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EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
REVERSE FLOW REACTOR OPERATION

TECHNOLOGY CODE: 4.1.2

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1. Technology

Nowadays, transient operations open new ways in process intensification, which may offers considerable advantages for the performance of a process if a dedicated procedure can be developed (Budhi, 2005). In practice it means that permanently one or more process variables are intentionally perturbed according to some schedule, which either disturbs the steady state of a process or even may prevent that a process becomes steady. Improvement of reactor performance has become a key issue over the past decade. In particular, the reactor design and development have deeply focused on improving conversion and selectivity as well as reducing energy consumption for heterogeneously catalyzed gas phase processes in fixed bed reactors. Various improvement methodologies have been proposed with general topic as the key elements in *process intensification*. Among methods in process intensification, dynamic operation concerns an important role at all levels of process improvements that cannot be achieved by steady state operation. In addition, the transient processes are at the apex of chemical reaction engineering due to involvement of accumulation effects next to convection, dispersion, and reaction as occurs in a steady state.

The transient operation of catalytic reactors is receiving increased attention due to its capability to influence the temperature and concentration profiles inside the fixed bed, leading to the possibility for improvement of conversion and selectivity. The application of the transient reactor is also gaining broad interest as an efficient method for energy saving. This technology may be considered as an attractive alternative to various catalytic reactions in which heat storage and catalytic coverage can be manipulated for the process improvement.

The research field of *dynamic reactor operation* is deliberately devoted to the developments of transient operation and control procedures for catalytic reactors with the objective to improve their performance. In transient reactor, one great challenge is to increase the reaction's conversion or selectivity through manipulation of the catalyst's surface coverage or heat storage capacity by suitable perturbations of the reactant inlet conditions or by dedicated flow reversals. From this research emerged the idea that under deliberately and artificially created unsteady state conditions, it is possible to increase the productivity, conversion, or selectivity, and to reduce the heat consumption of a catalytic process as a whole when compared to steady state performance. This issue is interesting from a viewpoint of *process intensification* (Stankiewicz and Moulijn, 2004).

Among the various options for transient operation, periodic operation offers the combined benefits of a permanent unsteady-state regime and a constant time-average regime. Periodically changing the flow direction through the reactor, better known as Reverse Flow Operation (hereinafter referred to as RFO), has been widely applied for exothermic reactions from a viewpoint of energy saving and for improvement of conversion or selectivity. The use of the reverse flow principle as transient operation procedure for a catalytic reactor becomes interesting by the combination of dynamic properties at a microscale (catalyst) and at a macroscale (reactor). It may produce more favourable concentration and temperature profiles for the catalytic process (Ferreira et al., 1999).

Former applications of reverse flow reactor (RFR) were focused on the energy saving (Boreskov et al., 1982; Boreskov and Matros, 1983; Matros and Bunimovich, 1996; Matros, 1985, 1989; Froment, 1990; Neophytides and Froment, 1992). Further study on transient kinetic studies were performed to identify the relevant elementary reaction steps and to quantify the kinetic rate coefficients that are used in supporting modeling studies (Smith and Bobrova, 2002; Budhi, 2005). Basically, this might be a chievable by a dedicated operation procedure for a fixed bed reactor with periodic flow reversal, aiming at selectivity improvements with respect to the desired product, or avoiding that the undesired products are detected at the reactor outlet.

The contemporary issue of the development of RFO technology has been diversely explored in a wide range, not only for the issue of exothermic reactions, but also for coupling reactions, selectivity manipulation, control strategy and stability etc. In this contribution, possible operations and methods of fixed bed reactors in reverse flow mode are presented. This chapter outlines how the RFO technology has developed.

1.1 Description of technology / working principle

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

Figure 1 depicts a schematic illustration of a fixed bed reactor for a steady state, once-through operation (1a) and for a reverse flow operation (1b). In the reverse flow operation, the flow passes 1-2-R-3-4 during the first half of each cycle, and during the second half of each cycle, the flow passes 1-2’-R-3’-4. This scheme is periodically repeated to maintain the dynamic process variables along the bed, which can be characterized by the heat front and the concentration front. Neophytides and Froment (1992) investigated two phenomena competing with each other and are responsible for the main characteristic of the heat front. First, chemical reaction accompanied by the release of heat leads to a temperature increase in the catalyst bed for exothermic reaction. Second, the flow of the cool inlet reaction mixture through the previously heated catalyst bed, together with the interface heat exchange, extracts heat from the bed in the direction of flow. The created transient temperature and concentration fields posses a number of characteristics, which are great of practical importance (see **Figures 2**). The dynamic properties of the catalyst may change due to modification of the surface structure and the near-surface composition (see **Figures 3**). It was also proven that the transient operation may be used to manipulate the catalyst surface coverage (Budhi et al., 2004a; Budhi, 2005).

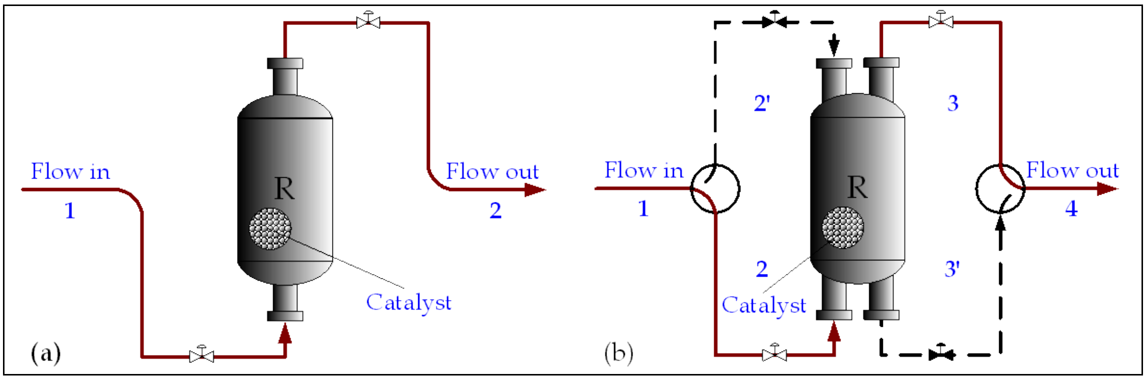

Fig. 1. Schematic illustration of a fixed bed reactor: (a). once-through reactor operation; (b). reverse flow reactor operation.

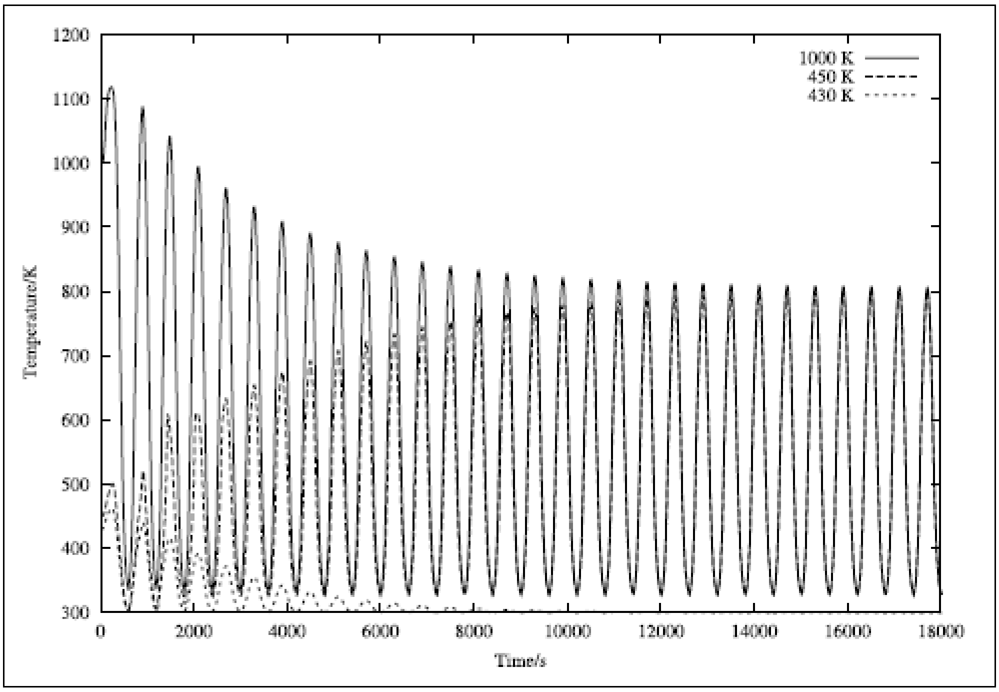

Fig. 2. Transient evolution of the solid temperature at the mid point of the catalyst with three initial conditions (1000 K, 450 K, and 430 K) (adopted from Smith et al., 2002).

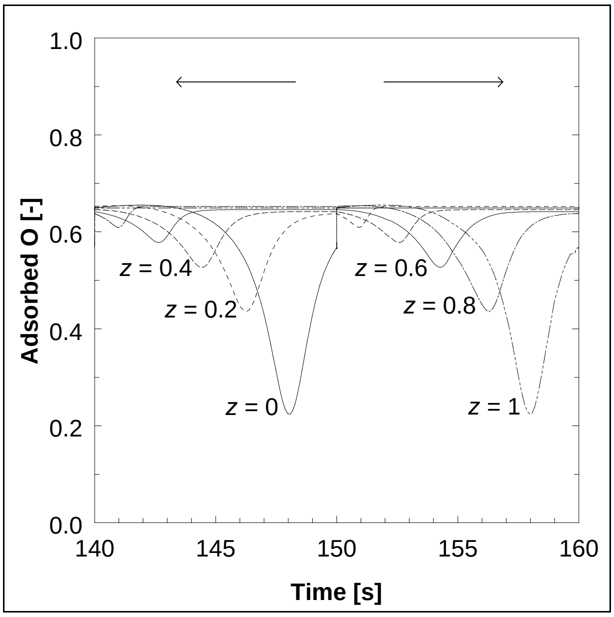

Fig. 3. Simulated adsorbed oxygen coverage at various axial positions in the reactor in regular RFO as a function of time. T = 800 K, τ_o = 10 s, FR = 1:1, and t_s = 10 s. Arrows show the flow direction (adopted from Budhi, 2005).

According to the switching time period and regime of operation, the reverse flow reactor can be distinguished as follows:

1. Switching time period:
   - *Symmetric operation*:
     Time period between forward and backward flows are similar.
   - *Asymmetric operation*:
     Time period between forward and backward flows are different.
2. Regimes of operation:
   - *Quasi-steady state regime*:
     Defined as a condition during reverse flow operation, in which the switching time of flow reversal is much larger than the gas residence time if the same reactor is operated under steady state, once-through operation.

- *Dynamic regime*:
  Defined as a condition during reverse flow operation, in which the switching time of flow reversal is near to the gas residence time of the same reactor, operated under steady state, once-through operation.
- *Relaxed or sliding regime*:
  Defined as a condition during reverse flow operation, in which the switching time of flow reversal is less than the gas residence time if the same reactor is operated under steady state, once-through operation.

The terminology of the asymmetric and symmetric operations may also be found for the case of different feed composition between forward and backward flows. The particular case can be seen for coupling exothermic and endothermic reactions. During forward flow, the mixtures of methane and air are introduced into the reactor to conduct the methane combustion, while during backward flow, the mixtures of methane and steam are introduced into the reactor to conduct the steam reforming. Detailed review of this topic can be obtained in Kolios et al. (2000).

The time scale of flow reversals in an isothermal fixed bed reactor for manipulation of the selectivity appears in the order of seconds, which is significantly smaller than the order of minutes, used in the classical reverse flow application for energy saving (Matros and Bunimovich, 1996; Budhi et al., 2004a). A first estimate of the time scale can be obtained from the ratio of the storage capacity of the catalyst and the feed flow rate of the reactant. It means that manipulation of the reactor selectivity requires considerably more frequent flow reversals in order to keep the catalyst surface in a dynamic state. If the reaction rate is fast compared to reversing the flow direction, then there is essentially a steady-state present for the reaction rate and corresponding catalyst surface coverages. If an antipode situation exists, then real unsteady-state behaviour holds for the system.

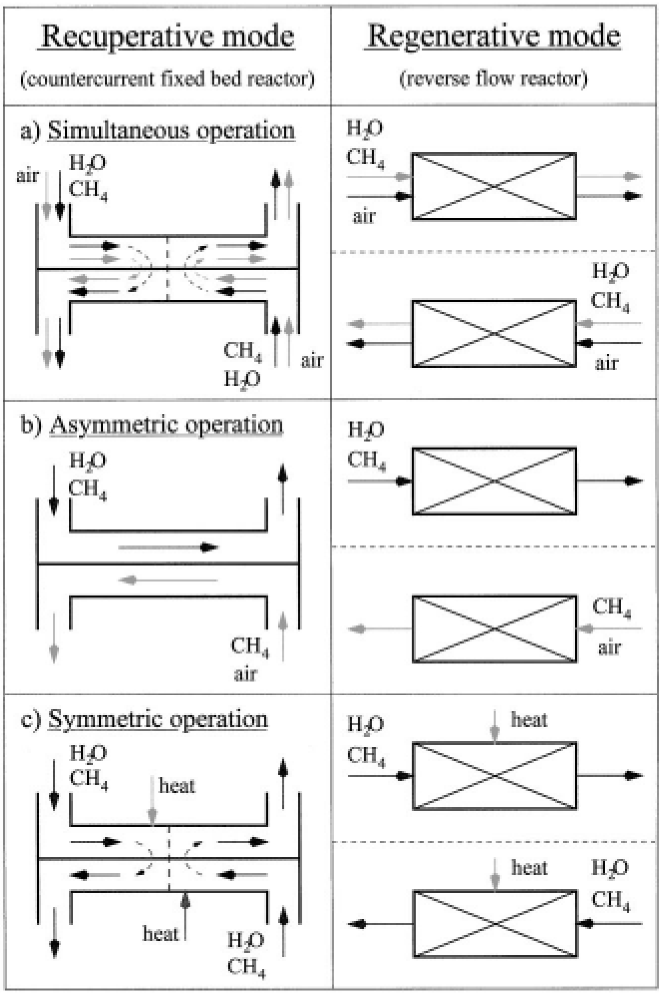

Fig. 4. Simultaneous, symmetric and asymmetric operations for the coupling of exothermic and endothermic reaction (methane combustion and methane steam-reforming) (adopted from Kolios et al., 2000).

1.2 Types and "versions"

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

The genuine concept of reverse flow reactor was initially proposed by Cottrell (1938) for the removal of pollutants. The recent applications both on the levels of academic interest and industrial scale were strongly motivated by the successful application of reverse flow reactor for SO_2 oxidation in Rusia (Boreskov et al., 1979; Boreskov and Matros, 1983). The further exploration of RFR roadmap (see **Figure 5**) has expanded remarkably since its beginning, which broadens to various aspects in chemical engineering both on the level of thermodynamic regime and kinetic regime.

According to Dudukovic (1999), the novel concepts in catalytic reaction engineering consists of a new simultaneous approach to the problem of catalyst and reactor selection, the enhanced level of understanding used in describing the various terms of the balance equations, and consideration of novel models of reactor operation. A transient operation according to the reverse flow principle gives rise to complicated dynamic behavior of the fixed bed reactor, as has been reported on several occasions for the classical application of energy saving (e.g. Salinger and Eigenberger, 1996; Khinast and Luss, 2000). The complexity is due to the non-linear dynamics of the whole system, caused by the usually non-linear reaction kinetics on the scale of a catalytic active site, in combination with heat transfer aspects on the scale of the reactor. Even a single, first order, exothermic reaction, carried out in a reverse flow reactor, may show five regions with different bifurcation diagrams, the

Damköhler number being the bifurcation parameter (Khinast and Luss, 2000). The existence of stable periodic states depends on the bifurcation parameter value and on the route that leads to the specific position in the bifurcation diagram. Knowledge of the bifurcation behaviour is important for reactor design and reactor control in order to avoid unstable operation. It is also important to assess a safe reactor start-up procedure, which includes a start-up period as short as possible.

So far, the research and application domains of reverse flow reactor may be categorized into *four types* as described underneath:

1. Reaction
    a. Heat of reaction: exothermic and endothermic
    b. Direction of reaction: irreversible and reversible reactions
2. Storage method
    a. Energy saving
    b. Feedstock saving
3. Reactor design
    a. Regular fixed bed reactor with feed at the reactor ends
    b. Modified fixed bed reactor with side feeding
4. Type of operation method, control, and stability
    a. Combination with concentration programming
    b. Symmetric and Asymmetric
    c. Control
    d. Stability

The research and application on each type may be carried out via modeling-simulation and experiment. There also exists an interaction among these types (see also **Figure 6**).

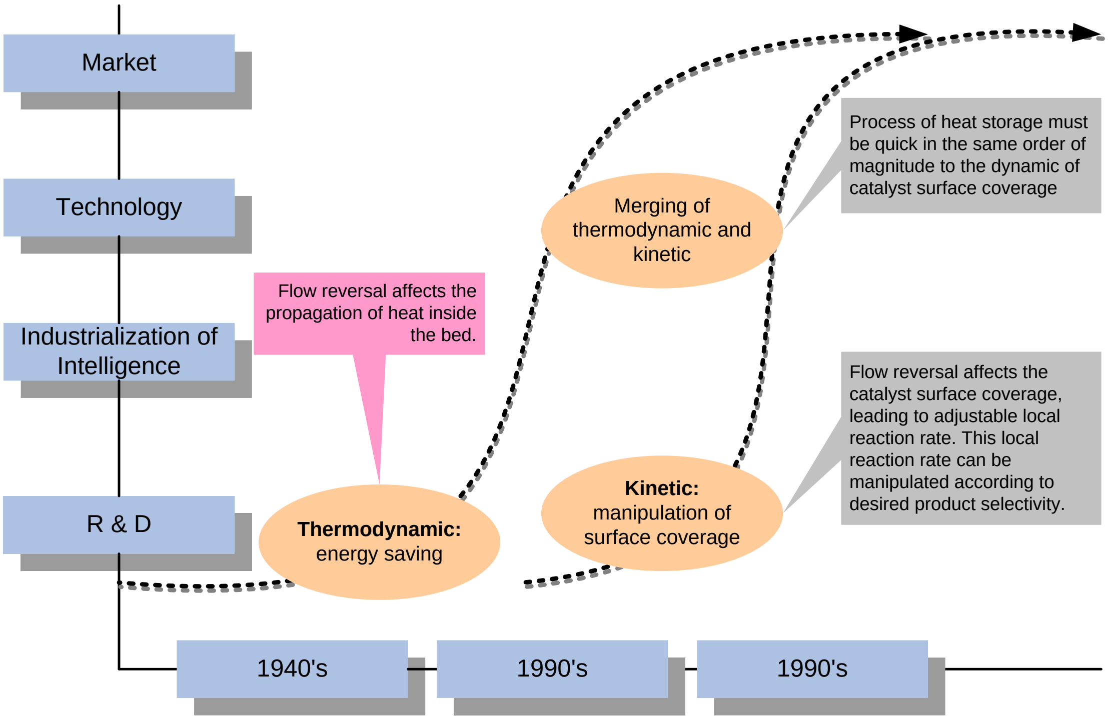

Fig. 5. Roadmap of research of reverse flow reactor.

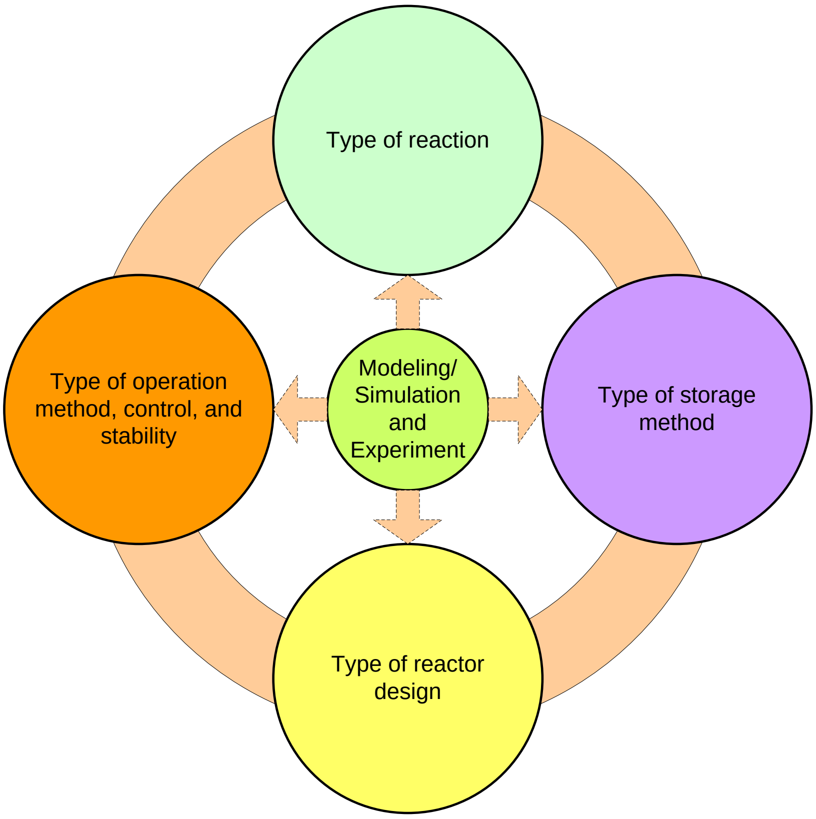

Fig. 6. The research structure of reverse flow reactor

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).

Most important advantages of the RFO technology in comparison with traditional steady state, once-through operation are:

1. The fixed bed catalyst can act both as heat and mass accumulators. It can also be used as a regenerative countercurrent heat exchanger. For exothermic reaction, this method may allow autothermal operation.
2. The catalyst surface can behave more dynamics, leading to possibility for manipulation of selectivity.
3. The heat front can be controlled by reversing the flow direction, leading to conditions thermodynamically favorable for reversible reactions such as a declining temperature profile for exothermic and increasing temperature profile for endothermic reactions.
4. Flow reversal at proper switching time may be used for heat trapping, which allows higher efficiency of heat recovery.
5. The concept of reverse flow operation has also been investigated for coupling reactions (endothermic and exothermic reactions).
6. Controlling the heat front along the catalyst bed may avoid the hot spot of catalyst, leading to longer life time.
7. Excluding the preheater as usually employed in conventional steady state operation may give rise to smaller reactor unit size and more simplification of unit flow diagram, etc.

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	Depending on the type of operation. One case reported for heat recovery higher than 50%.	Various applications of RFO for energy saving since this reactor can achieve autothermal operation. This method strongly suitable for very lean inlet gas, even beyond the flammability limit. The heat recovery was reported up to 60-70%. For methanol synthesis was reported up to 50%.
Increased conversion	Depending on the type of operation. One case reported 5-12%.	The conversion increase may result from the increase of reaction rate, which is induced by heat front, or by direct perturbation of flow reversal. The use of reactor side feeding in ammonia oxidation at its minimum switching time may yield conversion of 12% higher than steady state operation.
Increased selectivity	Depending on the type of operation. One case reported >2-13%.	As an engineering tool, RFO can also be used to for manipulation of selectivity due to improved surface coverage related to desired product. The use of side feeding in ammonia oxidation at its minimum switching time may yield selectivity to NO of 13% higher than steady state operation.
Increased productivity	Depending on the type of operation. One case reported > 5%.	Obviously, as the conversion and selectivity may be improved, this affects the productivity accordingly.
Less emissions	Depending on the type of operation. One case reported removal up to almost 100%.	NOx and CO emissions, fugitive VOC and CH_4
Longer catalyst life time	Depending on the type of operation. One case reported > 100%.	Oxidation of NH_3 to produce NO in a nitric acid plant, usually conducted at elevated temperature (1125 K), can be performed at lower temperature with conversion and selectivity to NO remain high. If the life time of catalyst is usually 2-8 months, it can be longer when the reaction temperature can be carried out at lower temperature with similar conversion and selectivity to NO.
Cost savings	No data available, but it can be advantageous.	Cost savings can result from: • Longer catalyst life time • Avoiding catalyst replacement frequently due to hot spot
Economic evaluation	One case reported capital costs 20-80% lower, 5-20% lower operating costs.	Example is in RFO for sulfuric acid production.

1.4 Stage of development

Various applications of the reverse flow reactor have been carried out since its initial development. Most of them are still predominantly developed in the laboratory stage. Several industrial applications have shown successful operation. Three commercially implemented processes are known where periodic operation with flow reversal is employed. They are oxidation of volatile organic compounds (VOC) for purification, SO_2 oxidation, for sulfuric acid production, and NOx reduction by ammonia in an industrial exhaust gas. Currently, some university research groups have been performing like the group of Kuipers at the University of Twente investigates reverse flow catalytic membrane reactor for synthesis gas production, the group of Schouten at the Eindhoven University of Technology was working on ammonia oxidation with reverse flow reactor for manipulation of selectivity, the group of Keith at Michigan

Technological University developed a modified reverse flow reactor with internal cooling as a control mechanism to maintain reactor temperature for proper removal of VOC, the group of Budhi at Institute of Technology Bandung is currently working on reverse flow reactor for tar reduction in producer gas and automotive catalytic converter to get faster start-up, and many others that cannot be mentioned in this report. Some well-known companies are also conducting such as Shell Global Solution International in Amsterdam, the Netherlands (a reverse flow reactor with integrated separation for combustion of volatile organic compounds over Pd catalyst, see in Bos (2007)).

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 reverse flow reactor technology is widely growing with creative methods and innovative applications. When talking about the existing technology, there are two approaches that can be described:

1. Steady state, once-through operation (SSO):
   Various implementations of SSO can be found in the chemical process industries. For example, the industrial production of NO from NH_3 over catalytic platinum/rhodium gauzes, known as the Ostwald process, is currently performed in the Netherlands by DSM AGRO, Yara, and Kemira Agro. Extremely short contact times, elevated temperatures, and intermediate pressure (typically over 1073-1173 K and 5 atm) are applied. One tries to reach 100% NH_3 conversion in order to avoid downstream formation of NH_4NO_3. The actual NH_3 conversion of the process over platinum group metal is around 95-97% (Perez-Ramirez et al., 2004). The selectivity to NO is around 96% if that high reactor temperature is maintained. The selectivity to N_2O is 1.5–2%, and the remainder is N_2. Under 773 K, the reactor would produce mainly N_2, which indicates that the reaction selectivity is strongly depending on the applied temperature. Another example is the industrial production of the synthesis gas (mainly the mixture of CO and H_2), which is traditionally conducted in multitubes packed bed reactor to perform methane steam reforming.

2. Conventional reverse flow operation:

   In the so-called 'conventional' reverse flow operation, the time scale for reversing the flow direction seems in the order of dozens minutes. This large time scale corresponds to high heat capacity of the inert material to store energy. At this time scale, the propagation of heat through the bed may follow three regimes of operation, depending on the applied switching time. However, the concentration profile along the reactor might reach the steady state condition, or dynamic condition that is affected by the propagation of heat.

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)

The industrial applications of reverse flow reactor can be scarcely found. Some of chemical processes are reported as shown in Table 2.

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**
Chemical industry	EXXONMOBIL CHEMICAL	Manufacture of acetylene from methane	Not reported	2007	Increase the main product selectivity
Chemical industry	ATOFINA Chemicals	Hydrocarbon isomerization and phenol oxidation using a reverse flow chromatographic reactor	Not reported	2002	Increase the octane number of hydrocarbon via Isomerization
Chemical industry	Port Kembla Copper Ltd. Plant. Cooperation of Matros Technology and Hitachi Zosen Corporation (Osaka, Japan)	SO_2 Oxidation to SO_3	100,000 m^3/hr	2000	A decrease of metal needed by factor of 1.5-5, 30-50% reduction in pressure drop, 20-80% lower capital costs, 5-20% lower operation cost.
Chemical industry	A unit placed in Krasnouralsk, Russia	SO_2 Oxidation to SO_3	40,000 Nm^3/hr	1982	First commercial unit, treating of copper smelter gas.
Chemical industry	A unit placed in former Soviet Union	Regenerative Catalytic Oxidizer (RCO) technology for VOC oxidation from industrial sources		1980s	The technology was licensed by Monsanto Enviro-Chem. First plant using Matros's RCO technology.

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**
Chemical industry	Yount and Windes	Reverse flow reactor trays for vertical staged polycondensation reactor	1995	Increase the reaction rate for polymerization reactor
Chemical industry	Subramaniam and Snyder	Reverse flow strategy for ethylbenzene	1996	Keep the conversion and selectivity of

		dehydrogenation in a packed-bed reactor		ethylbenzene and energy efficiency at the maximum value and
Chemical industry	Smit and Zhang	Adiabatic reactor simulations of the reverse flow catalytic membrane reactor concept with perovskite membranes	2004	Increase the separation efficiency
Chemical industry	Fan and Keith	Reverse flow packed bed reactor for stable treatment of volatile organic compounds	2005	• time for the reactor to extinguish during lean conditions • used as a control mechanism to maintain reactor temperature for proper removal of volatile organic compounds
Chemical industry	Boreskov	SO_2 oxidation	1980s	• 5% conversion increase

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)

As aforementioned, the concept of reverse flow reactor was initially proposed by Cottrell (1938) for the removal of pollutants. The advantages of the so-called forced transient operation have been highlightened and enumerated some decades ago. The concept of RFO was refined and then extended to catalytic reactors by Boreskov et al. (1982). An implementation was made for SO_2 oxidation (Sapundzhiev et al., 1988, 1990; Bunimovich et al., 1990, 1995; Xiao et al., 1999), which was continued by the installation of a successful process on an industrial scale (Matros, 1990). Ferreira et al. (1999) proposed reverse flow operation as a way to decrease the hot spot temperature and to obtain a more favourable temperature distribution along the bed for o-xylene oxidation to phthalic anhydride. The reverse flow operation can also be successfully applied for selective reduction of NOx by ammonia (Bobrova et al., 1988; Jirat et al., 1999; Matros et al., 1999). Nevertheless, discussion of reverse flow reactor in literature are predominated by its application for energy saving.

During the last 25 years, a number of papers have been published both for aspect of theoretical analysis on the basis of simple first-order of reaction kinetics and elementary reaction steps, and for aspect of experiment laboratory including model validation. More than 30 academic research groups have expectedly contributed.

1. Combustion of pollutant:
    a. Catalytic incineration of carbon monoxide and/or propane (Züfle and Turek, 1997; Salinger and Eigenberger, 1996; Chan and Keith, 2006)
    b. Combustion of VOC (Haynes et al., 1995; Zagorijiko et al. 1996; Dobrego et al., 2005)
    c. Lean methane (Marín etal., 2005; Litto et al. 2006a; 2006b; Hevia et al., 2006; Gosiewski and Warmuzinski, 2007; Gosiewski, 2005)
2. Selective catalytic reduction of NOx (Borisova et al., 1997; Fissore et al., 2006a; 2006b)
3. Selective catalytic oxidation of NH_3 (Budhi et al., 2004a; 2004b; Budhi, 2005)
4. Selective hydrogenation of phenylacetylene to styrene (Stankiewicz and Kuczynski, 1995)
5. Regenerative processes (Unger et al., 1997; Matros et al., 1996)
6. Application to chemical heat pump (Lai and Li, 1996)
7. SO_2 oxidation (Gosiewski et al., 1996, Bunimovich et al., 1995)
8. Methane reforming - coupling reaction (Glöckler et al., 2006)
9. N_2O decomposition (Nalpantidis et al., 2006)

10. Catalytic converter (Liu et al., 2007)
11. Control (Edouard et al., 2005a; 2005b; Balaji et al., 2007)
12. Chemical synthesis:
    a. Ammonia synthesis (Babu and Angira, 2005)
    b. Methanol synthesis
    c. Synthesis gas in membran reactor (Smit et al., 2005; 2007a; 2007b; 2007c)

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?
Reaction engineering	The kinetic model employed in RFR spans from the general stoichiometry till elementary reaction step. Depending on the level of study, each can be used for accommodating the reaction rate in the source term. The elementary reaction steps do fit when the switching frequency is extremely high. In isothermal operation, the manipulation of surface coverage by RFR requires rather high flow reversal frequency to keep the adsorbed component in dynamic states. It opens a new way for manipulation of selectivity.	Laboratory or research group and research centre at the university, in collaboration with chemical industries and equipment manufacturers.
Storage method	Selection and improvement of inert material for energy saving are still of interest. Novel method for direct usage in coupling endothermic and exothermic reactions are also new interest, particularly by the use of membrane reactor.	Laboratory or research group and research centre at the university, in collaboration with chemical industries and equipment manufacturers.
Reactor design	Among various researches on RFR have been carried out on laboratory scale. Only a few have been commercially constructed.	Laboratory or research group and research centre at the university, in collaboration with chemical industries and equipment manufacturers.
Reactor operation, control, stability	Modification of reactor operation and development of control method have become an important need. Knowledge of the bifurcation behaviour is important for reactor design and reactor control in order to avoid unstable operation. It is also important to assess a safe reactor start-up procedure, which includes a start-up period as short as possible.	Laboratory or research group and research centre at the university, in collaboration with chemical industries and 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?**
Extremely high flow reversal frequency	The flow reversal frequency might be limited by the speed of directing valves, which seem likely in the order of seconds. Much faster frequency may be indispensable when the kinetic needs to compete to flow reversal perturbation. Extreme high flow reversal frequency may induce small influence to subsequent unit.	This challenge should be addressed in the laboratory or research group at the university to develop the fundamental concept.
Endothermic reactions	Some chemical industries employ endothermic reactions (methane reforming, tar reforming). The heat required might be supplied by partial oxidation, which may exclude the conventional fired heater.	This challenge should be addressed in the laboratory or research group at the university in collaboration with manufacturers or vendors.
Equilibrium reactions	A number of equilibrium reaction with temperature dependence are quite well-known in industry. In practice, intercoolings were applied in order to approach the equilibrium conditions. RFR has been investigated for methanol and ammonia synthesis as typical reactions of equilibrium with temperature dependence.	This challenge should be addressed to manufacturers and producers of industrial-scale.
Reactor design and operation	Some reactor modifications have also been studied with typical motivations. The application of novel reactor design and operation to various reactions is challenging.	This challenge should be addressed in the laboratory or research group at the university in collaboration with manufacturers or vendors.
Control	Since progress in automatic process control nowadays brings essentially every forcing function within reach, there is no mandatory to maintain the process steady state from that point of view. Such tendency is also backed-up by the increase of computational capabilities, which indicates that full-transient modeling could be implemented in more sophisticated control strategies. Also the reactor perturbation is still possible for unsteady state operations if dedicated procedures and cycle times are within reasonable bounds.	This challenge should be addressed in the laboratory or research group at the university in collaboration with manufacturers or vendors.

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**
Balaji, S., Fuxman, A., Lakshminarayanan, S., Forbes, J.F., and Hayes, R.E. (2007). Repetitive model predictive control of a reverse flow reactor, *Chemical Engineering Science*, 62, 2154-2167.	Research paper	Control strategy
Smit, J., Bekink, G.J., van Sint Annaland, M., and Kuipers, J.A.M. (2007). Experimental demonstration of the reverse flow catalytic membrane reactor concept for energy efficient syngas production. Part 1: Influence of operating conditions. *Chemical Engineering Science*, 62, 1239-1250.	Research paper	Novel concept of membrane reactor with flow reversal
Chan, F.L. and Keith, J.M. (2006). Designing reverse-flow packed bed reactor for stable treatment of volatile organic compounds, *Journal of Environmental Management*, 78, 223-231.	Research paper	Reactor design and stability
Nalpantidis, K., Platte, F., Agar, D.W., Turek, S. (2006). Elucidation of hybrid N_2O decomposition using axially structured catalyst in reverse flow reactor. *Chemical Engineering Science*, 61, 3176-3185.	Research paper	Structured catalyst in reverse flow reactor
Litto, R., Hayes, R.E., Sapoundjiev, H., Fuxman, A., Forbes, F., Liu, B., and Bertrand, F. (2006). Optimization of a flow reversal reactor for the catalytic combustion of lean methane mixtures, *Catalysis Today,* 117, 536-542.	Research paper	Optimization-operation
Babu, B.V. and Angira, R. (2005). Optimal design of an auto-thermal ammonia synthesis reactor, *Computer and Chemical Engineering*, 29, 1041-1045.	Research paper	Optimization-reactor design
Dobrego, K.V., Gnesdilov, N.N., Kozlova, I.M., Bubnovich, V.I., and Gonzalez, H.A. (2005). Numerical investigation of the new regenerator–recuperator scheme of VOC oxidizer. *International Journal of Heat and Mass Transfer*, 48, 4695–4703.	Research paper	Novel regenerator–recuperator scheme for VOC combustion
Edouard, D., Hammouri, H., and Zhou, X.G. (2005). Control of a reverse flow reactor for VOC combustion, *Chemical Engineering Science,* 60, 1661-1672.	Research paper	Control
Gosiewski, K. (2005). Efficiency of heat recovery versus maximum catalyst temperature in a reverse-flow combustion of methane. *Chemical Engineering Journal*, 107, 19-25.	Research paper	Heat recovery
Budhi, Y.W., Jaree, A., Hoebink, J.H.B.J., and Schouten, J.C. (2004). Simulation of	Research paper	Manipulation of selectivity

reverse flow operation for manipulation of catalyst surface coverage in the selective oxidation of ammonia, *Chemical Engineering Science*, 59, 5365-5377.		
Budhi, Y.W., Hoebink, J.H.B.J., and Schouten, J.C. (2004). Reverse flow operation with reactor side feeding: analysis, modeling, and simulation. *Industrial and Engineering Chemistry Research*, 43, 6955-6963.	Research paper	Modification of RFR with side feeding
Bunimovich, G.A., Vernikovskaya, N.V., Strots, V.O., Balzhinimaev, B.S., and Matros, Yu.Sh., (1995). SO_2 oxidation in a reverse-flow reactor: Influence of a vanadium catalyst dynamic properties, *Chemical Engineering Science*, 50 (4), 565-580.	Research paper	SO_2 oxidation
Matros, Yu.Sh. and Bunimovich, G.A. (1996). Reverse-flow operation in fixed bed catalytic reactors, *Catalytic Reviews Science and Engineering*, 38 (1), 1-68.	Review	Extensive overview on RFR
Budhi, Y.W. (2005). *Reverse Flow Reactor Operation for Control of Catalyst Surface Coverage*, Ph.D. Dissertation, Eindhoven University of Technology, The Netherlands.	Book	Control procedure of surface coverage
van Sint Annaland, M. (2000). A novel reverse flow reactor coupling endothermic and exothermic reactions, Ph.D. Dissertation, University of Twente, The Netherlands.	Book	Coupling endothermic and exothermic reactions
Irick, D.K. and Nguyen, K. (2004). *Energy efficient thermal management for natural gas engine aftertreatment via active flow control*, Annual Technical Progress Report, The University of Tennessee.	Report	Efficient thermal management

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
US 5,534,142	Frederick E. Bernardin Ronald L. Peterson	Flow-reversing system for series connected reaction chambers
US 4,478,808	Method of producing sulphur trioxide	Matros; Jury S. (Novosibirsk, SU), Boreskov; Georgy K. (Novosibirsk, SU), Lakhmostov; Viktor S. (Novosibirsk, SU), Volkov; Viktor J. (Odessa, SU), Ivanov;

		Alexei A. (Novosibirsk, SU)
US 4,877,592	Method of catalytic cleaning of exhaust gases	*Matros*; Jury S. (Novosibirsk, SU), Chumachenko; Viktor A. (Novosibirsk, SU), Zudilina; Ljudmila J. (Novosibirsk, SU), Noskov; Alexandr S. (Novosibirsk, SU), Bugdan; Evgeny S. (Novosibirskaya, SU)
US 4,978,519	Process for producing elemental sulphur	*Matros*; Jury S. (Novosibirsk, SU), Zagoruiko; Andrei N. (Novosibirsk, SU), Malakhova; Irina V. (Novosibirsk, SU), Eremin; Oleg G. (Moscow, SU)
US 5,366,708	Process for catalytic reaction of gases	*Matros*; Yurii S. (St. Louis, MO), Yeo; Robert A. (Ballwin, MO), McCombs; David E. (Chesterfield, MO
US 5,401,479	Process for the removal of nitrogen oxides from off-gases	*Matros*; Jury S. (Novosibirsk, RU), Noskov; Alexandr S. (Novosibirsk, RU), Bobrova; Ljudmila N. (Novosibirsk, RU), Slavinskaya; Elena M. (Novosibirsk, RU)
US 5,451,300	Process for stripping a volatile component from a liquid	*Matros*; Yurii S. (St. Louis, MO), McCombs; David E. (Chesterfield, MO
US 5,658,541	Process for removal of divalent sulfur compounds from waste gases	*Matros*; Yurii S. (St. Louis, MO), Meyer; Steven F. (Flor., MO)
US 5,768,888	Emission control system	*Matros*; Yurii Sh. (Chesterfield, MO), Bunimovich; Grigorii A. (Creve Coeur, MO), Strots; Vadim O. (Clayton, MO)
US 5,823,770	Process and apparatus for oxidizing components of a feed gas mixture in a heat regenerative reactor	*Matros*; Yurii Shaevich (Chesterfield, MO), Bounimovitch; Grigori Abramovich (St. Louis, MO), Strots; Vadim Olegovich (Clayton, MO)
US 6,261,093	Heat regenerative oxidizer and method of operation	*Matros*; Yurii S. (Chesterfield, MO), Bunimovich; Grigori A. (St. Louis, MO), Roach; Christopher A. (Richmond Heights, MO)
US 6,314,722	Method and apparatus for	*Matros*; Yurii Sh.

	emission control	(Chesterfield, MO), Bunimovich; Grigori A. (St. Louis, MO), Strots; Vadim O. (Clayton, MO)
WO 9,619,415; AU 4,169,396; US 5,560,823; US 5,667,698; EP 0,799,162; JP 11,504,254T; DE 69,512,271E	ABITIBI PRICE INC	Reversible flow supercritical water oxidant reactor
WO 02,051,865; NL 1,016,975C; AU 2,002,225,513; JP 2,004,523,342T	BIOMASS TECHNOLOGY GROUP BV	Cracking in packed bed reverse flow reactor
WO 9,942,540; NL 1,008,361C; AU 3,278,799	BIOMASS TECHNOLOGY GROUP BV	Gasification of biomass-comprising material
WO 2004,013,075	CALGON CARBON CORP	Production of bisphenol-A
US 2002,020,113	KENNEDY L A	Continuous generation of combustion products from fuel-rich reactant mixture
WO 0,128,674	KTH HOLDING AB	Continuous catalytic process for reacting fluid phase reactant in Heck reaction and hydroformylation
US 4,506,599	POLSKA AKAD NAUK	Ethylene removal from fruit storage chamber
WO 2006,045,765	SHELL INT RES MIJ BV	Reverse-flow reactor useful in removal of contaminants e.g. water
NL 1,003,547C	STICHTINGS SCHEIKUNDIG ONDERZOEK IN NEDER	The catalytic treatment of process gases containing flammable impurities
NL 1,003,547C	STICHTING TECH WETENSCHAPPEN	The catalytic treatment of process gases containing flammable energy usage
CN 1,528,661; CN 1,270,967C	WANG J	Method for continuous concurrent preparation of sulfoxide chloride and phosphorus oxychloride

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**
Michigan Technological University (Prof. Keith)	USA	Reactor stability and dynamics, including scale-up issue.
University of Houston (Prof. Luss)	USA	Reactor perturbation and stability.
University of Twente (Prof.	The Netherlands	Coupling endothermic-

Kuipers)		exothermic reactions in membrane reverse flow reactor
Eindhoven University of Technology (Prof. Schouten)	The Netherlands	Control of catalyst surface coverage for manipulation of selectivity
Institute of Technology Bandung (dr. Budhi)	Indonesia	Optimization of recuperator and exhaust gas treatment
University of Stuttgart (Prof. Eigenberger)	Germany	Exhaust purification and heat integration concept using RFR
National University of Singapore (dr. Lakshminarayanan)	Singapore	Model predictive control of a reverse flow reactor
University of Alberta (Prof. Hayes)	Canada	Optimization of RFR for lean methane combustion
Shell Global Solutions International BV (dr. Bos)	The Netherlands	RFR with integrated separator

5. Stakeholders

5.1 Suppliers and developers

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

To the best of our knowledge, no suppliers of commercial-scale of RFR are known, while manufacturer of laboratory scale of reverse flow reactor is presented in table 9.

Table 9. Supplier and developers

Institute/Company	**Country**	**Remarks**
VTA Technology GmbH	Austria	The VTA reverse flow disintegration unit
J&L Aquatics Calcium Reactors	USA	Precision Marine Systems' RFCa (reverse flow) Series Calcium Reactors employ a unique method for scavenging CO_2 and recirculating it back through the water pump. This makes more efficient use of the carbon dioxide used to lower the pH in the reactor. The reverse direction of water flow prevents channeling and allows for more even distribution of water and CO_2. This results in a more efficient calcium reactor than others.

5.2 End users

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

The potential end users of RFR technology may be all chemical industries which concern air pollutions, such as VOC, hydrocarbon, CO, CH_4, SO_2 etc. In some cases, the combustion of those pollutants can eliminate their existence in the air, as well as can produce extra energy for electricity or heater.

6. Expert’s brief final judgment on the technology

(maximum 5 sentences)

The technology of reverse flow reactors have grown up remarkably in the last decade as can be seen from their various applications for the improvement of dynamic properties at a microscale (catalyst) and at a macroscale (reactor). As their capability to open new ways in process intensification, the reverse flow reactor technology nicely exhibits potential methods from a viewpoint of energy saving and for manipulation of catalyst surface coverage. The development stage of the reverse flow reactor technology is still predominated by research on the level of laboratory. With such an effort, this technology will create a new class of industrial catalytic processes that can be hardly achieved by classical method of once-through operation. In the future, inline with the increased competitiveness and globalization, the reverse flow reactor might be much superior when compared to steady state operation.