European Roadmap of Process Intensification

- Technology Report -

Technology: Monolithic Reactors

Technology Code:

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1. Technology

1.1 Description of technology / working principle

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

Catalysis is one of *the* enabling technologies for Process Intensification in the (petro-) chemical production plant (and in many processes protecting the environment) . New catalysts enable more efficient routes and, associated herewith, more compact plants operating at higher efficiency and production of lower amounts of waste. Intimately connected with a satisfactory catalyst is the reactor, housing the catalyst.

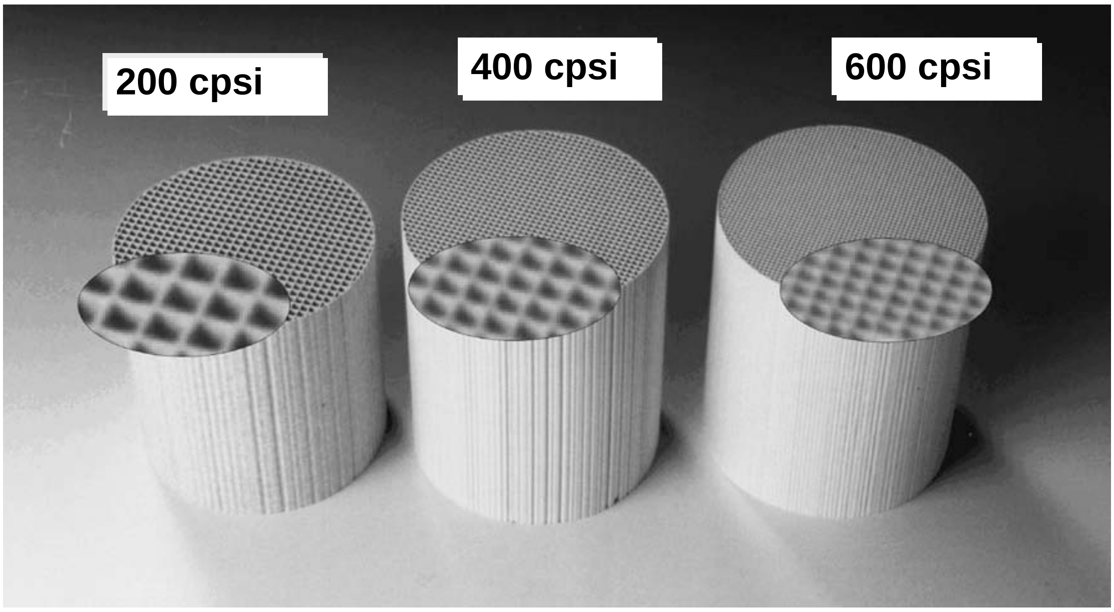
Catalytic reactors roughly can be divided in random and structured reactors.
Apart from high activity, reactors can be judged according to

- catalyst quality on a microscopic length scale (quality, number of active sites),
- catalyst quality on a mesoscopic length scale (diffusion length, loading, profiles),
- ease of catalyst separation and handling,
- heat supply and removal,
- hydrodynamics (regimes, controllability, predictability),
- transport resistance (rate and selectivity).
- safety and environmental aspects (run-aways, hazardous materials, selectivity),
- scalability
- costs

Although in chemical production industry usually random packed bed or slurry reactors are used with respect to many of these criteria they often are inferior to structured reactors. A monolith is the most applied structured catalytic reactor, see Fig 1. Dependent on the point of view it can be considered to be a reactor or a catalyst: the borders between catalyst and reactor vanish.

Monolithic reactors offer high precision, high control and decoupling of hydrodynamics and particle size. As a consequence, high selectivity can be reached and energy can be saved (for so-called Taylor flow conditions) while mass transfer *increases*. The latter is striking as in PI much work is presented aiming at maximizing energy dissipation expecting that this will lead to increased mass transfer and, as a consequence, intensified processes. The explanation is that in monoliths the flow pattern is laminar and there is no sense in trying to increase turbulence by dissipating more energy. Two phase laminar flow leads to higher mass transfer than conventional turbulent contactors. In fact, mass transfer under Taylor flow conditions is increased by reducing the energy dissipation.

Because the production reactor is essentially identical to the bench scale reactor scale-up is easy (provided good inlet/ outlet design).



1890 **2740** **3440**

Fig 1. Typical examples of monolithic catalysts with different cpsi (cells per square inch). The numbers below the monoliths represent the volumetric surface area ($m^2_{geometric}/m^3_{reactor}$).

1.2 Types and "versions"

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

Monolithic catalysts can be produced by extrusion of support material (often cordierite is used, but various types of clays or typical catalyst carrier materials such as alumina, titania etc. are also used), a paste containing catalyst particles (e.g. zeolites, V-based catalysts) or a precursor for the final product (e.g. polymers for carbon monoliths).

Alternatively, catalysts, supports or their precursors can be coated onto a monolithic support structure ('washcoating'). All major catalyst support materials, ceramic and polymeric, have been extruded as monolith. Metallic support structures (usually not produced by extrusion) are only used for automotive applications. The choice for a certain catalyst type will strongly depend on the balance between maximising the catalyst inventory and catalyst effectiveness. For slow reactions a high catalyst loading is desired and the pure catalyst-type monolith is desired, while for fast reactions or if diffusion is slow a thin coating with a maximum geometric area is preferred.

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
More compact reactors	2-10	Normalized to Reactor volume (ms gas phase reactors, multiphase (Taylor flow))
Higher selectivity in production	2-10	Plant size (Less separation)
Higher yields		Higher selectivity, higher conversion (finishing reactor)
Less waste	2	Less end-of-pipe
Higher throughput	2	Lower pressure drop, finishing reactor
Safer		Reduced risk of run-away
Energy savings	2-10	Lower pressure drop; good mixing at laminar conditions (Multi phase (Taylor flow))
More compact plants	2-5	Multifunctional reactors (catalytic distillation, ..)

1.4 Stage of development

Monoliths are industrially mainly produced by extrusion. Because of the enormous market in cars they are produced in very large numbers. This leads to the attractive situation that, although they are sophisticated structures, the standard systems are robust structures and they are commercially available at reasonable costs. It should be noted that when a specific type is desired an extensive development program might be unavoidable.

It is useful to distinguish between the following (potential) areas of application;

1. Gas phase systems
    a. Cleaning of exhaust gases (three-way catalysts, diesel gas cleaning systems, de-NOx in power plants, oxidation VOCs, etc)
    b. Catalytic postreactors (ammonia oxidation, phthalic anhydride production, ..)
    c. Production at ms time scales (syngas, HCN, olefins via oxidative dehydrogenation, etc)
2. Multiphase systems
    a. Bulk chemicals (H_2O_2, hydrogenation Pygas, etc.)
    b. Fine chemicals (benzaldehyde hydrogenation, production amines, etc.)

The stages of development are extremely different for these sectors. For 1a monolithic reactors are state-of-the-art and 1b is already commercial, whereas for the multiphase systems, except for the large-scale commercial production of H_2O_2, the others are objects of increasing attention in academic and industrial research, but commercial applications are scarce.

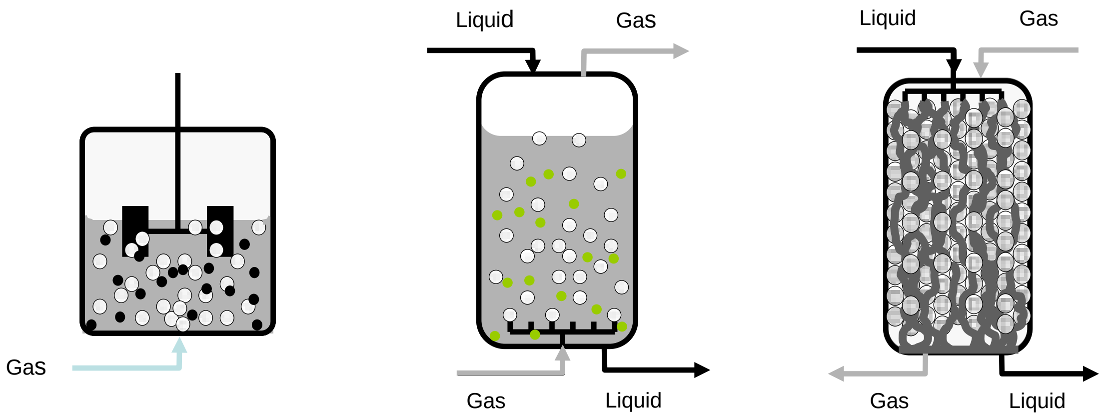
2. Applications

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)

Several types of reactors are in use in the chemical industry and in environmental control. Gas phase (catalyzed by solids) reactions are usually carried out in fixed bed reactors. For multiphase applications the slurry-type and fixed bed reactors are conventionally applied. Replacing slurry reactors by monolithic reactors has several advantages:

- Less pollution
    - Lower waste disposal
    - Lower loss of metals (catalyst)
- Less maintenance
- Much more compact



Slurry **Bubble Column** **Trickle Bed**

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)

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
Bulk chemicals	AKZO NOBEL	Hydrogenation step in anthraquinone H_2O_2 production	200 ktpy	early 1990s	
	Lurgi	Finishing reactor in Phthalic anhydride production	2 commercial plants	Ca 2000	Increased conversion
Fertilizer industry	Boreskov Institute of Catalysis Russian Nitric acid plants	Replacement of Pt gauses by base metal/ monolith systems	10 plants	Ca 2000	Less loss of Pt
Environmental	De-NOx (SCR)	Reduction with NH_3 or urea	Widely applied in	End 1970s	Works well

			power stations, etc		
	EmeraChem/ de-NOx	Catalytic absorption process	Stationary gas turbines	Some commercial applications	Works well, price an issue
	Exhaust purification Otto engines	3-way catalysis	Otto engines	End 70s	Very large scale
	Idem diesel	Abatement NOx, soot and HCs	Diesel engines	2000	

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.)

The interest in academia and industrial laboratories is large and increasing (see fig with publication/ patent numbers). Moreover the industry is not very open. Therefore, in table 3 only a (biased) selection is presented.

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
Bulk chemical industry	Haldor Topsoe	Methanol to folmaldehyde	now	Yield increase (96-99 %) at half the pressure drop
	TUD (CE)	Several multiphase hydrogenations		High selectvity, high rates
	TUD (CE) and University of Dortmund (Chem Eng)	Reactive stripping		
	Air Products/ Johnson Matthey	Hydrogenation nitroaromatics in the aniline production		Rather far developed process
Energy	Catalytica	Low NOx gas turbine	now	Demonstration success
Water treatment	Nippon Shokubai	Catalytic Wet Air Oxidation of waste water		Demonstrations successful

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)

Besides the above examples it is fair to draw the atrention to applications in the biotechnology and in water purification (bio or catalytic). These are often large-scale multiphase applications and monolithic reactors are an option.

In the fine chemistry big stirreed tank reactors are normally used. Monolithic loopreactors are an option for retrofitting.

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?
Catalyst availability	In replacing existing technology new catalysts have to be developed and produced	Cooperation industry (producers and technology providers) /academia
Catalyst loading	Catalyst loadings for reactors based on coatings are usually much lower than packed bed reactors; this does not apply to sluury reactro systems	Develop integrated extruded monolithic catalysts; standardization; select examples where catalsyt loading is not critical / industry and knowledgecenters
Price	Catalytic monoliths are more expensive than presently available catalyst powders	Standardization / idem
Stability	Often the orice is such that the catalytic monolith has to be used for a long time. This implies good stability and regenerability	
Experience in multiphase applications	New technology calls for development, in particular reactor design including in- and outlet.	Develop pilot processes/ industry and knowledge centers
Exothermal reactions	Most commercial monolithic structures are poor heat conductors.	Novel materials (based on metals) Other engineering, e.g. loop reactors
Safety	Monolithic reactors might be intrinsically safer than trickl bed reactors	Demonstration / engineering companies and knowledge centers

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)

In table 5 overlap with table 4 is avoided. It is not always clear if a certain aspect is an 'issue' or a 'challenge'.

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Production coated monoliths	Instead of applying commercially available (powdered) catalyst a dedicated coating has to be made with good activity, selectivity and stability	Produce standard catalytic monoliths. Knowledge centers & catalyst producers
Design scale-up reactors	The low pressure drop can result in mal-distribution. Inlet design critical. Reactors have to be packed with monolithic elements. What is optimal?	Computational efforts and experimental demonstrations. Knowledge centers and energy providers.
Selection of processes with the highest potential for monoliths	For a fast penetration in the chemical industry demonstrations will be most convincing.	Make evaluations n teams composed of scientists. Chemical engineers of knowledge centers and industry.

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
'Structured Catalysts and Reactors, eds A. Cybulski and J. A. Moulijn, WIley 2006	book	
'Multiphase monolithic reactors: Chemical reaction engineering of segmented flow in microchannels', M. T. Kreutzer, F. Kapteijn, J. A. Moulijn and J.J. Heiszwolf, Chem Eng Sci 60 (22) 5895-5916, 2005	Research/review	Co-current multiphase; Taylor flow
'Monolithic catalysts for nonautomotive applications', S. Irandoust and B. Andersson, Catal. Rev. Sci. Eng. 30, 341, 1988	review	
'Experimental and theoretical study of reactive stripping in monolithic reactors, I. Mueller, T. J. Schildhauer, A. Madrane, F. Kapteijn, J. A. Moulijn and E. Y. Kenig, Ind Eng Res 46 (12) 4149-4157, 2007	Research	Counter-current film flow reactor
"Catalytic Air Pollution Control: Commercial Technology', R. M. Heck and R. J. Farrauto, Wiley 2002	book	
'Development of a monolith-based process for H_2O_2 production: from idea to large-scale implementation', R. Edvinsson Albers, , M. Nyström, M. Siverström, A. Sellin, A. -C. Dellve, U. Andersson, W. Herrmann and Th. Berglin Catalysis Today, Volume 69, Issues 1-4, 15 September 2001, Pages 247-252	research	Treats (carefully) process development H_2O_2 production
'Mathematical models of cataluytic combustors', G. Groppi, E. Tronconi and P. Forzatti, Catal. Rev. Sci. Techn. 41, 227, 1999	review	

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.)

In the field of monoliths a very large number of patents have been applied for. In the following figure the numbers of publications (in five years intervals) together with the patents are given. The large numbers and the fact that many are very recent make it impossible to give an evaluation withour spending considerable time in analysis. Therefore it was decided not to fill in the table.

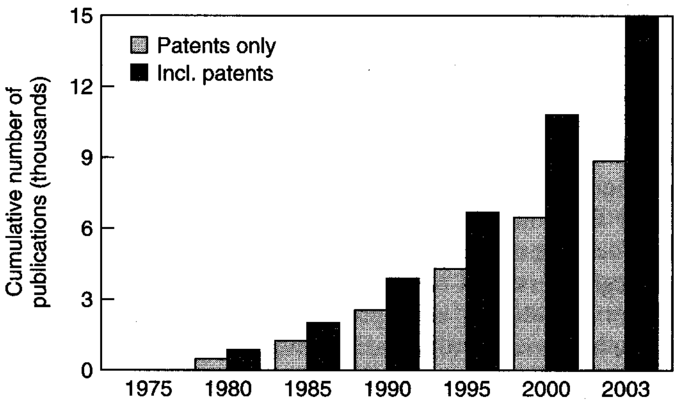


Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
n.a.	n.a.	n.a.

4.3 Institutes/companies working on the technology

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

From the large numbers of patents and publications it will be clear that the number of groups working in the field is enormous. Table 8 contains a list selected accoding to a personal taste.

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Corning	USA	Market leader for three way catalytic converters Have been very active in development
Boreskov Institute of Catalysis	Russia	Inventor, process developer
Akzo Nobel, Eka Chemicals	Sweden	Inventor and user
Johnson Matthey	UK	In earlier stage JM/AP cooperation
Air Products	US	In earlier stage JM/AP cooperation
Catalysis Engineering, TUD	The Netherlands	Mainly multiphase
Dip de Chimica, Politécnico di	Italy	Mainly gas phase

Milano (Tronconi)		
BASF (Engelhard)	Germany, US	Catalyst producer

5. Stakeholders

5.1 Suppliers and developers

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

In the industry a lot of development takes place. It is neither useful nor possible to list them all. Moreover, because the technology is relatively new industry treats it as confidential. Therefore in table 9 only the major companies are listed.

Table 9. Supplier and developers

Institute/Company	Country	Remarks
Corning	US	
NGK	Japan	
Boreskov Institute of Catalysis	Russia	
BASF (Engelhard)	German	
Johnson Matthey	UK	
MAST	UK	Small company developing and selling carbon monoliths

5.2 End users

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

In biotechnology large-scale multiphase reactors are applied. The same applies for waste water treatment,

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

The technology has proven itself for gas phase cleaning catalytic reactors. In other applications this is not the case, although from a theoretical analysis they are quite promising.

Hurdles are:

- Lack of experience
- Price of catalytic systems and, associated herewith, stability and regenerability
- Availability of catalytic monolithic reactors, in particular in the fine chemistry
- In the case of coated monoliths low catalyst load; this is in particular important for the bulk chemistry and refineries

Catalyst production and standardization should be given a lot of attention. In particular for the fine chemistry in-hous development is nearly impossible. For industry here is a market. For instance why not offering a set of cartridges containing standardized monoliths?