EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Microwave Reactors for Non-Catalytic and Homogeneously Catalyzed Liquid-Phase Processes

TECHNOLOGY CODE: 3.3.3.4.1

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1. Technology

1.1 Description of technology / working principle

(Feel free to modify/extend the short technology description below)

Microwave (or dielectric) heating of materials has been known for a long time and development of microwave ovens has more than 50 years of history. The classical publication by Gedye et al. (1986) has opened a period of very intensive investigations of the microwaves effect on chemical reactions.
In general, microwave frequencies range from 0.3 to 300 GHz, which corresponds to the wavelength between approximately 1 mm and 1 m. Much part of this range is occupied by the radar and telecommunication applications and in order to avoid interference the industrial and domestic microwave appliances operate at several standard allocated frequencies, most often at 2.45 GHz. Molecules that have a permanent dipole moment (e.g. water) can rotate in a fast changing electric field of microwave radiation. Additionally, in substances where free ions or ionic species are present, the energy is also transferred by the ionic motion in an oscillating microwave field. As a result of both these mechanisms the substance is heated directly and almost evenly. Heating with microwaves is therefore fundamentally different from conventional heating by conduction. The magnitude of this effect depends on dielectric properties of the substance to be heated.
Authors generally agree about the ability of microwave heating to accelerate organic reactions and acceleration factors from several to more than thousand are reported. Also, increase of the product yield has been reported in some cases as a result of microwave heating.
The discussion about how the highly polarizing radiation of microwaves promotes and accelerates chemical reactions is still going on. Microscopic hot-spots, molecular agitation and improved transport properties of molecules have been mentioned as potential mechanisms of activation (Jacob et al., 1995). Other hypothetic effects, such as changing the molecules collision pattern, positioning of the transitions states or decrease of the activation energy in Arrhenius law were also postulated and discussed (Howarth and Lockwood, 2004). Recently more and more authors agree that the effect of microwaves has a purely thermal character (Lidström et al., 2001, Kuhnert, 2002, Kappe,. 2004), although for others this appears still a too simplistic explanation (Perreux and Loupy, 2001, 2002, De la Hoz et al., 2004).

1.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Two basic types of microwave reactors can be distinguished:

<u>Monomode microwave reactor</u>:
In the monomode devices a single standing microwave is created inside an electromagnetic waveguide. The sample is located in the place where the amplitude of the wave is the highest. In a basic modomode reactor the wave penetrates the sample cavity only from one side. Recently, CEM Corporation claims to have developed a laboratory microwave reactor, in which a cylindrical sample is uniformly irradiated with a monomode wave from several directions (Fig. 1).

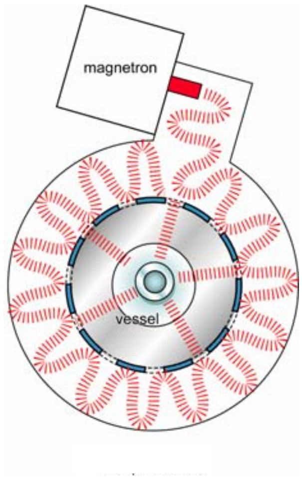

Fig. 1. CEM monomode microwave reactor

Multimode microwave reactor:
A multimode microwave reactor operates in a similar manner to a kitchen microwave oven. It contains a “field diffuser” to reflect the microwaves at different angles. Reflections of microwaves from the cavity walls results in different wave forms while standing waves are mostly avoided.

The achievable specific power density in monomode devices is usually greater than 1000 W/L and is up to ca. 2 orders of magnitude higher than in the multimode reactors. However, this high power density can be applied only to small volumes, as the maximum cavity size of the monomode reactors usually does not exceed 0.25 L, while multimode microwave devices cavities of hundreds of liters are often met. Accordingly, the potential application areas for the monomode and multimode microwave reactors differ considerably.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	Only in specific cases, 40% saving reported in one case	When used purely for heating of a non-reacting liquid, microwave requires ca. 30% more primary energy than the conventional steam heating (due to electricity as the intermediate stage). Overall energy savings can only be expected in the following cases: • Selective heating (e.g. only catalyst particles are heated) • Better yield/selectivity (energy savings in downstream processing) • Less heat losses in the heat-up or cool-down periods (faster heating) Obviously, in the future the green electricity generation (wind, solar etc.) is expected to provide a decisive argument towards using a MW heating instead of gas-fired steam boilers (fossil fuel savings/no CO_2 emission).
Less CO_2 emission	No data available	See remarks concerning energy above.
Cost savings	No industrial data so far, however can be substantial (> 50%)	Cost savings can result from: • Faster processing (shorter batch times, 5-fold reduction in batch processing time reported for

		the only commercial application known) • Smaller equipment volume/capacity ratio • Higher product yield (see further) • Catalyst saving (see further) • Better product quality (see further) • Less maintenance (e.g. due to less fouling)
Increased yield/selectivity	Up to ca.10%	In specific cases. Much faster heating-up leaves less room for side-reactions to take place.
Increased safety	No data available	Safety increase can result from: • Smaller inventory of chemicals in equipment • Possibility of instantaneous cut-off of the heat supply by switching off the microwave, in case of possible overheating/runaway conditions
Fouling prevention	No data available	Contrary to the conventional heating by conduction, the volumetric MW heating creates no temperature gradients and uses no heat-exchange surfaces, which should lead to reduction of fouling.
Catalyst savings	Up to 100%	In some cases catalyst can be totally eliminated, as it is in case of the Sairem plant – see further)
Better product quality	No data available	MW creates a uniform temperature in the whole volume of processed liquid (no gradients). Uniform reaction conditions may lead to a better product quality.

1.4 Stage of development

Contrary to other microwave applications like drying, sintering of materials, polymer processing or heterogeneous catalysis (see other Technology Reports), microwave reactors for liquid-phase reactions are still basically in the laboratory phase of development. Several vendors (see further) offer laboratory-scale microwave reactors, both monomode and multimode, batch as well as continuous. Some university groups, such as University of Jena (Germany) have pilot-scale set-ups, with processing capacities of e.g. 25 l/hr. So far, only one commercial-scale microwave reactor has been announced (see further).

2. Applications

2.1 Existing technology (currently used)

(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)

Vast majority of batch non-catalytic or homogeneously catalyzed liquid-phase reactions are carried out in stirred-tank reactors with heating/cooling jackets and/or coils. Continuous processes are usually carried out in stirred-tank reactors in-series or in tubular flow reactors. Depending on process temperature various heat transfer media are applied, such as steam or mineral oils.

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

So far, only one commercial application of the microwave reactors has been reported, in the specialty chemicals & pharma sector.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity /Plant size	Year of application	Reported effects
Specialty chemicals & pharma	BioEurope, Sairem and De Dietrich/Laurydone	microwave generator on a batch recycle reactor	Reactor size: 1 m^3	2003	• 40% less energy; • 5 times shorter processing time; • Catalyst totally eliminated

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

No demonstration projects on microwave reactors for non-catalytic and homogeneously catalyzed liquid-phase reactions are known.

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Aimed year of application	Reported effects
				•

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

The literature concerning the enhancement effects of the microwaves on chemical reactions, homogeneous liquid-phase organic reactions in particular, is exceptionally rich. Since the original articles of Gedye et al. (1988) hundreds of research papers have been published and there exist several good reviews on this subject (Lidström et al., 2001, Hayes, 2002, Larhed et al., 2002, Kappe, 2004). However, the research in this field has been so far dominated by organic chemists and therefore the focus of the papers is clearly on the synthesis side and on the applications. Microwave effects have been reported in the following classes of chemical reactions:

- Acylations
- Alkylations
- Aromatic and nucleophilic substitutions
- Condensations
- Cycloadditions
- Deprotection and protection reactions
- Esterifications and transesterifications
- Heterocyclization
- Organometallic reactions

- Oxidations
- Rearrangement reactions
- Reductions.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Engineering & design concepts for commercial-scale devices	MW reactors have been developed on the laboratory scale, so far. New design concepts are needed of commercial-scale continuous flow reactors, which would also address the issues of energy efficiency, low penetration depth of the microwave (integrated mixing devices?) and the way of irradiation. This may need the development of new geometries of magnetrons as well. Also, materials issues are of importance here (reactor walls and elements transparent to the MW, etc.)	R&D projects carried at the universities, in collaboration with equipment manufacturers and producers of industrial-scale magnetrons
Modeling and scale-up methodologies	Research in the field of MW reactors was almost entirely dominated by the organic chemists and attracted only very little attention of chemical engineers, so far. Robust and reliable mathematical models of the microwave reactors have to be developed, together with the scale-up methodologies for those devices.	R&D projects carried at the universities, in collaboration with equipment manufacturers and producers of industrial-scale magnetrons
Control systems for commercial-scale MW reactors	Proper control of the chemical reactions carried out in the MW reactors is of crucial importance for the reliability and safety of the operation. In most cases the MW generator has to be used in and intermittent way, to avoid overheating and possible temperature runaways.	R&D projects carried at the universities, in collaboration with MW equipment vendors

3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Small irradiation depth of the microwave	The irradiation depth of the microwave in water medium does not exceed 2 cm. This brings an important question concerning the maximum production capacity achievable in a microwave	This challenge should be addressed in the R&D projects on engineering & design concepts for

versus the required scale of production	reactor. To illustrate the issue: in a single-tube flow reactor of 3 cm I.D. operating at 0.5 m/s liquid flow velocity, the maximum production capacity could reach ca. 10,000 t/year. Possible (partial) solutions to this problem could be for example: integrated intensive mixing devices in larger diameter tubes (to renew the irradiated liquid layer continuously) or multitube reactor designs.	commercial-scale MW reactors (pos. 1 in Table 4).
Narrow applicability of microwaves in terms of the type of media used in the process	MW are only applicable to the liquids with specific dielectric properties, containing dipoles and/or ions. In other systems introduction of an extra MW-sensitive solvent or a MW-absorbing solid phase can be considered	Feasibility studies at the end-user for each specific case
Limitations related to the constructional materials of MW reactors	Tubes in MW flow reactors have to be made of materials transparent to the microwave radiation, which excludes metals as constructional materials. This may put constrains on the conditions, in which such reactors can be applied on industrial scale.	This challenge should be addressed in the R&D projects on engineering & design concepts for commercial-scale MW reactors (pos. 1 in Table 4).
Safety	Operations involving microwaves require certain safety precautions as MW irradiation is dangerous for the human health. Current technology of MW ovens enables a fully safe use of these devices.	Process development has to involve the vendors of the MW-devices.

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L. and Rousell, J., 1986, The Use of Microwave Ovens for Rapid Organic Synthesis, Tetrahedron Letters, 27 (3), 279-282	Research paper	First paper in the field
Jacob, J., Chia, L. H. L. and Boey, F. Y. C., 1995, Thermal and non-thermal interaction of microwave radiation with materials, J Materials Sci, 30, 5321-5327	Review	
Lidström, P., Tierney, J., Wathey, B. and Westman, J., 2001, Microwave assisted organic synthesis – a review, Tetrahedron, 57, 9225-9283	Review	Extensive chemical overview of the MW-enhanced reactions
Howarth, P. and Lockwood, M., 2001, Come of age, tce, 756, 29-31	Review	
Perreux, L. and Loupy, A., 2001, A tentative rationalization of microwave effects in organic synthesis according to reaction medium, and mechanistic considerations, Tetrahedron, 57, 9199-9223	Review	Non-thermal MW effect postulated

Loupy, A. (ed.), 2002, Microwaves in Organic Synthesis, Wiley-VCH Verlag GmbH, Weinheim, Germany,	Book	
Kuhnert, N., 2002, Microwave-Assisted Reactions in Organic Synthesis – Are There Any Nonthermal Microwave Effects?. Angew Chem Int Ed, 41 (11), 1863-1866	Review	Purely thermal MW effect postulated
Hayes, B. L., 2002, Microwave Synthesis – Chemistry at the Speed of Light, (CEM Publishing, Matthews, NC, USA)	Book	
Larhed, M., Moberg, C. and Hallberg, A., 2002, Microwave-Accelerated Homogeneous Catalysis in Organic Chemistry, Acc Chem Res, 35 (9), 717-727	Review	Chemical overview of the MW-enhanced reactions
Nüchter, M., Ondruschka, B. and Gum, A., 2004, Microwave assisted synthesis – critical technology overview, Green Chem, 6, 128-141	Review	
Kappe, C. O., 2004, Controlled Microwave Heating in Modern Organic Synthesis, Angew Chem Int Ed, 43, 6250-6284.	Review	Extensive chemical overview of the MW-enhanced reactions; purely thermal MW effect postulated
De la Hoz, A., Díaz-Ortiz, A. and Moreno, A., 2004, Microwaves in organic synthesis. Thermal and non-thermal microwave effects, Chem Soc Rev, 34, 164-178	Review	Thermal and non-thermal effects of MW postulated
Tierney, J. P., Lindström, P. (Eds), 2005, Microwave assisted organic synthesis, Blackwell, Oxford	Book	

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
WO 97/13137: Microwave assisted chemical process	CEM Corporation	
US 6455317: Method of controlling a chemical process by microwave radiation	CEM Corporation	
US 6649889: Microwave-assisted chemical synthesis instrument with fixed tuning	CEM Corporation	
US 6713739: Microwave-assisted chemical synthesis instrument with fixed tuning	CEM Corporation	
WO 03/089133: Microwave-assisted synthesis instrument with controlled pressure release	CEM Corporation	
US 6403939: Microwave apparatus and methods for performing chemical reactions	Personal Chemistry I Uppsala AB	
US 6614010: Microwave heating	Personal Chemistry I	

apparatus	Uppsala AB	
EP 1521501: Microwave heating device	Personal Chemistry I Uppsala AB	
WO 2004/054707: Method and apparatus for control of chemical reactions	Personal Chemistry I Uppsala AB	
WO 2004/054705: Microwave heating system	Personal Chemistry I Uppsala AB	

All the above listed patents concern lab-scale microwave reactors.

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

No institutes or companies are known to work specifically on the development of microwave reactors for production purposes. In Table 8 some research groups carrying out research on MW-assisted non-catalytic or homogeneously catalyzed reactions are listed.

Table 8. Institutes and companies working on the technology

Institute/Company	**Country**	**Remarks**
Friedrich Schiller University Jena (Prof. B. Ondruschka)	Germany	Broad range of research activities, including scale-up issues
University of Graz (Prof. O. Kappe)	Austria	Focus primarily on the synthesis with MW
University of York (Prof. J. Clark)	UK	Focus on green synthesis
Université de la Réunion, Saint Denis (Prof. F. Chemat)	France	Focus on mechanisms behind MW effects
Universidad de Castilla La Mancha (Prof. A. De la Hoz)	Spain	Focus on mechanisms behind MW effects

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

No suppliers of commercial-scale MW reactors are known. Manufacturers of laboratory MW reactors and manufacturers of large-scale microwave equipment for other operations (drying, heating, sintering, etc.) can be seen as potential stakeholders here. Some of these manufacturers are listed in Table 9.

Table 9. Supplier and developers

Institute/Company	**Country**	**Remarks**
CEM Corporation	U.S.A.	World's biggest developer and manufacturer of microwave reactors for laboratory applications (both monomode and multimode, batch and

		continuous)
Milestone	Italy	Manufacturer of microwave reactors for laboratory applications (both monomode and multimode, batch and continuous)
Biotage (formerly Personal Chemistry)	Sweden	Manufacturer of microwave reactors for laboratory applications (multimode, batch), mostly for synthetic, analytical and medicinal chemistry.
Anton Paar	Austria	Offers one type of multimode batch MW reactor for organic synthesis
Plazmatronika	Poland	Offers one type of multimode batch MW reactor for organic synthesis; also manufacturer of commercial-scale MW dryers
Hitec Engineers Pvt.	India	Manufacturer of commercial MW dryers
Industrial Microwave Systems, LLC	U.S.A.	Manufacturer of commercial MW dryers and cylindrical heating systems
Püschner GmbH	Germany	Manufacturer of commercial MW dryers
Advanced Manufacturing Technologies (AMT)	Australia	Manufacturer of commercial MW furnaces for sintering
Linn High Term GmbH	Germany	Manufacturer of laboratory double-frequency MW ovens
Microdry Inc.	U.S.A.	Manufacturer of commercial MW ovens for drying and tempering

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Potential group of end users includes companies operating in the fine chemical & pharmaceutical sector, as well as some manufacturers of the consumer products.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Microwave reactors for non-catalytic and homogeneously catalyzed reactions present a promising technology for niche applications in the fine chemical/pharmaceutical and consumer product sectors, in small-to-medium scale processes. The technology remains in an early stage of development and an interdisciplinary R&D effort is needed in order to arrive at significant number of commercial applications. With such an effort industrial-scale MW reactors could be developed and implemented within next 5-10 years. On the long term, with the further growth of green electrical energy generation, this technology may become a heating method of choice for small-to-medium scale chemical processes, superior to the natural gas-based steam heating in terms of the fossil fuel usage and CO_2 emission.