

EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:

Millisecond (gauze) reactors

TECHNOLOGY CODE:

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1. Technology

1.1 Description of technology / working principle

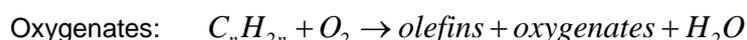
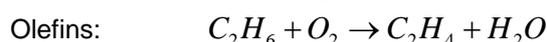
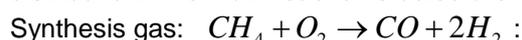
(Feel free to modify/extend the short technology description below)

The concept of catalytic reactions over metallic gauzes at millisecond contact time has been known for decades. Three processes are of actual industrial importance:

- the ammoxidation of methane to form HCN (Andrussov process), Pt/10%Rh gauze
- the oxidation of NH₃ to NO as the first step of nitric acid production, Pt/10%Rh gauze
- the partial oxidation of methanol to formaldehyde, Ag-crystals, short packed bed

These applications have been operated for decades at large scale and have been optimized for safe, efficient and reliable operation. Although the experiences concerning engineering and safety issues might be of interest, these well established industrial processes will not be further discussed in this technology report.

More recently, Schmidt and coworkers (Hickman and Schmidt, 1992, Huff and Schmidt, 1993) suggested the use of millisecond reactors for the catalytic partial oxidation (CPOX) of alkanes at high temperatures, and reported on the effect of very short contact times on the product distribution. The main reaction studied are:



The working principle of the millisecond reactor can be described using a two-zone model: A fuel rich gas feed is passed over a (structured) oxidation catalyst at contact times between 0.5s and 0.5ms. The reactor works under near adiabatic conditions and reaches 800 to 1000°C depending on the feed composition and the product distribution. Mainly short monoliths or metal gauzes are used.

After ignition of the reactor, the reactants are rapidly heated within ca.100µs by the highly exothermic total oxidation of a part of the feed. The maximum temperature near the reactor entrance usually reaches 1000-1200°C, depending on feed composition and initial temperature, type and structure of the catalyst as well as gas velocities and flow patterns. Oxygen is consumed in this hot zone near the entrance. Within the following part of the reactor decomposition of the remaining alkanes and/or reaction of products with fuel molecules and/or with water occurs.

Transformation rates are generally high enough to achieve high conversions at millisecond contact times.

Product selectivities have been shown to depend on active metal type, catalyst structure, feed composition and temperature as well as reaction pressure. It is interesting to note that in many cases maximum product yields are achieved for C/O feed ratios at or near the reactions' stoichiometric values.

To which extent heterogeneous catalytic reactions in the second zone of the reactor contribute to the final product composition is still subject to discussion. While in some cases the formation of products others than CO₂ and H₂O were ascribed to purely homogeneous pathways (Schmidt, 2000), recent results (e.g. Quiceno et al., 2007) indicate that the contribution of heterogeneous catalytic reactions can not be neglected.

Since the initial publications mentioned above, considerable efforts have been dedicated to various millisecond reactor applications. With the emerging issues of mobile hydrogen production for fuel cell applications and the industrial use of stranded natural gas resources, most recent research has focused on synthesis gas and H₂ production from methane and renewable feedstocks as ethanol or biodiesel.

1.2 Types and “versions”

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

The performance of millisecond reactors is strongly influenced by the catalyst geometry and its composition, the temperature profile over the catalyst, and the gas flow pattern. Mainly Pt or Pt/Rh is used as catalyst. Two general types of catalyst geometries are dominant in the literature:

Structured ceramic supports:

Structured ceramic supports are generally used in the form of ceramic foams or honeycomb monoliths with bed lengths in the range of 1-5 cm. In spite of their relatively low thermal stability at temperatures above 1000°C and at fast temperature variations, foams are generally preferred due to their favorable radial mixing characteristics.

Usual active metal loadings on the ceramic supports are around 0.1–20 wt%, ranging from highly dispersed particles to continuous films. For the majority of applications one or more noble metals as catalytically active phase are used.

Temperatures over the reaction zone inside the monolith stay above 900°C, the oxygen is generally completely consumed inside the catalytic structure.

Single metal gauzes:

Gauzes and similar structures like cloths and felts usually consist of bulk catalyst metal or alloys. In the case of noble metal catalysts, considerably high catalyst costs as compared to supported catalysts on ceramics result. The pressure drop characteristics of gauze structures are comparable to those of ceramic foams. The thermal stability of gauze catalysts exceed that of ceramic monoliths. Severe conditions of temperatures around 1500°C and fast temperature variations are possible without destruction or deactivation.

In partial oxidation processes over single gauze layers, part of the reactant gas is rapidly heated on the gauze surface and quenched directly downstream of the gauze by cold gas bypassing the catalytic wires. Most of the oxygen is consumed by homogeneous (mainly radical) reactions downstream the catalyst layer.

An alternative way to distinguish different millisecond reactor versions is the way in which the extremely high reaction rates necessary to reach high conversions in milliseconds are realized. The majority of applications discussed in the literature is based on the total oxidation of a small fraction of the feed to generate temperatures around 1000°C. A more efficient use of the generated heat can be achieved in a short reverse-flow reactor. Neumann and Vesper, 2005, observed a high selectivity to syngas at even shorter contact times compared to adiabatic systems. This allows a further process intensification at comparable product yield. Another way to achieve high conversions in milliseconds at lower temperatures (<100°C) is the use of alternative energy like non thermal plasma in combination with catalysts. This technology has been recently suggested for the production of hydrogen from H₂S (Subramanyam et al, 2007) using catalytic filters in a cross-flow setup.

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; CO₂ 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
Cost savings		Considerable savings both in investment and operational costs are expected from millisecond reactor applications. They can result from: <ul style="list-style-type: none">– Higher productivity per reactor volume as compared to existing technologies– Catalyst savings due to increased catalyst stability and productivity at high reaction-temperatures– Process flexibility concerning production rates without decrease in product yield– Favorable product distribution
Catalyst stability	n.a.	Due to the high reaction temperature of many applications, catalyst poisoning (e.g. S poisoning of noble metals) is effectively avoided.
Catalyst savings	Substantial, possibly 1-2 orders of magnitude	Industrial Catalysts for oxidation reactions often contain expensive noble metals. Therefore, compact reactor design resulting from the extremely high reaction rates at temperatures around 1000°C lead to considerable reduction of the amount of catalyst used in the process

Process flexibility	n.a.	In contrast to (autothermal) stream reforming reactors, millisecond reactors display virtually constant conversion and product yields over a broad range of flow rates/contact times during the production of syngas and H ₂ from various alkanes
Easy scale up and scale down	n.a.	Millisecond reactors can be operated almost adiabatically in reaction volumes as small as 1cm ³ . Thus, variations in process scale are considered straightforward. In this context, special attention is given to small scale mobile applications like H ₂ production for automotive fuel cells.
Increased yield/selectivity		In the case of monoliths, intense convective heat transfer in the catalytic bed creates a more even axial temperature profile. As partial oxidations are favored by high temperatures, this can increase product yields in certain applications
Favorable product composition		CPOX of methane produces syngas with a H ₂ /CO ratio ideal for methanol synthesis. Costly recycle of H ₂ rich off-gas is avoided

1.4 Stage of development

While millisecond contact time reactor technology has been used in large scale processes for decades (see 1.1), applications concerning catalytic partial oxidations of alkanes are still in the laboratory phase. A limited number of pilot-scale projects are mentioned in the literature, but no commercial scale application has been announced so far.

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)

- The production of syngas as one of the most promising applications of millisecond reactor technology is currently based on steam reforming (SR) and autothermal steam reforming (ATR) of natural gas or naphtha as well as, to a smaller extent on non-catalytic partial oxidation processes, mainly in large scale applications.
- The complete production of olefins is currently based on steam cracking technology.

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)

Commercial scale applications of millisecond gauze or monolith reactors are limited to three well established processes:

- production of HCN (ammoxidation of methane)
- partial oxidation of NH₃ as the first step of nitric acid production (see 1.1).
- Partial oxidation of methanol to formaldehyde

All three technologies have been known for decades and will not be considered further in this report.

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
					•

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.)

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
syngas	EniTecnologie S.p.a. (Italy)	Syngas production by catalytic partial oxidation of various feedstocks at GHSV between 50,000 and 250,000h ⁻¹	no information	No information
Decentralized H ₂ -production	Coordinated by: Infracerv GmbH & Co KG, Höchst (Germany)	Multi-fuel station with a 50 Nm ³ /h on-site hydrogen production via catalytic partial oxidation of methane	2006	No information

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)

Various applications of millisecond reactor technology have been discussed in the literature, all of which are based on partial oxidation reactions:

- Synthesis gas production from methane, ethane and higher alkanes. Recently, research has extended on renewable sources, e.g. ethanol and bio-diesel
- Production of unsaturated hydrocarbons, namely ethylene, by catalytic dehydrogenation of various alkanes.
- Mixed oxygenates from various feedstocks
- H₂ and S^o from H₂S

Expected advantages of short contact time reactors for partial oxidation are

- the potential use of various refinery hydrocarbon streams including those with high aromatic and sulfur content
- the use of natural gas for the production syngas with a composition of H₂/CO=2, useful for low temperature Fischer-Tropsch synthesis, thus avoiding the recirculation of syngas.
- the realization of small and simple installations for hydrogen production for stationary fuel cell application

- Schmidt and coworkers did pioneering research work, coining the term “millisecond contact time reactors” in the process (Hickman et al, 1992; Huff et al, 1993) . By now, an extensive amount of research papers is available on the subject, especially concerning synthesis gas and H₂ production. However, the number of reviews focusing on millisecond reactor

technology is somewhat limited (Schmidt, 2000; Basini, 2005; Bharadwaj, 1995; Schmidt, 2000)

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 pilot- and commercial-scale devices	Product yields in millisecond reactor applications can increase considerably with the feed temperature. Different reactor concepts including regenerative heat integration have been demonstrated in the literature, reaching heat integration efficiencies up to 70% (Veser et al., 2000; Neumann and Veser, 2005). Engineering and design concepts will have to address this issue, e.g. by adapting reverse flow technology to industrial scale.	R&D projects on pilot scale carried out at universities, essentially in cooperation with equipment manufacturers
Scale-up methodology	Although scale-up of millisecond reactors is considered straightforward, surrounding equipment like feed preheaters and product separation units will have to be adapted to large scale production. One aspect of particular interest might be the question, as to which extent the millisecond reactor could be directly integrated into existing technology, e.g. for hydrogen production	R&D projects on pilot scale carried out at universities, essentially in cooperation with equipment manufacturers

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?
Influence of reaction pressure on conversion and yield	Product yields in millisecond reactors can decrease considerably with increasing reaction pressure. This is generally explained by the increasing influence of non-selective homogeneous reactions. However, the industrial application of millisecond reactor technology depends on the possibility of running the reaction at higher pressure.	As laboratory experiments at high pressures are limited due to safety and costs, this challenge should be addressed in R&D projects on the pilot plant scale

Thermal catalyst and support stability	Maximum catalytic bed temperatures e.g. in the combustion region of millisecond CPOX reactors may well exceed 1000°C. Notably the long term thermal stability of commercially available foam catalysts does not extend to these regions. This issue could be addressed by efficient temperature control, including adapted O ₂ -concentrations in the feed gas.	
Safety	Partial oxidation processes necessitate the formation of potentially flammable gas mixtures. Especially in large scale industrial applications this raises the issue of fast and efficient mixing of reactants.	

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
Goetsch D.A., Schmidt L.D., 1996, Microsecond catalytic partial Oxidation of Alkanes, Science 271, 1560-1562	Research paper	First paper on oxygenate production in millisecond gauze reactors
Schmidt LD, 2000, Millisecond Chemical Reactions and Reactors, Studies in Surface Science and Catalysis 130, 61-81	review	
Schmidt L.D., Siddall J, Bearden M, 2000 New Ways to Make Old Chemicals, AIChE Journal 46 (8), 1492-1495	review	Summary of work done on ethylene production in millisecond reactors
Hickman D.A., Schmidt L.D., 1992, Synthesis Gas-Formation by direct oxidation of methane over PT-Monolith, Journal of Catalysis 138, 267-282	Research paper	First paper on millisecond contact time effects
Basini L, 2005, Issues in H ₂ and synthesis gas technologies for refinery, GTL and small distributed industrial needs, Catalysis Today 106, 34-40	short review	
Bharadwaj SS, Schmidt LD, 1995, Catalytic partial oxidation of natural gas to syngas, Fuel Processing Technology 42, 109-127	review	
Quiceno R, Deutschmann O, Warnatz J, Pérez-Ramirez J, 2007, Catalysis Today 119, 311-316	Research paper	First 3-D simulation of methane-CPOX over metal gauze catalyst
Huff M, Schmidt LD, 1993, Ethylene Formation by oxidative Dehydrogenation of Ethane over Monoliths at Very Short Contact Times, J.Phys. Chem 97, 11815-11822	Research paper	
Neumann D, Vesper G, 2003, Catalytic Partial Oxidation of Methane in a High-Temperature Reverse-Flow Reactor, AIChE Journal 51 (1), 210-223	Research Paper	
Vesper G, Frauhammer J, Friedle U, 2000, Syngas formation by direct oxidation of methane Reaction mechanisms and new reactor type, Catalysis Today 61, 55-64	Research 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
US4940826: Process for the production of mono-olefins by the catalytic oxidative dehydrogenation of gaseous paraffinic hydrocarbons having two or more carbon atoms	BRITISH PETROLEUM CO PLC (GB)	
WO9613475: Catalytic Oxidative Dehydrogenation Process	UNIV MINNESOTA (US)	
US5648582: Gas-phase process and catalysts for the ultra-low residence time partial oxidation of methane in the manufacture of synthesis gas.	UNIV MINNESOTA (US)	
WO9726987: Catalytic Oxidative Dehydrogenation Process	UNIV MINNESOTA (US)	
US5654491: Catalytic partial oxidation of hydrocarbon for producing oxygenate(s) cheaply, rapidly and efficiently - by passing mixture of oxygen containing gas and hydrocarbon gas through metal catalyst structure having specified transparency	UNIV MINNESOTA (US)	
US6452061: Catalytic oxidative dehydrogenation process	UNIV MINNESOTA (US)	
WO200511668: Production of olefin with functional group, by mixing fuel source and source of oxygen to provide fuel and oxygen mixture, and contacting fuel and oxygen mixture with catalyst.	UNIV MINNESOTA (US)	
US200613587: Catalyst comprising a metallic support and process for the production of olefins	-	
RU2126781: Method of Producing Unsaturated Hydrocarbons	TOPSOE HALDOR AS (DK)	
US7214331: Catalyst configuration and methods for syngas production	-	
US2005131255: Catalyst systems for converting alkanes to alkenes and to their corresponding oxygenated products	-	
WO0180992: Rhodium Cloth Catalyst for Partial Oxidation of Hydrocarbons	CONOCO INC	
US7122170: Catalysts for SPOCTM enhanced synthesis gas production	CONOCOPHILLIPS CO (US)	
US6946111: Short contact time catalytic partial oxidation process for recovering sulfur from an H ₂ S containing gas stream	CONOCOPHILLIPS CO (US)	
US7108842: Process for the catalytic partial oxidation of H ₂ S using staged addition of oxygen	CONOCOPHILLIPS CO (US)	
US7138101: Two-stage catalytic process for recovering sulfur from an H ₂ S-containing gas stream	CONOCOPHILLIPS CO (US)	

4.3 Institutes/companies working on the technology

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

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
University of Minnesota (Prof Schmidt)	USA	
University of Patras (Prof Verykios)	Greece	
Dow Chemical	USA	
Politecnico di Milano (Prof Forzatti)	Italy	
Eindhoven University of Technology (Prof Schouten)	The Netherlands	
Norwegian University of science and Technology (Prof. Holmen)	Norway	
McGill University, Montreal	Canada	
University of Pittsburg (Prof. Vesper)	USA	

5. Stakeholders

5.1 Suppliers and developers

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

Some suppliers of catalytic gauzes and foams as well as ceramic supports are listed in Table 9

Table 9. Supplier and developers

Institute/Company	Country	Remarks
Degussa	Germany	
Corning	USA	
BASF Catalysts LLC	USA	
W. C. Heraeus GmbH,	Germany	
Johnson-Matthey	GB	
Vesuvius High Tech Ceramics	Belgium	
Goodfellow	GB	
K.A. Rasmussen	Norway	
Hi-Tech Ceramics	USA	

5.2 End users

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

Potential end users include manufacturers of H₂-based automotive systems, decentralized H₂ supply technology as well as companies operating in the petrochemical sector

6. Expert's brief final judgment on the technology

(maximum 5 sentences)

Millisecond (short contact time) reactors are an attractive alternative to classical large scale installations for syngas and hydrogen production. In particular for distributed production of hydrogen for stationary fuel cell application millisecond reactors may become important. In addition, the high flexibility allowing the utilization of different hydrocarbon feedstocks is advantageous for syngas production.

Based on the positive results obtained on laboratory scale, first pilot plants are designed to proof the commercial advantages of this technology.