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EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Microwave Reactors for Heterogeneously Catalyzed Chemical Processes

TECHNOLOGY CODE: 3.3.3.4.2

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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 heterogeneously catalyzed reactions and increase in the product yield is usually reported.

The discussion about how the highly polarizing radiation of microwaves influences chemical reactions in heterogeneous catalysts is still going on. Several mechanisms are postulated in the literature:

1. Temperature difference between reactants and the catalyst (reactants colder than the catalyst)
2. Higher temperature of catalyst nano-particles than that of the support (support colder than nano-particles)
3. Spatial hot-spots in catalyst beds (due to inhomogeneity of microwave field)
4. Arcing and plasma formation within catalyst

1.2 Types and “versions”

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

No specific types of the microwave reactors for heterogeneously catalyzed reactions have been developed so far, neither on industrial nor laboratory scale.

In the laboratory heterogeneous catalytic reaction are usually carried out in standard microwave reactors, two basic types of which 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).

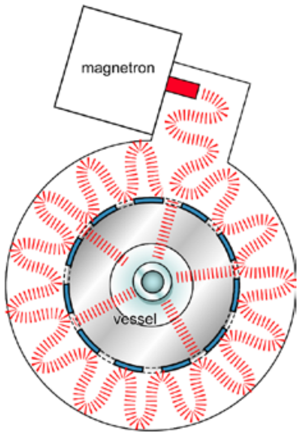

Fig. 1. CEM monomode microwave reactor

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	No exact data, can be substantial (>50%)	Overall energy savings can only be expected in the following cases: • Low-temperature instead of high-temperature processes • Selective heating (e.g. only catalyst particles are heated) • Better yield/selectivity (energy savings in downstream processing) 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 • Higher product yield (see further) • Catalyst saving (see further)

Increased yield/selectivity	Up to ca. 3 times	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
Catalyst savings	No data available	Higher yield save amount of catalyst needed. Lower temperatures save catalyst lifetime.

1.4 Stage of development

Contrary to other microwave applications like drying, sintering of materials or polymer processing, microwave reactors for heterogeneous catalytic reactions are still basically in the laboratory phase of development. Although microwaves have been reported to be used on the commercial scale in the Fluid Catalytic Cracking (see further), their role there is limited to quickly heating-up of the circulating catalyst.

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.

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 heterogeneously catalyzed liquid-phase reactions are carried out continuously operated fixed-bed (gas and liquid), fluidized-bed (mostly gas) or slurry (liquid) reactors.

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 irradiation in relation to heterogeneous catalytic process has been reported. Coastal Catalyst Technology Inc. (Houston, TX) developed a continuous fluid-bed reactor using microwave energy to quickly heat-up and oxidize the cracking catalyst from 25 to 850^{o}C. Here, 150 kW of microwave energy is used to heat and reactivate a 300 kg/hr flow of catalyst, with a resident charge of 2000 kg of catalyst. The technology has been applied at Eagle Point Oil Refinery in New Jersey.

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
petchem	Eagle Point Oil Refinery	Fluid Catalytic Cracking - MW used to heat-up and reactivate the catalyst	300 kg/hr catalyst flow	1999	•

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)

Applications of microwaves in heterogeneous catalysis should primarily be sought in endothermic processes.

The literature concerning the enhancement effects of the microwaves on heterogeneously catalyzed chemical reactions is much more limited than one concerning the homogeneous organic processes.
Microwave effects have been investigated in the following reactions:

<u>Decomposition of hydrogen sulfide</u>
Here a substantial conversion increase due to an apparent “shift” in the equilibrium constants has been reported (Fig. 2 - Zhang, et al., 1999). The observed shift was explained by a much higher temperature at some sites in the catalyst than the temperature measured.

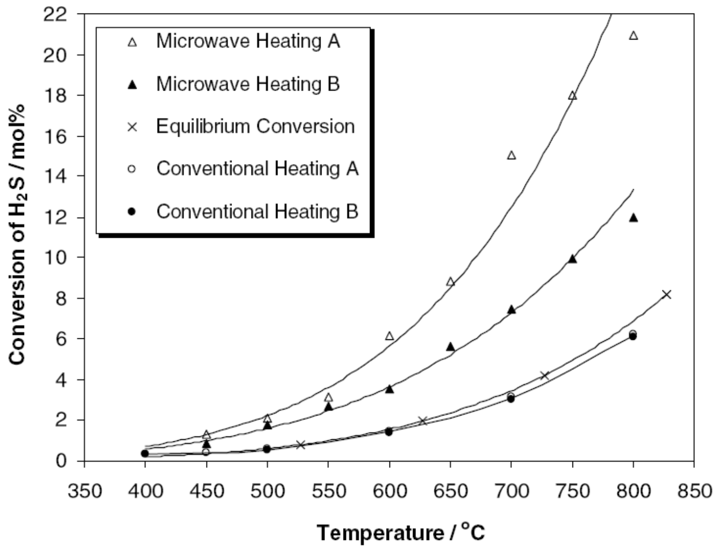

Fig. 2. Influence of microwaves on decomposition of hydrogen sulfide

<u>Reduction of SO_2 with methane</u>
Also here substantial differences in the achieved conversions with MW and with conventional heating have been observed (Fig. 3 – Zhang et al., 2001).

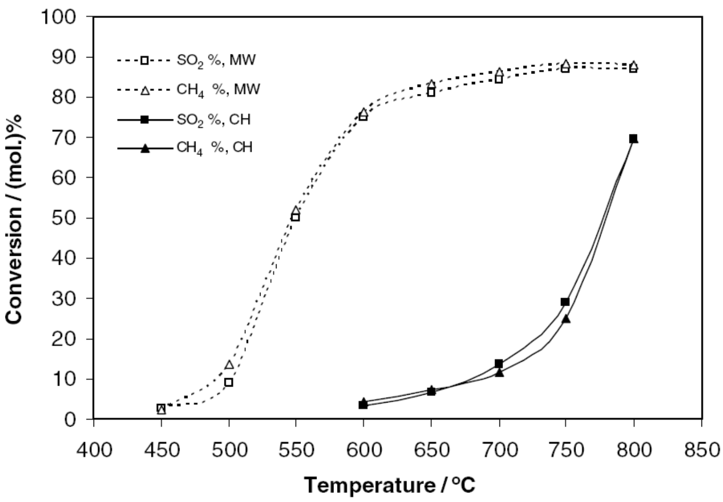

Fig. 3. Microwave effect on reduction of SO_2 with methane (MW-microwaves, CH – conventional heating).

<u>Reforming reactions</u>
In reforming of methane with carbon dioxide, especially in lower temperature range microwave heating delivered much higher conversions than the conventional one (Fig. 4 – Zhang et al., 2003a). Yanguas-Gil et al. (2004) report on microwave-induced non-catalytic reforming of ethanol at room temperature. The thermal efficiency is increased dramatically here by the plasma discharge induced by microwaves. Also reforming of methanol (Lee Perry et al., 2002) and hexane (Sekiguchi and Mori, 2003) were investigated.

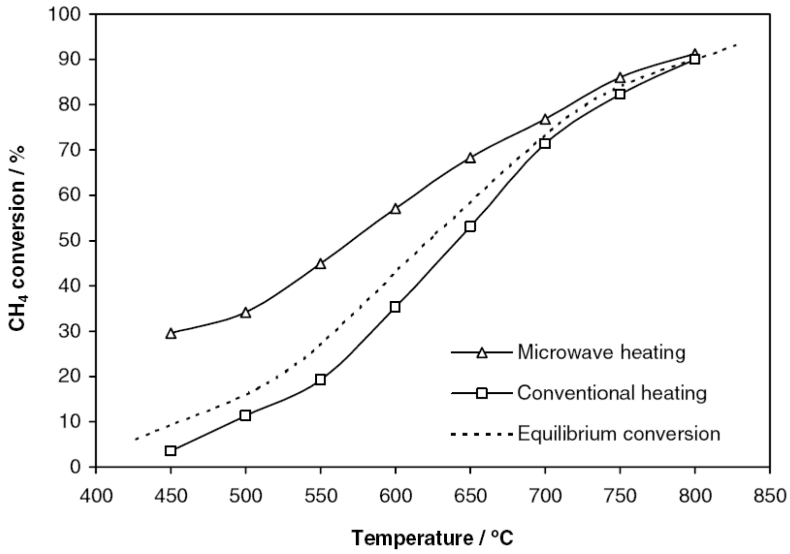

Fig. 4. Microwave effect on methane reforming with CO_2.

Hydrodesulfurization of tiophene
In this exothermic process no substantial effects of microwaves upon tiophene conversion were observed (Zhang et al., 2003b).

Oxidative coupling of methane to higher hydrocarbons
With microwaves similar conversions have been obtained at ca. 200^{o}C lower temperature than with conventional heating (Fig. 5 – Zhang et al., 2003c). The effect is explained by arcing and the formation of CH_4 plasma.

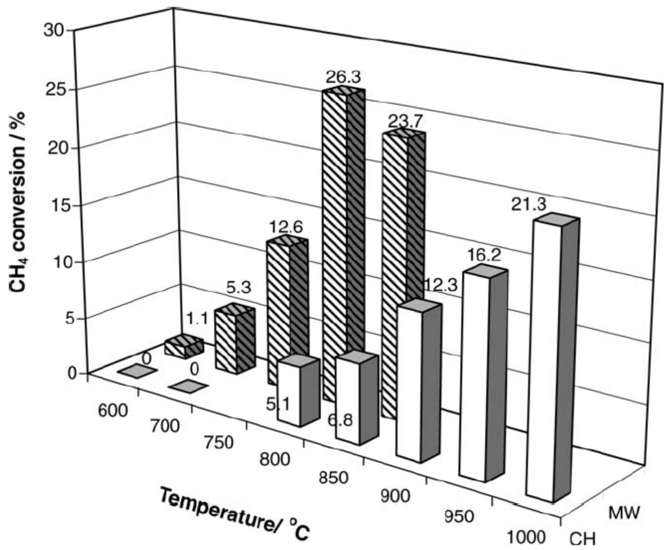

Fig. 5. Microwave effect on oxidative coupling of methane.

Esterification reactions
In heterogeneously catalyzed esterification reactions carried out with MW-assistance up to 15% higher product yields than in conventional heating were observed (Chemat, et al., 1998)

Isomerization reactions
Seyfried et al. (1993) reported a 1.3-2 fold selectivity increase in isomerisation of hexanes on alumina-supported platinum catalyst.

Other applications discussed in the literature include selective hydrocarbon oxidations, dehydrogenations and NO_x decomposition.

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. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) 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 <u>new geometries of magnetrons</u> as well. Also, <u>materials issues</u> 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 versus the	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 reactor. To illustrate the issue: in a single-tube	This challenge should be addressed in the R&D projects on engineering & design concepts for commercial-scale MW

required scale of production	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.	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.
Control	Proper control of microwave-operated reactors is of key importance not only to the safety of operation (overheating, runaways, etc.), but also to their energetic efficiency.	Reliable models, control policies and devices have to be developed for the on-line control of microwave reactors in continuous operation.

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
X. L. Zhang, et al., 1999, Chem. Commun., 975	Research paper	
X. L. Zhang, et al., 2001, Appl. Catal. B., 33, 137	Research paper	
X. L. Zhang, et al., 2003a, Catal. Lett., 88, 129	Research paper	
X. L. Zhang, et al., 2003b, Catal. Lett., 88, 33	Research paper	
X. L. Zhang, et al., 2003c, Appl. Catal. A, 249, 151	Research paper	
X. L. Zhang and D. O. Hayward, 2006, Inorg. Chim. Acta, 359, 3421	Review paper	
F. Chemat, et al., 1998, J. Microwave Power Electromagnetic Energy, 33, 88	Research paper	
A. Yanguas-Gil, 2004, Appl. Phys. Lett., 85, 4004	Research paper	
W. Lee Perry, 1997, Catalysis Letters, 47, 1	Research paper	Internal temperature gradients in catalyst insignificant
W. Lee Perry et al., 2002, AIChEJ, 48, 820	Research paper	

H. Sekiguchi and Y. Mori, 2003, Thin Solid Films, 435, 44	Research paper	
L. Seyfried, et al., 1994, J. Catal., 148, 281	Research paper	
H. Will, et al., 2004, Chem. Eng. Technol., 27, 113	Review paper	

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 apparatus	Personal Chemistry I 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 catalytic 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 Hull (Dr. X. L. Zhang)	U.K.	Focus on heterogeneous catalysis with MW
Delft University of Technology (Prof. A. Stankiewicz)	The Netherlands	Focus on reactive separations, microsystems, scale-up

5. Stakeholders

5.1 Suppliers and developers

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

No suppliers of commercial-scale MW catalytic 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 petrochemical, bulk-chemical and fine-chemical sectors.

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Microwave reactors for heterogeneously catalyzed reactions present a still largely unexplored but promising technology for various applications in chemical manufacturing. Mostly applications in the endothermic processes, such as cracking or reforming can be expected. The technology remains in an early stage of development and a substantial 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 10-15 years.

Also, important applications of microwave-assisted catalytic reactors beyond the chemical industry, for instance in distributed/mobile hydrogen production via reforming for automotive or energy applications, can be expected.