop an intermittent microwave heating model considering Maxwell equations and variable dielectric properties validate the model comparing the temperature distribution obtained from a TIC (Thermal Imaging Camera) and simulation and investigate the temperature redistribution due to intermittency. It shows that the hot spot is concentrated in a region with a maximum temperature rise of 63.9^0C after 60s of heating. As expected, after tempering for 150s, temperature redistributes due to conduction and hot spot disperse. Thus intermittency facilitates reduction in non-uniform temperature distribution which may contribute to improve food quality. In the case of drying, the tempering period removes the accumulated moisture on the surface. Thus combining microwave with convective drying creates unique drying system with high energy efficiency. During the experimentation, it was observed that microwave power is more efficient in the initial stage of drying. As a consequence, the final stage of drying should include power reduction or tempering time should be increased to avoid burning. More involved simulation studies need to be carried out to optimize the power level and tempering time.

1.2.5 Asakuma et al. [32] described mechanism of microwave heating through molecular orbital method and bubble size profiles. Mechanism of microwave heating on water was investigated through a combination of the experimental and simulation works on bubble formation. Fine bubbles were firstly observed and confirmed at the temperature below the boiling temperature of water using a reactor equipped with DLS system. It was hypothesized that thermal non-equilibrium condition such as a hot spot was formed under microwave irradiation. Secondly, the initial stage potential of bubble nucleation (clathrate), which consists of water molecules, was calculated through a molecular orbital method. From the experimental and simulation results, it was found that high energy was generated by the bubble collapse, reconstruction of water molecule clathrate, and repetition of clathrate formation and collapsing cause higher heating efficiency of microwave. Thus, it can be deduced that microwave heating is greatly influenced by clathrate formation and the collapse. Bubble sizes were measured during and after microwave irradiation and mechanism of microwave heating was discussed. Bubble sizes rapidly increased during irradiation, and gradually became smaller after the irradiation was turned off. The maximum bubble sizes were strongly influenced by the type of particle and bubbles were generated at below the boiling temperature due to the hot spot of thermal non-equilibrium condition of microwave irradiation. The profiles of the bubble sizes during and after irradiation can be explained by the bubbles growth, contraction due to temperature drop and the self-pressurizing effect of nano-bubbles. Moreover, energy of the original and collapsing clathrates was estimated using a molecular orbital method. It was found that high energy is released after the clathrates collapse. Therefore, apart from the friction of water molecule, based on the experimental data and molecular orbital method based simulation, behaviors for the formation and the collapse of clathrate were found to be influential in microwave heating.

1.2.6 Aguilar-Reynosa et al. [33] reported an overview on microwave heating processing (MHP) as alternative of pretreatment in second generation biorefinery. The development of a feasible biorefinery is in need of alternative technologies to improve lingo-cellulosic biomass conversion by the suitable use of energy. MHP is emerging as promising unconventional pretreatment of lignocellulosic materials (LCMs). MHP applied as pretreatment induces LCMs breakdown through the molecular collision caused by the dielectric polarization. Polar particles movement generates a quick heating consequently the temperatures and times of process are lower. In this way, MHP has positioned as green technology in comparison with other types of heating. Microwave technology represents an excellent option to obtain susceptible substrates to enzymatic saccharification and subsequently in the production of bioethanol and high-added compounds. However, it is still necessary to study the dielectric properties of materials, and conduct economic studies to achieve development in pilot and industrial scale. This work aims to provide an overview of recent progress and alternative configurations for combining the application of microwave technology on the pretreatment of LCMs in terms of biorefinery.

When the microwave energy vibrates, these molecules are strongly heating resulting in hot spots formation [34]. High heat and vibrational motion could result in the rupture or explosion from some LCMs components, causing the crystalline cellulose relocation. Some hot spots are created within the material, and their explosion is generated due to the heat increase. The blast effect created between the particles by microwave heating improves the crystalline structures relocation [35]. Hot spots formation starts when the temperature uniformity is lost and their location depends on the heating period and water evaporation. This fact modifies the maximum energy point and then hot spots can relocate in the regions where there is still some moisture content [36].

1.2.7 Horikoshi et al. [37] studied the generation of hot-spots by microwave electric field (E-Field) and magnetic field (H-Field) and their Impact on a microwave-assisted heterogeneous reaction in the presence of metallic Palladium nanoparticles on an activated carbon support. The present study examined the conditions under which hotspots are generated and their influence on a chemical reaction chosen to be the synthesis of 4-methylbiphenyl by a Suzuki

Miyaura heterogeneous coupling reaction [38] as model reaction to further clarify the feature(s) of hot-spots. Hot-spots are easily formed under E-field conditions but scarcely under H-field conditions. Moreover, the generation of hot-spots on the type of microwave generator used (magnetron vs semiconductor), and the possible disadvantage of hot-spots as well as magnetic field heating in microwave chemistry.

The generation of hot-spots (electric discharge) in a heterogeneous-catalyzed reaction system occurring in a nonpolar solvent when subjected to the microwaves E-field conditions has been confirmed and clarified by recording the events with a high-speed camera. The efficiency of generating hot-spots depended on the nature of the microwave generator used: semiconductor versus magnetron. Although normal expectations dictate that the efficiency of chemical syntheses should be the same whenever based solely on the macroscopic temperature determined under conditions of the microwaves' E- and H-fields, for a heterogeneous catalyzed reaction (as investigated herein) it becomes relevant to ascertain the outcome of the reaction from the gap between the solution bulk temperature (macroscopic area) and the temperature inherent at the surface of the catalyst (Pd/AC, microscopic area). The latter could not be measured by conventional thermometers (e.g., fiber optic, etc.). The microwaves H-field from the semiconductor generator operated effectively in the chemical reaction yielding greater product yields. The hot-spots generated at the activated carbon (AC) support for the Pd particles under E-field conditions, and at which the temperature was no doubt much higher than that of the bulk solution, had a negative impact on the reaction product yields as they caused aggregation of the catalyst particles on the AC support, one of the related factors affecting product yields. Most important are the observations that hot-spots may impact either positively (activate) or negatively (deactivate) the chemical reactions [39]. Accordingly, it is necessary to control the formation of hot-spots in microwave-assisted E-field induced chemical reactions, especially when these are carried out in heterogeneous media. This article has demonstrated that whenever hot-spots have a negative impact on a reaction, the reaction can be carried out with microwaves under H-field conditions as the latter have been shown to avoid formation of hot-spots. Moreover, hot-spots also play an important role in the synthesis of heterogeneous catalysts. In this regard, Siamaki and coworkers [40] reported an efficient method to generate highly active Pd nanoparticles supported on graphene (Pd/G) by the microwave-assisted chemical reduction of the corresponding aqueous mixture of a palladium salt and dispersed graphite oxide (GO) sheets. Dispersed Pd nanoparticles supported on the graphene may not be formed when performing the process under excessive E-field irradiation.

1.2.8 Das et al.[41] reported the microwave energy absorption, increases with increase of temperature is the cause of local thermal runaway and formation of hot-spot resulting in local melting of material, evaporation, or forming liquid, gas or plasma respectively. This thermal runaway hot-spot formation and process of phase change depicted as 'plasma' formation during the process of drilling with microwaves [42].Dimension of hotspot is also calculated by the help of $\rho C_p\, \delta^2 / k_{th} >> \tau$ where $\tau = 2\pi / \omega$ is period of the EM wave. This also quantifies timescale separation. Solid state microwave drill system can be developed with metered system of hot spot temperature regulation.

1.2.9 Skocpol et al. [43] reported self-heating hotspots in superconducting thin-film microbridges. Heating effects of Hotspots are analyzed by microbridges model. Simple model of a localized normal hotspot can be understood by Joule heating. Self-heating appears to be the principal cause of both the hysteresis of the 1-V characteristics at low temperatures, and the loss of phase coherence (and hence the ac Josephson effect) at high voltages. Iwanyshyn and Smith[44] presented extensive calculations of heating effects at high power levels in idealized point-contact geometry, and have concluded that a number of experiments in S-N and S-S point contacts should be reinterpreted because of the probable growth of a normal hotspot.

Heat generated in localized dissipative regions in such bridges is transferred in two ways: by thermal conduction within the film and by surface heat transfer across the temperature discontinuity which develops at the boundary with the substrate. It has been concluded that the electrical behavior of thin-film superconducting microbridges can be understood in terms of the simple physical idea of the growth of a normal hotspot due to localized dissipation in the microbridge. Among the important effects which are explained are hysteresis at low temperatures and loss of superconducting phase coherence at high voltages. In the latter case the performance of a variety of types of super conducting weak links were compared and found microbridges are somewhat better than proximity-effect bridges, but not as good as oxide tunnel junctions and some point contacts. However, changes in the geometry of thin-film microbridges which improve their cooling could help to improve their performance. In any case, the great importance of heating effects in microbridges, proximity effect bridges, and perhaps some point contacts shows that the shunted-Josephson-junction model is not sufficient by itself to serve as a universal model of superconducting weak-link behavior.

1.2.10 Bond et al. [45] reported recent applications of microwave heating in the areas of catalyst preparation, catalyst characterization and catalytic reactions. Oxidative coupling of methane was carried out using sodium aluminate as a catalyst. Both conventional and microwave drying was applied to study the comparative results. The drying of impregnated catalyst precursors in a microwave field offers three significant advantages over conventional drying methods. Firstly, microwave drying is more rapid. Secondly, as a result of the phenomenon known as moisture levelling, the distribution of metal on the support is much more uniform in microwave dried catalysts. Thirdly, microwave dried materials are physically stronger than conventionally dried materials. The possibility that the measurement of bulk temperature is incorrect in the microwave experiments has been discarded as the temperature has been monitored by two independent methods. There does, however, remain the possibility that the temperature within the catalyst bed may be non-uniform. This is especially likely when the catalyst is non-homogeneous or consists of more than one component as different areas will adsorb the microwave energy to differing extents. This will result in different intensities in the electric field within the catalyst bed. As a result heating will occur preferentially where the electric field is most intense and a hot spot will be generated. However, the position of these hot spots will not be fixed as the position of maximum electric field will change as heating proceeds. Hence these hot spots may occur at random throughout the catalyst bed. The existence of such hot spots is a hypothesis which has neither been proved nor disproved at this stage. However, we intend to use a thermal imaging camera to try to establish if localized hot spots are generated in catalytic materials during microwave heating.

1.2.11 Yeo et al. [46] analyzed theoretically catalytic reaction systems under microwaves to save energy. When a chemical reaction was conducted in a heterogeneous medium with microwave heating, the reaction rate and the yield were found to be increased compared to conventional heating under the same reaction conditions. This is due to hot spots generated by selective heating of the catalyst pellet, resulting in an increased reaction rate. Temperature profiles were obtained by solving the partial differential equations using the finite difference method. The higher steady-state temperature for microwave radiation indicates that uniform volumetric heating by microwave radiation is more efficient to transfer heat than conventional surface radiation with the same power deposition. From modeling and simulations we could see that the temperature at the center of the pellet under microwave heating is higher than that under surface radiation. Thus we can see that uniform volumetric heating by microwave is more efficient than surface radiation with the same power deposition. When the heterogeneous chemical reaction under microwave heating is compared with that under conventional heating of the same bulk fluid conditions, the difference in the temperature at the center of pellet and the bulk fluid phase under microwave heating is larger than that under conventional heating. The difference depends on the temperature dependence of the dielectric property of the catalyst. In the model used in the present work, the difference in the temperature under microwave heating and under conventional heating for exothermic reaction is larger than that for endothermic reaction. With microwave heating, the reaction rate and the product yield increase compared to conventional heating under the same conditions. This is due to selective heating of the catalyst pellet creating hot spots, resulting in an increased reaction rate. In short, direct heating of catalysts by microwaves was found to be effective to enhance the reaction rate and the production yield.

1.2.12 Horikoshi et al. [47] carried out the heterogeneous Suzuki–Miyaura cross coupling reaction for the synthesis of 4-methylbiphenyl in toluene solvent in the presence of Pd/AC (activated carbon) catalyst and examined the mechanism experimentally and electromagnetic simulation, by which the hot spots are generated through particle aggregation observed by means of a high-speed camera; the influence of particle size was also examined. After close examination a decreased catalytic activity was observed indicating that formation of hot spots has a negative effect on synthesis reactions. Accordingly, it becomes imperative that formation of hot spots be controlled for cases where needed. This led us to examine some possible methods to control the generation of these micro-plasmas, expose the reaction only to the magnetic field (H-field) component of the microwave radiation so as to minimize, or otherwise suppress the formation of hot spots [48]; make use of carbon micro-coils rather than activated carbon particles as the support for the Pd catalyst particles[49]; use microwaves at a frequency of 5.8 GHz rather than the 2.45 GHz microwaves typically used in nearly all microwave assisted syntheses [50] and control of hot spots formed on Pd/AC particles using the hybrid internal/external heating method [51]. By the help of optical fiber thermometer, it has been observed that the greatest difference in the heating rate occurred when the AC particle size was between 0.6 mm and 0.65 mm. Thus, it was anticipated being able to control the generation of hot spots particle sizes below 0.6 mm, and indeed hot spots did form easily at less than 0.6 mm. On the other hand, no hot spots were observed when the activated carbon size was less than 0.03 mm. Although hot spots formed under **E**-field conditions; they did not under **H**-field irradiation. Evidently, heating of AC particles by microwave radiation does not necessarily lead to the generation of hot spots. The generation of hot spots and the heating efficiency are likely unrelated. Also, hot-spots were generated whenever the particles were separated by very small distances; however, when the distance was 0 nm no hot spots formed, at least none were observed. Such a phenomenon resembles surface enhanced resonance (SERS) that occurs between metal nanoparticles wherein the electric field of light is concentrated between nanoparticles when the gap is narrow [52]. When hot spots occurred, the efficiency of the Suzuki–Miyaura cross-coupling reaction decreased significantly, whereas the Suzuki–Miyaura homo-coupling side reaction did not decrease by much. In heating with an oil bath, the yields of 4- methylbiphenyl and biphenyl were 21.3% and 8.8%, respectively (ratio, 2.4 to 1). Compared with oil bath heating, the efficiency of the cross-coupling reaction was increased by H-field irradiation (no generation of hot spots), while that of the Suzuki–Miyaura homocoupling process was affected negatively (a decrease in efficiency).For instance, generation of a hot spot could be suppressed in the flow-through reaction using a fixed bed reactor (catalyst deposited in the reactor). Moreover, it will work effectively since conductivity can be reduced by covering the catalyst surface with SiO_2.

1.2.13 Horikoshi et al.[53] examined the generation of hot spots and their impact on the yields of products in organic syntheses, as demonstrated by the formation of 4-methylbiphenyl from the heterogeneous Suzuki−Miyaura cross-coupling reaction in the presence of Pd/AC catalyst particles. Several factors were considered: the dispersiveness of the catalyst and substrates(i.e., mass transfer), pulsed wave versus continuous wave irradiation, and the presence of standing waves versus non-standing waves when microwaves were used to carry out the reaction. Generation of hot spots can be clearly controlled by the dispersiveness of the catalyst in solution. However, even though the heterogeneous dispersions were stirred at fairly high speeds (up to 2000 rpm), formation of hot spots could not be suppressed completely. On the other hand, microwave irradiation with pulsed waves versus irradiation with continuous waves appears to have little or no impact on the formation of hot spots. Nonetheless, it was possible to control the formation of hot spots with microwave selective heating of Pd/AC catalyst particulates by power-saving microwave irradiation using standing waves.

1.2.14 Liao et al. [54] forged electronic mathematical model based on the Finite Element Method (FEM) to predict the temperature distribution. Meanwhile, a new computational approach based on the theory of transformation optics is first provided to solve the problem of the moving boundary in the model simulation. This structure is based on the theory of phase shifting but is totally different from other cavity structures. The cavity structure is efficient, relatively inexpensive and user-friendly. Infrared camera and optical thermometer verified that the model and computational results are reliable. The theory of transformation optics was first introduced to overcome the difficulty of multi-physics calculations for a moving boundary. Thereafter, an elaborate experiment was designed to measure some point temperature histories and spatial temperature distribution, which are compared with model predictions at the same time.

1.2.15 Jerby et al.[55] reviewed potential applications of Localized microwave-heating (LMH) intensification. The LMH effect is associated with the localized hotspot formation due to the thermal-runaway instability. LMH intensification in solids and powders enables various applications using the microwave-drill technique, as reviewed in this paper. These include for instance local heating, up to >10^3 K, also by LDMOS transistors.The microwave drill [56] intentionally utilizes the LMH effect by purposely exciting thermal-runaway instability [57]. It generates a small hotspot (with a diameter ~102 shorter than λ), which enables local temperature increase to >1000°C in heating rates of >100°C/s.The temperature- dependent dielectric permittivity, consequently modified along the resonator, is coupled to the higher-order modes. These enable the sharper sub-wavelength intensification of the EM dissipated power Q_d (z, t), initially distributed as the original fundamental mode (with a $\sin^2 \pi z/L$ profile). As the LMH instability proceeds, Q_d becomes significantly intensified and confined at the hotspot region. The localized temperature profile is sharpened accordingly to intensify the hotspot.The various LMH aspects reviewed in this paper differ from the common microwave-heating paradigm by the intentional concentration and local intensification of the microwave-heating energy into a heat-affected zone (HAZ) much smaller in size than the microwave wavelength. The relatively high power density concentrated within this small volume enables the hotspot melting, evaporation, and even breakdown to plasma.

1.2.16 Coleman et al. [58] reported hotspots formation by both perturbation and numerical means. The phenomenon of hotspots is the existence of thermal instabilities. By the linear perturbation analysis, it has been noted that the hotspot phenomena is over before there is any significant dispersion of the initial perturbation profile. Although such effects can be troublesome, there is now some evidence that they can also be used to advantage in the production of specialized metal alloys [59]. Consequently, it is important that further theoretical work be undertaken in order to aid the development of these processing techniques. In these circumstances, however, the dissipation is so strong that that interaction between the electromagnetic and thermal fields cannot be neglected.

1.2.17 Alcolado et al. [60] investigated profile and the stability of hot spots in one and two dimensions using Kriegsmann’s model with exponential nonlinearity. The linearized problem associated with hot spot type solutions possesses two classes of eigenvalues. The first type are the large eigenvalues are associated with the stability of the hot spot profile and in this particular model there cannot be instability associated with these eigenvalues. The second type is the small eigenvalues associated with translation invariance. It showed hot spots can become unstable due to the presence of small eigenvalues and characterized the instability thresholds. In particular, the material with low heat conductivity (such as ceramics), and in the presence of a variable electric field, the hot spots are typically stable inside a plate (in 2D) but can become unstable for a slab (in 1D) provided that the microwave power is sufficiently large. On the other hand for materials with high heat conductivity, the interior hot spots are unstable and move to the boundary of the domain in either one or two dimensions. For materials with moderate heat conductivity, the stability of hot spots is determined by both the geometry and the electric field inside the microwave cavity.

The two dimensional case is more difficult to analyse due to the appearance of the logarithmic singularity in the free-space Green's function. Unlike the one-dimensional case, the stability is independent of the power p, and the hot-spot will be stable provided that the diffusion $d << 1$ and $f(x)$ has an interior maximum. Moreover, two-dimensional hot-spot can be stable even when $d = O(1)$. By contrast, the one dimensional hot-spot is unstable when $d = O(1)$, regardless of the shape of $f(x)$.

It is well known that scalar local reaction diffusion systems cannot give rise to stable hot-spot type solutions [61]. On the other hand, the addition of a nonlocal term has a stabilizing effect [62, 63] Even then, two or more hot-spot solutions are found to be unstable – similar phenomenon was discussed in [64] in the context of reaction-diffusion systems. It is an open question as to whether several hot-spot solutions can be stabilized

1.2.18 Wang et al. [65] reported Numerical Simulation of Hot-spot Effects in Microwave Heating due to Existence of Strong Microwave-Absorbing Media. Silicon carbide (SiC) as a representative of strongly microwave absorbing media, and simulated hot-spot effects when SiC was put into and surrounded by weak microwave absorbers under simultaneous microwave irradiation. Investigation of heat transfer issues related to hot-spot effects was facilitated by measurements of actual thermal generation. Hot-spot effects were shown quantitatively in micro and instantaneous scales. Understanding hot spot intensity and other effects will be beneficial for its proactive utilization and the optimization of microwave heating processes. The overall heating of SiC particles was experimentally measured and only temperature gradients inside and outside the particles was simulated. The ANSYS software package—a large computer-aided engineering tool, integrating fluid dynamics with electronics, magnetism, and temperature—was employed. The influences of particle size, irradiation time and heat generation were also considered. Hot-spot profiles vary for different SiC particle geometry, heat generation, or heat transfer. Larger particle sizes, higher heat generation rate, and smaller heat transfer share all highlight the temperature difference of the hot spot from surrounding media. The temperature difference can exceed several hundred degrees Celsius under certain conditions. The magnitude of the effect depends on how quickly the heat generated in the strongly absorbing medium can be transferred to the weakly absorbing media. Prominent hot spots could be intentionally created, including the use of microwave discharges, and the temperature differences employed to enhance chemical reactions, such as macromolecule decomposition, pollutant removal, etc.

1.2.19 Yang et al. [66] reported Influence of Microwave Irradiation on Calcium Sulphate Crystal Phase but also detected small quantity of calcium sulphate hemihydrates with microwave heating. By multiphysics calculation and experimental measurement confirmed that the formation of calcium sulphate hemihydrates is induced by hot spots during the microwave heating. It is well known that calcium sulphate hemihydrates can only be produced above 107

°C. There are quite difference between the measured macroscopical temperature of the reaction system and local temperature during the high power microwave heating. The coupled Maxwell's equations, fluid field equations and heat transport equations were solved by using finite-element (FEM) method.

1.2.20 Haneishi et al. [67] reported the generation of hot spots between catalyst particles under microwave heating reaction rate of the dehydrogenation of 2-propanol over a magnetite catalyst was enhanced 17- (250 °C) to 38- (200 °C)fold rather than an electrical furnace. Coupled simulations of the electromagnetic field distribution and heat transfer using a model of the packed beds to analyse the distribution of the electromagnetic field and the temperature in the beds under MWs. Visible camera and an emission spectrometer were used to demonstrate the existence of high-temperature regions. This study clearly confirms that the local high temperature regions occurred at the vicinal contact points between the catalyst particles under MW irradiation. These local high temperature regions can be exploited to enhance fixed-bed flow reactions.

Synthesis of Heterocyclic Compounds: The above description and theory associated with microwave-induced reactions have received significant attention to the synthesis of diverse organic molecules including heterocycles. Clearly, microwave-induced processes are different than reactions performed thermal, photo or sound-induced conditions. It is observed that reactions that need high activation energy can be conducted easily due to microwave facile energy transfer and this can happen because of the formation of hot spots.

Conclusions

Hotspots creation was just a generalized theory in past times. This review leads us to, not only experimental but numerical simulation results which confirm the practical existence of hotspots with proper explanations. Hotspots formation can also be manipulated manually by the help of mathematical models. This application is highly useful in organic synthesis of carbocyclic and heterocyclic compounds using catalytic surfaces where reaction rates can be increased as needed.

The results of experimental and mathematical models are compiled herewith in diverse applications, which will be highly helpful to propose any conclusions based on microwave heating applications.

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