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Perspectives of Microwaves-Enhanced Heterogeneous Catalytic Gas-Phase Processes in Flow Systems

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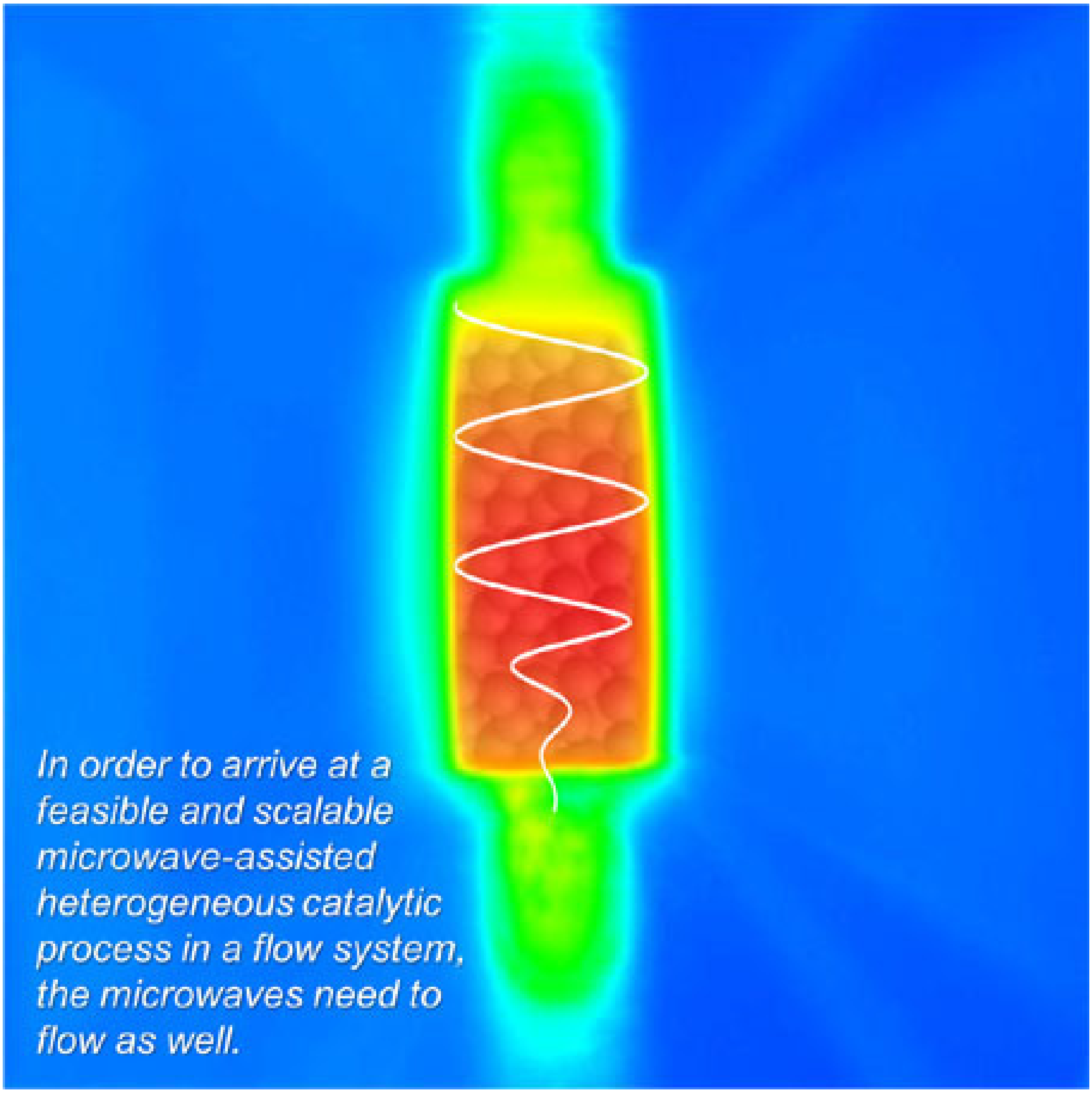

In order to arrive at a feasible and scalable microwave-assisted heterogeneous catalytic process in a flow system, the microwaves need to flow as well.

Abstract: The paper discusses the currents status and future perspectives of the utilization of microwaves, as a selective and locally controlled heating method, in heterogeneous catalytic flow reactors. Various factors related to the microwave-catalyst interaction and the design of microwave-assisted catalytic reactor systems are analyzed. The analysis clearly shows the superiority of the traveling-wave systems over the mono-mode and multi-mode cavity-based systems when it comes to the design and application of microwave flow reactors at relevant production scales.

Keywords: Microwave Heating, Flow Reactor Systems, Heterogeneous Catalysis, Large-Scale, Modularity

1. Introduction

With the growing importance of renewable electricity as a primary energy source on Earth, the significance of the electricity-based technologies in process industries is also expected to increase. Microwave heating is a well-established electricity-based industrial technology utilized on the commercial scale in various operations, such as drying, thawing, pasteurization or sintering. Carrying chemical reactions under the microwave irradiation has been investigated for more than thirty years, first in liquid-phase homogeneous systems and later also in the heterogeneous gas-phase catalytic processes. Unfortunately, despite encouraging results of various laboratory-scale studies, commercial implementations of microwaves in heterogeneous catalysis are non-existent. This is primarily due to the complexity of the interactions between the microwaves and solid catalysts, as well as to several important design factors influencing the performance of a continuously operated microwave-assisted flow reactor. The current paper examines the above interactions and factors and provides a perspective view on necessary developments in the technology that should lead to its industrial-scale applications.

2. Interaction of Microwave with Heterogeneous Catalyst

When a solid matter is introduced inside the electromagnetic field (EMF), e.g., microwave field, the solid matter generally transmits, reflects or absorbs the exposed field. The interactions between microwaves and different mediums and EMF distributions are illustrated in Figure 1. Materials which transmit the microwave are referred to as transparent materials. The microwave propagates within these materials with a little (or a negligible) attenuation due to low interaction with the EMF, see Figure 1a. For that reason, most of the transparent materials (e.g., quartz, borosilicate glass, PTFE) are being used as vessels in many microwave applications. Conductive materials, (e.g., aluminum, silver, copper) also known as opaque materials, reflect the microwave (Figure 1b) and they are the key components of the construction of transmission lines (e.g., waveguide, coaxial cable). Absorbing materials (Figure 1c) possess polar properties, they can absorb the microwave energy through the polarization converting it to heat.[1]

Microwave heating mechanism changes depending on the absorbing material composition. In heterogenous catalysis, most of the microwave absorbing catalysts are non-magnetic materials except some metal oxides (e.g., iron, nickel, and cobalt) in which the heating occurs through magnetic losses.[2] Non-magnetic microwave absorbing materials are also referred as dielectric materials such as zeolites, which are an important group of heterogeneous catalysts.[3] There are some zeolites that can be easily and efficiently heated to a glowing temperature.[4] In microwave heating, dielectric and conduction losses are the main two physical heating mechanisms. These loss mechanisms and their contribution are strongly dependent on the material composition, structure, temperature and the microwave frequency.[5] These dependences, especially the complexity of structures and chemical compositions of the matter, make it difficult to understand the contribution of each mechanism, i.e., dielectric and conduction losses. The group of Ohgushi[4,6] and Legras[7] intensely studied the microwave heating mechanism of Linde Type A (LTA) and Faujasite (FAU) zeolites regarding different compensate mobile cations (e.g., Na, K, Ca), Si/Al ratios, and hydration degrees, i.e., water uptake. In a recent investigation,[8] heating mechanism of zeolites under the microwave irradiation has been explained theoretically by means of the molecular dynamic simulation for cation movements.

At high frequencies, i.e., microwave frequencies, (commonly ca. 2.45 GHz), the dielectric loss (also known as

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Andrzej Stankiewicz - Full Professor and Chair of Process Intensification at Delft University of Technology, the Netherlands, and Director of TU Delft Process Technology Institute. With circa 40 years of industrial and academic research experience he is author of numerous scientific publications on process intensification, chemical reaction engineering and industrial catalysis. Prof. Stankiewicz is one of the pioneers of process intensification. He is principal author and co-Editor of the world's first book on Process Intensification. Prof. Stankiewicz is Editor-in-Chief of Chemical Engineering and Processing: Process Intensification (Elsevier) and Series Editor of the Green Chemistry Books Series (Royal Society of Chemistry). He was founder and first Chairman of the Working Party on Process Intensification at the European Federation of Chemical Engineering. He currently chairs the Board of the European Process Intensification Centre (EUROPIC). Current research interests of Prof. Stankiewicz focus on control of molecular interactions and intensification of chemical reactions using electricity-based energy fields (e.g. laser, microwave, UV). The research in that area has brought him prestigious Advanced Investigator Grant from the European Research Council.

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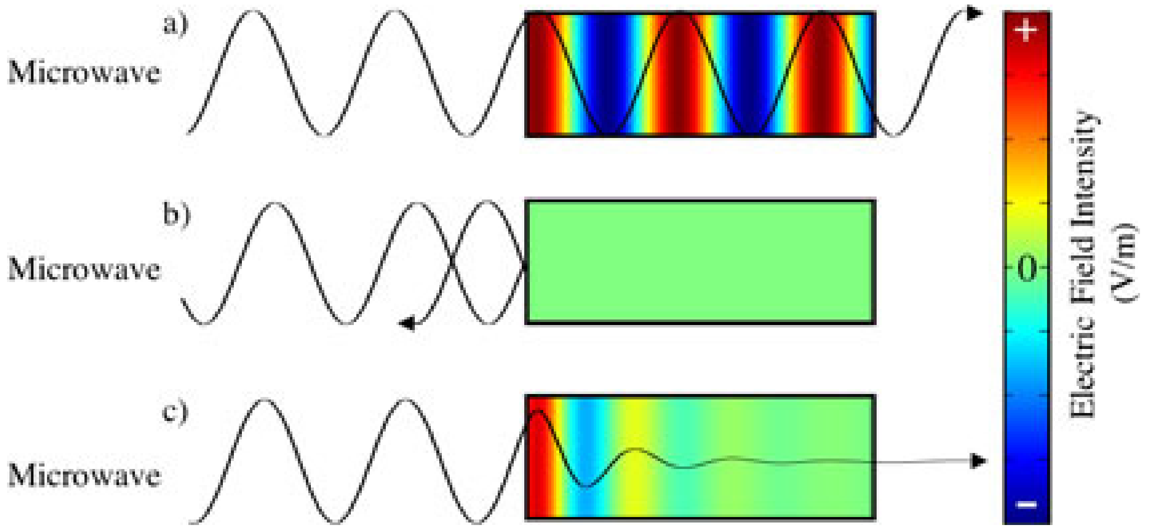

Figure 1. Interactions between microwaves and different materials and EMF distributions: A) transparent, B) conductor, and C) absorbing medium. The simulations were performed on COMSOL Multiphysics (v.5.3a) simulation environment using a Radio Frequency module.

dipolar polarization or dipolar reorientation) is the dominant mechanism.[9] EMF propagation and the loss mechanisms are characterized for dielectric materials by complex permittivity, which characterizes the material interaction with exposed EMF's electric field. The complex permittivity composed of a dielectric constant, ε', and dielectric loss, ε'', and generally represented in the dimensionless form with normalization to the free space's permittivity ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, $\varepsilon = \varepsilon_0 \varepsilon_r$) corresponding to the following equation:

$$\varepsilon_r = \left(\varepsilon_r' - j\varepsilon_r''\right) \tag{1}$$

where $j = \sqrt{(-1)}$ is the complex operator. Generally, The real part characterizes the ability to propagate microwave into material, whereas the imaginary part is the loss factor which shows the ability of a material to dissipate the microwave energy.[10] Therefore, in microwave-assisted catalytic systems, the catalysts' dielectric properties are the determining factors. The catalyst in those systems has a dual functionality, i. e., conversion of the electromagnetic energy, and of the reactant (s). The sufficiency of a dielectric catalyst for a particular reaction depends on the required operating temperature. In principle, less energy- demanding processes have higher potential to be applied in microwave-assisted systems with moderate dielectric materials. The needs of a catalyst with adequate dielectric property is more pronounced for endothermic reactions, where high temperatures are required (> 300 °C).

Furthermore, dielectric reactants and products may contribute to electromagnetic conversion to heat in the void spaces within the catalyst bed. Liquid reactants, such as water, have relatively higher dielectric constant than gaseous reactants. Consequently, the effects of microwave vary for each catalytic system, gas-solid or liquid-solid reactions. Table 1 highlights the dielectric properties of the common materials and reactants.

Table 1. Dielectric property of common materials and reactants at 2.45 and 2.5 GHz and ambient temperature.

Materials	Dielectric Properties ε'–ε''	Ref.	Materials	Dielectric Properties ε'–ε''	Ref.
Air	1.0–0	[11]	Benzene	2.3–n/a	[12]
Nitrogen	1.0–0	–	Water	77–13	[11]
Methane	1.3–n/a	–	Carbon[b]	26–∼10	[13]
Methanol	32.7–30[a]	[12]	Quartz	3.78–0.001	[11]
Ethanol	24.6–1.5[a]	[12]	Teflon	2.04–∼0	[11]

[a] Adapted results from reported tan(δ), [b] Relative density 36.8 %.

As described in Table 1 all gases have dielectric constants similar to air, ~1 because polarization depends on the particle density, which is low in the gases. Hence, for gas-solid reactions, heat generation depends on the dielectric properties of the catalytic bed material. In general, gas-solid reactions occur at high temperatures, which makes microwave-assisted systems for such reactions a challenging topic from the material perspective. For liquid-solid reactions, the effects of the microwave in the catalytic bed depend on the dielectric distinguishing between the solid catalyst and flowing reactant (s).

The use of microwave as an alternative heating technology has already demonstrated remarkable advantages over conventional heating methods, i. e., conduction, convection and radiation, that shapes the future of microwave technology for the chemical industry. The observed advantages of microwave were summarized from literature findings, which are interesting to validate for a specific catalytic reaction:

1. Higher heating rate is achievable via MW energy, if component(s)/material have a vigorous response to microwave as well as distinct products distribution.[14]
2. Controlled heating of reaction components to optimize reaction products by avoiding undesired reactions by selective heating nature of MW. For instance, mixture impurities with poor dielectric properties reduces the tendency of undesired products.[14–15]
3. Reported significant reduction in reaction time for several batch processes, which increase the throughput.[15]
4. Reaction acceleration under increased pressure conditions due to selective heating.[14]

Although numerous empirical studies in the literature reported various promising features of microwave-assisted catalytic reactions, there is still lack of understanding of microwave contribution into the reaction kinetics apart from heat generation. Researchers explain the enhancement in reaction conversion and selectivity as follows:

1. Microwave irradiation induces non-thermal effects by shifting reaction equilibrium to improve the reaction rate.
2. Microwaves heat up the catalytic bed selectively, without heating the reactant(s).
3. Hot-spots are formed within the catalyst due to the different heating rates between metal nanoparticles and the catalyst support.[16]

Some studies attributed the conversion and yield improvements in the microwave assisted-systems to the direct microwave effects on the reaction mechanism (the so-called “non-thermal effects”). However, this hypothesis remains unsupported, given the difficulties in obtaining comparable local temperature measurements under the convective and the microwave heating. In the microwave heating, temperature measurements rise critical challenges due to the lack of appropriate tools.[17] Zhang et al. reported significant conversion enhancements exceeding the equilibrium limit for the catalytic conversion of hydrogen sulfide. The improvements were attributed to the hot-spot formation between the active sites and the support, which led to the changes in the reaction rate changes and the equilibrium constant.[18] Therefore, the improvements of reaction activity may results from higher or lower operating temperature in the microwave-assisted systems that observed via thermal indicators such as infrared camera and fiber optic sensor. To validate microwave contribution, temperature measurement approach has to be reliable and comparable.

The advantage of microwave heating in solid/gas heterogenous catalytic systems is that the solid catalyst (microwave absorbing media) may be heated selectively when nonpolar solvent and gas used. For that reason, the temperature of the solid catalyst surface, where chemical reactions typically take place, has higher temperature than the gas phase. This selective microwave heating phenomenon may also lead to a significant energy efficiency unlike the conventional heating.[1a,19]

Coke formation is generally inevitable in heterogenous catalysis of hydrocarbons, and it hinders the catalyst activity. Several literature findings illustrated that coke formation was less pronounced in microwave-assisted systems. In conventional systems, the catalysts deactivation is compensated by introducing higher temperature to maintain a certain conversion. In contrast, the microwave interaction with the catalytic bed may improve with coke formation due to the excellent carbon dielectric property. On the other hand, however, non-homogenous coke formation in the catalytic bed may introduce larger temperature non-homogeneity.

Another critical challenge in the microwave-catalyst system is to find a good material for the microwave energy conversion and for the desired chemistry. Consequently, the optimum catalyst and chemistry for conventional heating and microwave heating can often be different. Microwave-assisted heterogeneous catalytic processes were investigated by numerous researchers – see for instance.[2,20] Table 2 lists several high-potential processes studied in microwave-assisted systems.

3. Basic Types of Microwave Reactor Systems

3.1. Reactors based on Multi-mode and Mono-mode Cavities

Microwave heating, whether in our kitchens or in the industry, always takes place in the so-called “microwave applicators” or “cavities”. There are three basic types of those applicators: multi-mode, mono-mode, and traveling wave.

Multi-mode applicators, which include household microwave ovens, can be simply described as rectangular metal cavities (Figure 2). Inside those cavities, microwaves are reflected from the walls and from the sample (load). Due to these reflections, multi-mode cavities are characterized by a chaotic interaction with the sample and a non-homogeneous microwave field which results in non-uniform heating profile and hot spots formation. To this end, a rotating disk and a mode stirrer (rotating reflector, see Figure 2) are used in those cavities to make the microwave field distribution as homogeneous as possible. Despite that problem with heating uniformity, the multi-mode cavities are frequently used in industry because of their low cost, simplicity of construction, and their versatility. A general problem in multimode

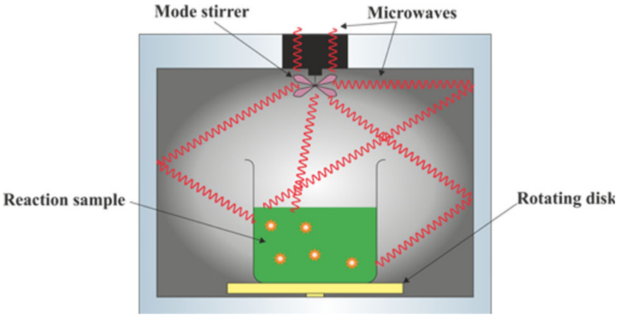

Figure 2. Multi-mode Microwave Cavity, adapted from reference,[24]

applicators is the low field density compared to the high generated microwave power (1000–1400 W) which results in a weak performance in case of small-volume samples.[23]

In the mono-mode cavities, on the other hand, only one mode is present and generates a standing wave inside the cavity. The irritated material is positioned in the place of the maximum intensity of the electromagnetic fields (Figure 3).[24]

This specific feature of mono-mode cavities makes them strictly limited in size to less than a half of the wavelength to provide a more uniform heating profile. Therefore, mono-mode applicators are usually employed to process volumes up to 200 ml, which is their main limitation.[24] However, compared to multi-mode cavities, mono-mode cavities can provide higher field strength with less energy consumption. Although, the microwave field pattern inside a mono-mode cavity can be strongly affected by frequency changes and also by the position and dielectric properties of the heated sample, Patil et al. have demonstrated the effect of shape and dimensions of a milli-reactor setup on controlled and efficient microwave heating in a mono-mode cavity.[25]

As one can see from the above, the applicability of typical multi-mode and mono-mode cavities is limited because both systems suffer from non-uniform heating and are strongly dependent on the frequency and dielectric properties of the sample. Those negative features may not be critical in case of drying or thawing; they are very much critical for controlled carrying out chemical reactions.

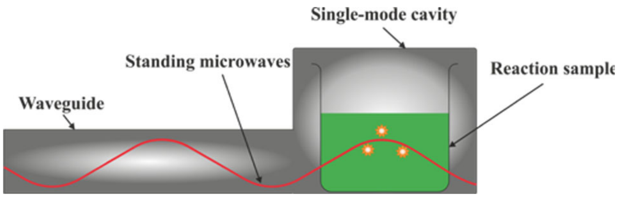

Figure 3. Mono-mode Microwave Cavity, adapted from reference.[24]

3.2. Reactors Based on Traveling Wave Principle

In contrast with the earlier described cavities, the traveling wave reactor (TWR) has the potential to provide highly uniform microwave heating, by avoiding reflections and resonant conditions.[26] In a properly designed traveling wave system, the microwave field inside the reactor travels in only one direction, to avoid non-uniform electromagnetic interference patterns and, consequently, non-uniform heating along the axial direction of the reactor.

Traveling wave reactors can be considered in various configurations. The most popular concept of TWR, with coaxial cable configuration, has been studied in the last few years.[10b,27] A cross-sectional longitudinal view of a coaxial traveling wave reactor is demonstrated in Figure 4, where, the microwave energy delivered at the inlet is absorbed by the catalyst and dissipated at a high heating rate.

The stainless-steel inner and outer conductors form a coaxial waveguide structure, and their diameters are adjusted such that the characteristic impedance of the waveguide is maintained at the characteristic impedance of the feed transmission system (50 Ω). This reactor is rotationally symmetric along the central axis of the inner conductor and catalysts of different shapes, e.g. particles, foam or monolith, can be placed in the annular space between the conductors and the process fluids/reactants flow in the axial direction through the catalyst load.

4. Design Challenges in a Microwave Reactor System

As described in the previous section, the microwave field pattern inside a mono-mode cavity can be strongly affected by frequency changes and also by the position and dielectric properties of the heated sample. This may result in a thermal runaway, hot spots within the material, and, in some cases, in losing the interaction between microwave energy and the material.

There are some mechanisms which can be considered in this system for the efficient transfer of energy to the material,

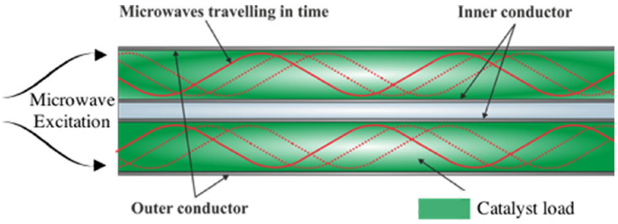

Figure 4. Coaxial Traveling Wave Reactor Configuration.

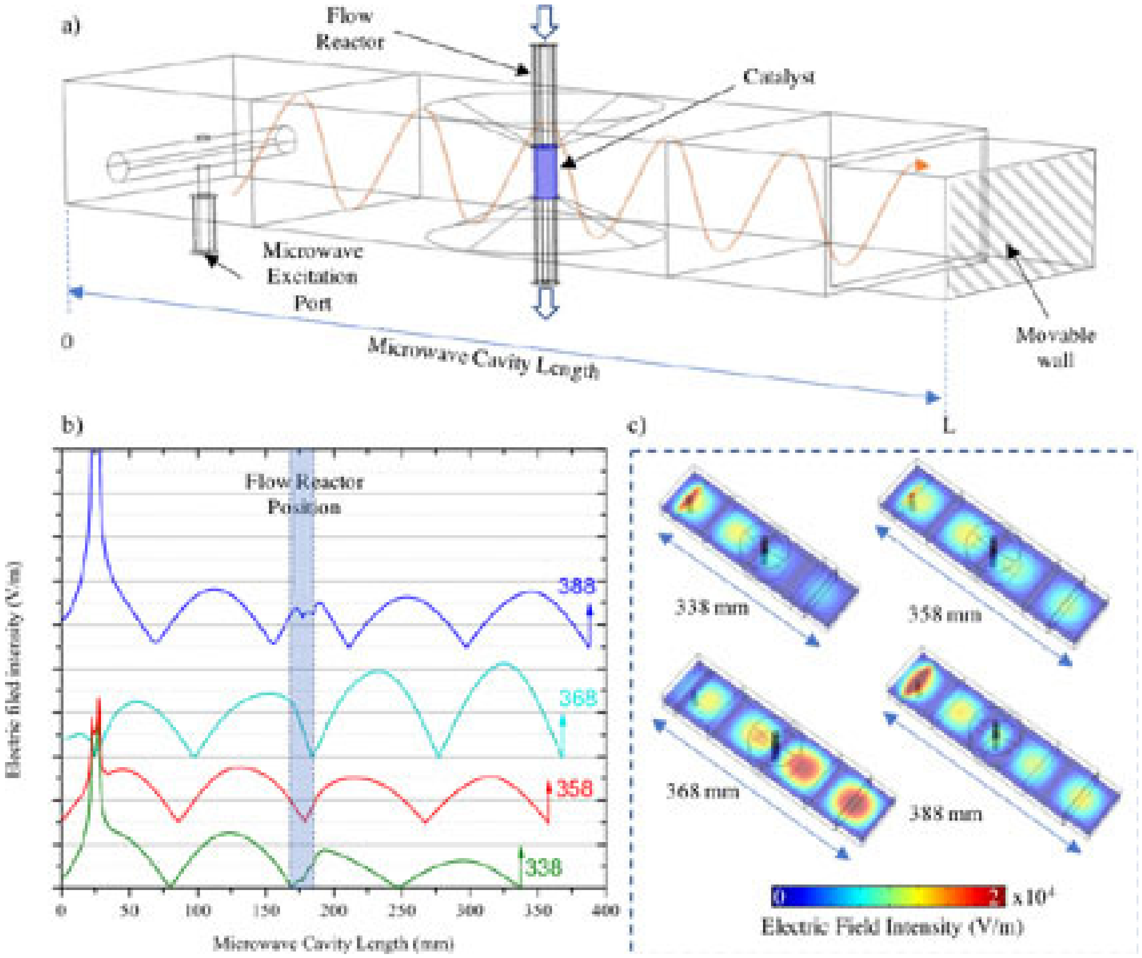

Figure 5. a) Perspective view of the mono-mode rectangular microwave cavity with an adjustable tuner (i.e., movable wall), and b–c) simulated normalized electric field distributions, at the centre along the cavity, in different microwave cavity lengths. The simulations were performed on COMSOL Multiphysics (v.5.3a) simulation environment using a Radio Frequency module at 2.45 GHz with an input power of 100 W.

to compensate for the varying dielectric properties and frequency and to keep the coupling between the material and the applicator during the process. Currently, the best solution to this problem is to use an in-line detection and feedback-control system for temperature actuation and microwave energy input, and auto-tuning of microwave field by tuning elements (e.g., stub-tuner and plunger = movable walls). The tuner's position affects both standing wave patterns and the electric field intensity along the waveguide, i.e., cavity. Because of that, the tuner basically changes the physical length of the cavity along the direction of microwave propagation. For that reason, tuners can adjust and maximize the interaction between different materials (with different dielectric properties) and the microwave. Figure 5 presents simulated different electric field patterns at 2.45 GHz in a mono-mode rectangular microwave cavity.

It is obvious that changing the cavity length changes the standing wave patterns inside the microwave cavity, see Figure 5b–c. Regarding the flow reactor position (Figure 5b), the optimum cavity length in this configuration is 388 mm. At this length, the maximum intensity of the standing wave matches the position of the flow reactor position. That match results in heating of the material (catalyst) contained in the reactor. It is important to stress that this simulation has been done at room temperature. In general, dielectric properties change with temperature and material composition. This may lead to different standing wave patterns. Thus, maximizing the interaction between the catalyst and the microwave field in a mono-mode cavity-based reactor requires continuous adjustment of tuners to maintain appropriate operating conditions. Otherwise, the material cannot be heated further. Moreover, the wave frequency is another variable which may change the electric field distribution inside the microwave cavity.

In contrast to the mono-mode cavity, in the traveling wave reactor there is no need to deal with frequency changes during the process. The only elements that should be taken into account in TWR design are the size of the reactor and the microwave reflections through the whole system, in order to ensure that there is no standing wave generated along the structure.

The reactor dimensions are selected based on restrictions concerning electromagnetic wave propagation, and due to this, the outer conductor, i. e., outer wall of the whole coaxial structure, diameter cannot exceed half of the electromagnetic wavelength. Thus, for the typical frequency of 2.45 GHz, the upper limit of the diameter is approximately 61 mm.[24]

Microwave reflection is an essential factor of the traveling wave reactor performance. A smaller microwave reflection leads to faster heating and less energy losses since more microwave energy penetrates into the sample. In order to minimize the electromagnetic reflections in the coaxial structure TWR, the characteristic impedance of the waveguide should be adjusted and maintained at the characteristic impedance of the feed transmission system. Furthermore, it is also important to keep the impedance matching when introducing the dielectric load (catalyst) inside the waveguide. For this, it is necessary to load the reactor gradually in order to avoid sudden impedance changes. Otherwise, it may reflect back a huge amount of the incident wave. This would result in creating a standing wave inside the waveguide, which would cause a non-uniform heating profile and hot spots formation.

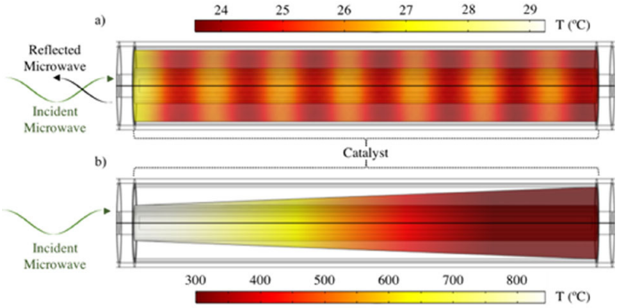

Figure 6. Simulated catalyst heating profile in coaxial traveling wave reactor in different catalyst loading configurations: a) Fully b) partially filled by catalyst.

Figure 6 shows a simulated heating profile in a traveling microwave reactor for two different loading patterns at the same conditions. As can be seen from Figure 7a, due to the large microwave reflections (more than 12 %), the catalyst cannot interact with the electromagnetic wave efficiently. Even at higher energy input the catalyst cannot be heated and hot spots appear inside the reaction zone. On the other hand, in Figure 7b, where the microwave load is gradually introduced to the system, the temperature profile is distributed more smoothly without forming any hot spots.

5. Microwave-assisted Flow Reactor Systems

Until now, besides multi-mode reactors, several mono-mode standing wave reactors and traveling wave reactors have been developed for heterogeneous catalysis.[15,17,20b,28] Because there is an unsatisfactory prediction and controlling on the heterogeneous reaction in multi-mode reactor system, here we focus on the flow reactor system of mono-mode standing wave and traveling wave with single propagation mode.

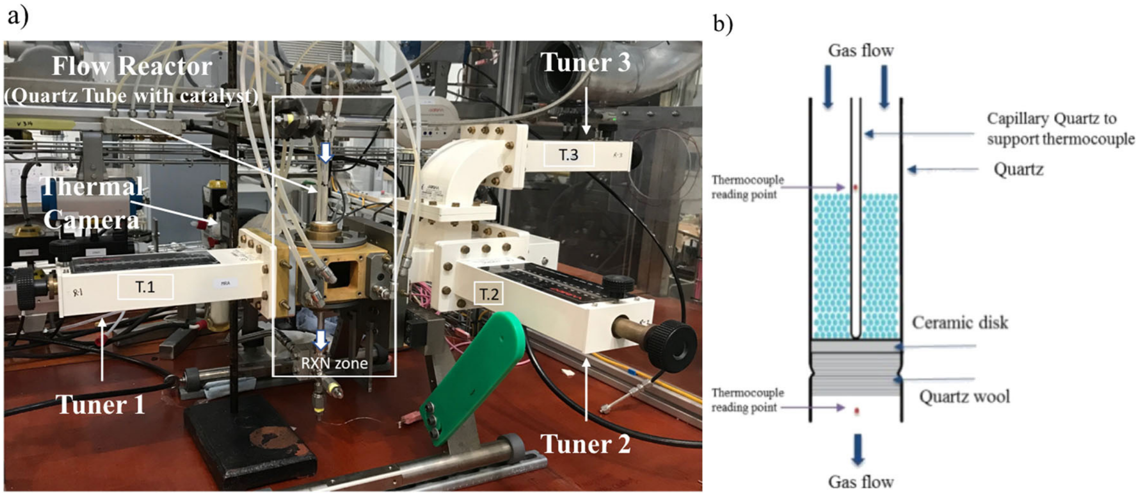

Figure 7. a) Custom designed microwave reactor system with a flow reactor inside, and b) schematic view of a flow reactor.

5.1. Lab-Scale Microwave Reactor Systems

A typical lab-scale microwave reactor system for heterogeneous catalysis study usually consists of a MW generator, a reactor tube with catalyst bed, control units, microwave tuning parts (T1, T2, T3), cooling, and gas supply units, as illustrated in Figure 8.

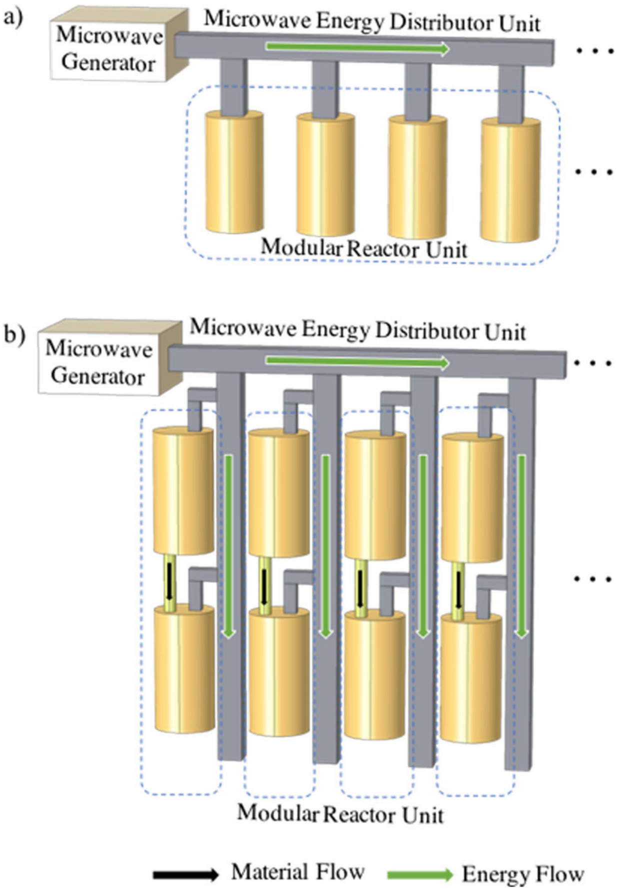

Figure 8. Conceptual design of integrated system for large-scale production by numbering-up strategy: a) reactor unit in parallel for step-wise capacity extension, and b) hybrid scale-up by combining reactor-in-series with numbering-up in parallel.

Several laboratory-scale mono-mode and traveling wave reactors with improved temperature/field control have been developed by different research groups.[17,28b–d] Still, there is plenty of room for further optimization of those systems.

5.2. Integrated System for Large-Scale Production

In the lab-scale microwave reactor systems, attention is usually focused on the microwave-heating and catalyst performance. However, when it comes to scale-up from a lab-scale to pilot-scale and finally industrial scale, more questions need to be answered, such as increased process throughput, reproducibility of lab-scale system performance, economics and response to the change of market-demand.

Conventionally, scale-up means increasing the system characteristic dimensions, hence volume, usually at the cost of some loss of the performance with respect to the lab-scale reactor system. Such conventional scale-up can be realized by shifting the frequency from 2.45 GHz to 915 MHz. However, such a frequency-shift scale-up strategy, requires in each case substantial additional studies concerning physical transport phenomena, frequency-related microwave-catalyst interaction and reaction performance. It will mean in fact an entirely different research story. Therefore, an alternative scale-up strategy should be considered.

In view of the above and in view of the limitation of the microwave penetration depth, a numbering-up strategy presents an attractive alternative that can maintain the performance of the lab-scale system. This strategy was initially proposed for organic synthesis in a mono-mode microwave-assisted flow system.[29] It can also be implemented in a heterogeneous catalytic process.

A general numbering-up concept is schematically illustrated in Figure 8a. In this concept, the lab-scale reactor is replicated, arranged in parallel and provided with a microwave energy distributor unit. This ensures the reproducibility of the lab-scale system performance and minimizes scale-up related issues. Microwave energy distributor design, to ensure uniform energy distribution from microwave generator to each reactor unit, presents a challenge related to this strategy.

In cases when a process requires reaction time longer than in the original lab-scale unit, a mixed, parallel-in-series numbering-up strategy can be applied, as illustrated in Figure 8b.

5.3. Microwave Energy Distributor

Microwave energy distribution is an issue in the conceptual design of an integrated system following the numbering-up strategy. Generally, energy and materials distribution in all the chemical process systems are ubiquitous and extremely important. Flow distributors for uniform materials distribution have been widely investigated and developed, which can be generally classified into tube orifice structure and fractal structure.[30] However, there are rare reports on energy distribution, especially microwave energy distribution, which will determine the feasibility of numbering-up strategy.

Similar to flow distributors, microwave energy distributors can be categorized into two conceptual designs: 1) perforated-waveguide distributors, and 2) fractal distributors. Preliminary attempts of designing microwave energy distributors have been reported by TU Eindhoven and Hitachi Ltd. and the results are encouraging.[29a,31] Still, there is a lot of room for fundamentally new conceptual design. Current microwave energy distributors are still very bulky in volume and complex in structure compared to the reactors. Solutions that would make the system more compact retaining uniform energy distribution are still pending.

5.4. Modularity

Modularity, a modern chemical engineering concept beyond unit operations, is explored in the context of continuous-flow processing and small-scale devices for process intensification.[32] In recent years, modular chemical plants receive wide attention from both academia and the industry due to its nature of fast, flexible production and the possibility for decentralized implementation. Compared to a conventional chemical plant, it offers significant economic and safety benefits together with time-saving in the design, engineering and construction.[33]

The earlier described numbering-up strategy of heterogeneous catalytic flow reactors fits very well in the concept of modular design and manufacturing. Although modular chemical plant presents an important trend for future development and global chemical markets, technical challenges still exist starting from the design of a single modular unit up to the integration of the whole system. Additionally, due to the loss of the economy of scale by shifting from large conventional plants to distributed modular ones, the economic-environmental assessment from the perspective of the overall supply chain for each given production process is a prerequisite.[34]

6. Conclusions

The most important conclusion resulting from the critical analysis presented in this paper is that in order to arrive at a feasible and scalable microwave-assisted heterogeneous catalytic process in a flow system, the microwaves need to flow as well. The cavity-based designs, whether standing-wave or multimode, cannot guarantee a uniform, well-controlled temperature distribution in the catalyst bed on larger scales. In the waveguide-based traveling-wave systems, on the other hand, that control can be achieved, among other things, by manipulating the dielectric properties distribution in the catalyst bed, its geometry and the frequency of the microwaves. The numbering-up strategy utilizing properly designed microwave energy distributors presents the best route towards the industrial-scale units. A pre-requisite of the success here is a multidisciplinary approach and collaboration involving catalysis, material sciences, electrical and chemical engineering.

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