

The reverse-flow operation of catalytic reactors: History and prospects

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ABSTRACT

The reverse-flow reactor concept means much more than just the reactor design concept. Actually, it reflects the overall general approach to engineering of catalytic reactions. The efficiency of the reverse-flow reactors for performance of exothermic reaction with low or moderate heat effect, especially in the area of purification of waste gases with low content of admixtures, was emphatically confirmed by 30 years of successful commercial application in hundreds of installations worldwide. Though some stagnation has been observed in this area during the last decade, the reverse-flow concept still has significant potential for new developments and applications. The most significant progress may be achieved in the area of catalytic reverse-flow processes with sorption enhancement, which may be applied, in particular, for production of hydrogen and for performance of various selective oxidation reactions.

KEYWORDS: reverse-flow operation, catalytic reactions, engineering, environmental protection

ABBREVIATIONS

DC/DA - double contact - double absorption

VOC - volatile organic compounds

RFR - reverse-flow reactor

INTRODUCTION

The technical progress in the chemical reaction engineering area is traditionally based on the

chemical, catalytic and engineering drivers, meaning the achievements in development of novel reaction pathways, new catalysts and new engineering approaches as a development basis. Usually, the main role is played by chemical and catalytic drivers; much less often the engineering ideas form a self-sufficient basis for new technology. The reverse-flow approach is an excellent demonstration of such a rare case, where the new process engineering concepts lead to the development of really new technologies applicable to a great variety of existing chemical reactions and catalysts.

Development history

The pioneering patent on the reverse-flow reactor (RFR) was filed by US inventor Frederick G. Cotrell in 1935 [1], though the heat regeneration principle, being a basis of the reverse-flow approach have been actually known and practically applied for air preheating since the beginning of the 19th century [2, 3].

Catalytic RFRs were proposed in 1950s both in the flow-sheet versions with stationary catalyst and heat regenerative beds and switching valves [4, 5] and with rotating catalyst bed [6]. The first theoretical description of the reverse-flow operation in respect to catalytic selective oxidation reaction [7] belongs to the same period.

First known attempt to create a commercial catalytic reverse-flow reactor for reduction of SO₂ by reducing gases was made in the late -1960s - early 1970s by Allied Chemical Corp. (USA) [8-9]. According to available information, this attempt was unsuccessful due to some technical problems with switching valves.

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The intensive theoretical and practical development of the reverse-flow approach has started in the mid -1970s, pioneered by the team of Prof. Yuri Matros in Boreskov Institute of Catalysis (Novosibirsk, Russia). This research has led to formulation of fundamental process concept and development of the mathematical simulation methods for the reverse-flow operation of catalytic reactors [10-38]. This work had also resulted in development, creation and startup of the first successful commercial reverse-flow reactors for SO₂ oxidation (Krasnouralsk non-ferrous smelter, Russia, 1982) and incineration of volatile organic compounds - VOCs (Novosibirsk Chemical Plant, Russia, 1984) [33].

Starting from the late 1980s the RFRs for various applications have become an attractive research object for scientists and engineers worldwide [39-77]. The most significant conceptual and scientific contributions into the development of the reverse-flow reactors were made during these years by Institut für Chemische Verfahrenstechnik, University of Stuttgart (Germany), Swingtherm Co. (Poland), Institute of Chemical Engineering (Poland), Department of Chemical Engineering, Technion-I.I.T. (Israel), Cullen College of Engineering, University of Houston (USA), Fakultät Bio- und Chemieingenieurwesen Technische Universität Dortmund (Germany), University of Twente (Netherland), Departamento de Ingeniería Química y Tecnología del Medio Ambiente, University of Oviedo (Spain), Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino (Italy).

Working principle of the reverse-flow technology

The reverse-flow technology is mostly targeted for performance of the exothermic chemical reactions between gaseous reagents in the packed bed of solid catalysts or non-catalytic materials. The main distinctive working principle common for all RFRs is periodic cyclically repeating reversals of the gaseous reaction mixture flow inside the packed bed of solid catalyst or non-catalytic heat regenerative material. The simplest flow-sheet of the reverse-flow reactor is given in Fig. 1.

The RFR is equipped with the system of switching valves, providing the periodical gas flow reversals inside the reactor (the directions of the gas flow filtration are shown in Fig. 1 by solid and dashed arrows).

The typical temperature profile along the reactor axis is shown in Fig. 2. Inlet gas is usually fed into the reactor with low (e.g., ambient) temperature without any preheating. In the inlet part of the bed this gas contacts the preliminary heated solid material, resulting in gas heating and solid material cooling. Then the heated reaction gas enters the

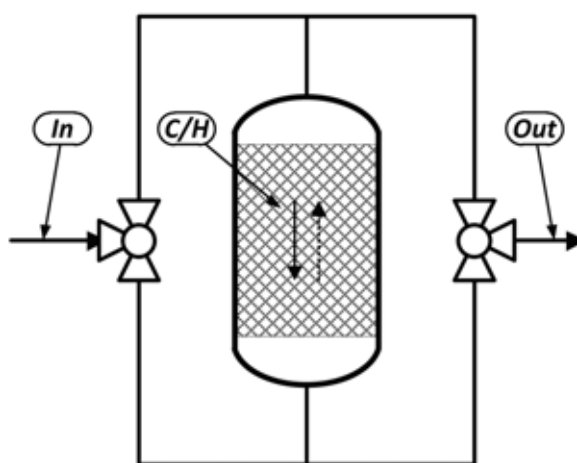


Fig. 1. Simplified scheme of the reverse-flow reactor. *In*, *Out* - inlet and outlet gas streams respectively, *C/H* - packed bed of solid catalyst (*C*) or non-catalytic heat regenerative material (*H*).

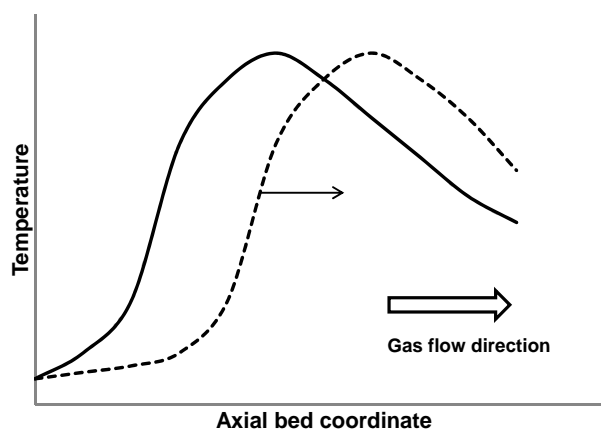


Fig. 2. Dynamics of the axial distribution of the temperature in the adiabatic reverse-flow reactor.

area where the temperature is sufficient for occurrence of the chemical reaction between the gaseous reagents. This reaction is accompanied by emission of reaction heat and heating of both solid material and gaseous flow. Finally, the heated gas passes through the outlet part of the packed bed, where gas cooling and solid material heating occur. The described phenomena lead to evolution of the temperature profile in form of a moving heat wave. Normally, such wave is moving in the direction of the gas flow filtration.

The flow reversal is performed when the high-temperature reaction zone reaches the outlet of the reactor. After the reversal, when the gas flow direction turns to opposite, the heat wave also starts moving in the backward direction. Such periodical reversals make possible to keep the high-temperature reaction zone within the reactor for an unlimited time.

Fig. 3 demonstrates the dynamics of the temperature profiles within the process cycles between flow reversals. It is seen that the final temperature profile in the operation cycle (Fig. 3, curve *c*) is completely symmetric to the initial profile (Fig. 3, curve *a*) in respect to the bed center. After the flow reversal the *c* profile will turn into *a* profile and the temperature evolution will be repeated in the next cycle. This indicates the established character of the cyclic regime in the reactor, meaning that such cycles may be repeated for an unlimited time (say, for years of continuous operation, if necessary).

Fig. 4 shows the axial temperature profile in the reverse-flow reactor averaged per cycle duration in the established cyclic operation regime. It is seen that the difference between average outlet gas temperature and inlet temperature is equal to the adiabatic heat rise of the reaction, in strict agreement with the energy conservation law.

At the same time, the difference between the maximum temperature in the reactor and the inlet temperature may be significantly higher than the adiabatic heat rise. Such super-adiabatic behavior is known for the heat waves of exothermic reactions moving in the direction of the gas flow filtration, when the energy is extracted by the gas flow from the heated regeneration material in the inlet part of the reactor and transported by this

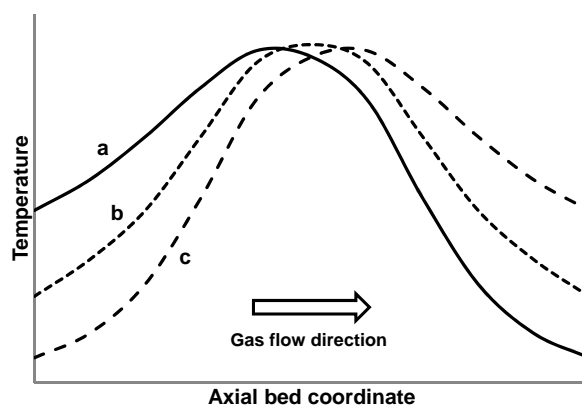


Fig. 3. Axial temperature profiles in the reverse-flow reactor in the established cyclic regime. a - beginning, b - middle, c - end of the cycle between flow reversals

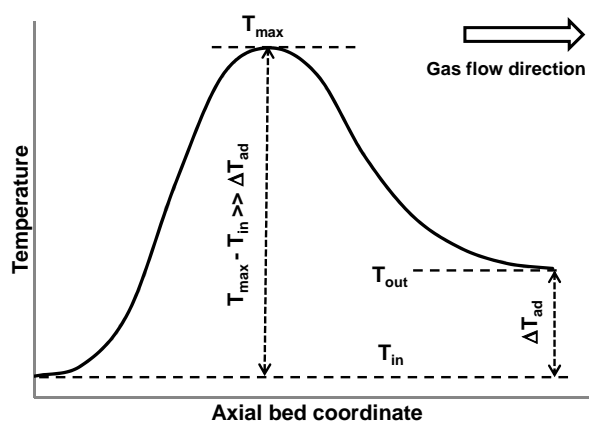


Fig. 4. The axial temperature distribution in the reverse-flow reactor averaged per cycle duration in the established cyclic operation regime.

flow to the reaction area in the central part of the reactor. Such energy transfer from lower temperature area to the higher temperature one, being in formal contradiction to the thermodynamics (which, of course, may be easily resolved by combined account of the heat energy and potential energy of exothermic chemical reaction), actually leads to super-adiabatic heat concentration or “heat pumping”, resulting in high maximum temperatures in the reactor even in case of lean reaction mixtures with low potential adiabatic heat rise.

In other terms, the RFR may be represented by the high-temperature reaction zone, surrounded by regenerative heat exchangers for preheating of the

gaseous reaction mixture. Due to the specifics of the temperature profiles formed, the regenerative heat exchange is especially efficient under periodic flow reversals with counter-current movement of heating and cooling gas streams. In general, the regenerative heat exchange here is a basis of the most important features of the RFRs. This fact is reflected in the related terminology, when RFRs are sometimes called regenerative reactors, for example, the catalytic and non-catalytic reactors for deep oxidation reactions are often termed as regenerative catalytic oxidizers (RCO) or regenerative thermal oxidizers (RTO) respectively.

Regenerative heat exchange is quite advantageous in case of gas-phase reaction mixtures with low concentration of reagents (and, thus, with low potential heat of reaction). This case is characterized with relatively low typical values of heat-exchange coefficients for the gas-solid heat transfer (under gas pressure closed to ambient) and low temperature gradients, resulting in increased requirements for the heat exchange surface area. The heat regenerative packing in the RFRs is characterized with very high heat exchange area (up to few thousands of square meters per cubic meter of packing), being much higher than that for recuperative heat exchanger.

Another advantage of the reverse-flow reactor is its improved operation stability under fluctuation of the process external parameters (e.g., gas flow rate, inlet temperature and composition) in time. It is explained by the fact that these parameters mostly influence the velocity of the heat wave movement in the reactor; therefore, it is only necessary to provide the flow reversals at the optimum time moments. These moments may be rather easily defined by achievement of the some fixed temperature in the fixed points of the reactor (for example, usual control procedure for the catalytic reverse-flow reactor involves switching of the flow when temperature at the interface between inlet heat regenerative bed and catalyst bed becomes lower than some fixed value).

Flow sheets of the reverse-flow processes

The catalytic RFR (Fig. 5) most often contains a packed bed (C) of the catalyst (in form of pellets or monoliths), surrounded by the packed beds of heat regenerative material (H) which is catalytically

inert [5, 13]. Usually the ceramic pellets (cylinders, saddles etc.) or monoliths are used, though the application of structured metal fibers media and different foams are also reported to be used for this purpose [78, 79]. To avoid the undesired adsorption/desorption phenomena at the beds ends it is recommended to use the heat regenerative materials with zero or minimum adsorption capacity in respect to reagents [80].

Such type of reactors is practically applied in the processes for VOC combustion in waste gases.

Fig. 6 demonstrates the RFR with improved heat management [81-83]. It may be applied for treatment of lean gases (requiring the additional supply of heat for provision of stable reverse-flow operation), as well as for treatment of gases with increased content of reagents (requiring the heat withdrawal for energy utilization purposes and in order to avoid the overheating of the catalyst beds). The gas cooling or heating is better to be performed between the sections of the catalyst bed (by means of internal or external heat-exchangers) - such positioning provides the most efficient heat management of the process.

Such reactors are applied in a heat addition mode for combustion of lean VOC-containing waste gases (characterized with own adiabatic heat rise below 20-30°C). Heat withdrawal mode may be realized in case of more reach fuels (adiabatic heat

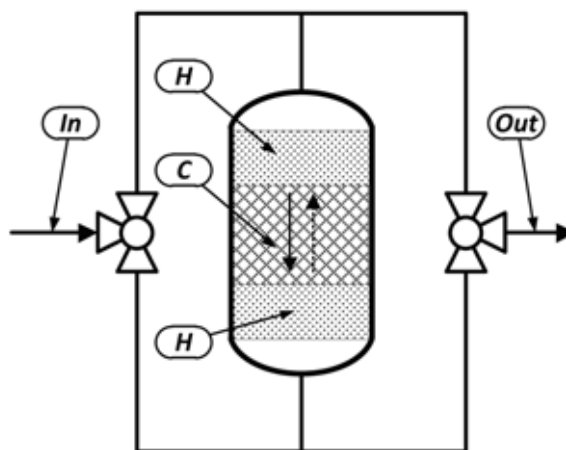


Fig. 5. Basic flow sheet of the catalytic reverse-flow reactor. *In*, *Out* - inlet and outlet gas streams respectively, *C* - packed bed of solid catalyst, *H* - packed beds of the heat regenerative material.

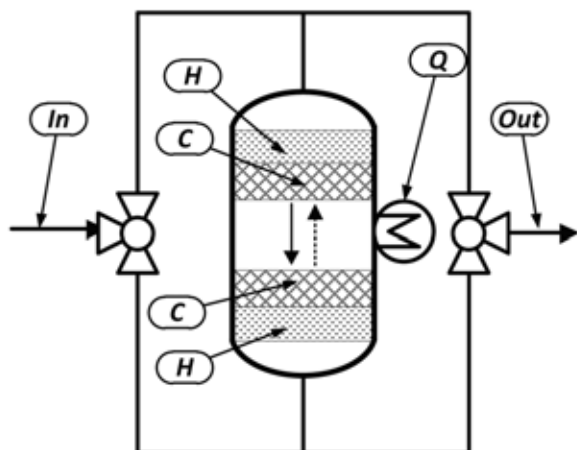


Fig. 6. Catalytic multi-bed RFR with heat addition/withdrawal in the central part. *In*, *Out* - inlet and outlet gas streams respectively, *C* - packed beds of solid catalyst, *H* - packed beds of the heat regenerative material, *Q* - heat exchanger.

rise above 100-150°C) with production of heat in the form of hot water or steam.

Majority of existing SO₂ oxidation reverse-flow reactors with 2 or 3 catalyst beds use the heat withdrawal between the beds for control of the catalyst temperature, which defines the equilibrium level of SO₂ conversion. In some cases, the excessive heat of SO₂ oxidation may be transferred from first stage of the DC/DA RFR to the second stage, that requires an additional heat input to provide the stable reverse-flow operation [84].

Non-catalytic RFR [85, 86] may have the simplest form, represented in Fig. 1, with only heat regenerative material in the packing inside the reactor. At the same time, there exists the version of the non-catalytic RFR with energy addition/withdrawal (Fig. 7), similar to the one, described above. Such reactor is widely used in heat addition mode for combustion of lean VOC-containing waste gases.

Non-catalytic RFRs compared to catalytic ones have lower efficiency in terms of conversion and energy consumption [51, 73]. On the other hand, non-catalytic reactors do not require the loading of the catalyst, which usually has a much higher price and much lower lifetime than the inert heat-regenerative packing, and this may lead to favorable capital and operating costs, as well as to improvement of process operation reliability.

Fig. 8 represents the reverse-flow reactor with the possibility of an additional feeding of one of the reacting streams into the central part of the reactor [87]. Such reactor configuration is, for example, applied in the processes of selective catalytic reduction of NO_x by ammonia, when ammonia (in the form of ammonia water or urea water solution) is introduced in the reactor center (In₂),

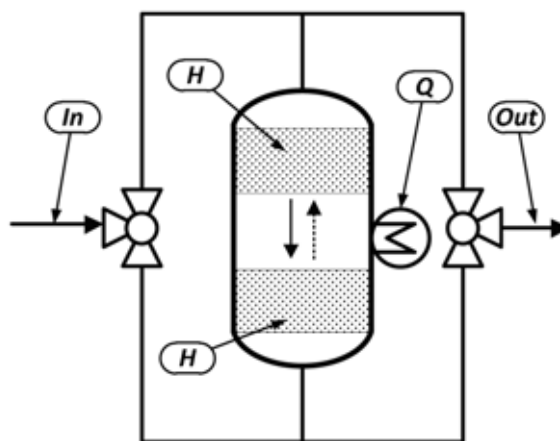


Fig. 7. Non-catalytic multi-bed RFR with heat addition/withdrawal in the central part. *In*, *Out* - inlet and outlet gas streams respectively, *H* - packed beds of the heat regenerative material, *Q* - heat exchanger.

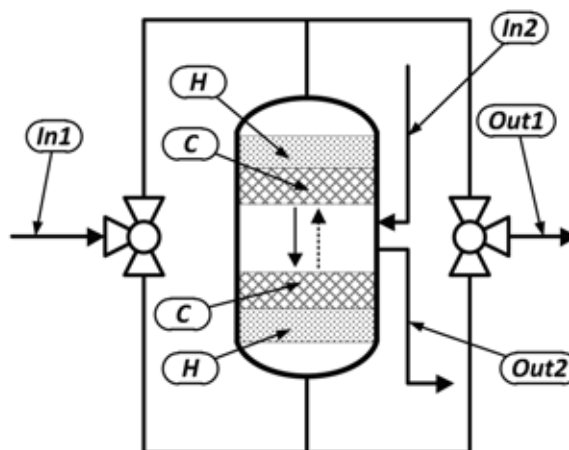


Fig. 8. Catalytic multi-bed RFR with central stream feeding/withdrawal. *In1/Out1* - basic inlet and outlet gas streams respectively, *In2/Out2* - alternative points streams feeding/withdrawal respectively, *C* - packed beds of solid catalyst, *H* - packed beds of the heat regenerative material.

while the main stream of NO_x-containing waste gases (In1) is fed through the inlet switching valve. Such an approach helps to avoid the undesired ammonia desorption from bed ends (which may happen in case of direct ammonia feeding into the inlet gas stream and result in significant ammonia slip due to ammonia desorption from the bed ends) and thus to provide high process efficiency.

The reactor configuration with partial gas stream withdrawal from the reactor may be used as a version of the process for heat withdrawal, when the extracted central stream is forwarded to the external exchanger.

Some flow-sheets of the reverse-flow process may include more than one flow reversal contour, e.g. double reverse-flow process, proposed for the performance of the Claus process [88] (Fig. 9).

Fig. 10 demonstrates the design of the rotating reverse-flow reactor [6, 88-92], where the flow direction is kept constant in respect to the reactor vessel body, while the periodical changing of the flow direction in the packed catalyst and heat regenerative beds is provided by continuous rotation of the packing. The volume above the packing may be used for addition/withdrawal of heat, as well as for side stream feeding or withdrawal. Such reactors are used for treatment of VOC containing waste gases.

Such a design does not include switching valves and it helps to minimize conversion losses occurring during flow switching, which is a typical problem for valve-based RFRs. On the other hand, rotating design may produce problems with sealing of the reaction volume under the rotating packing, resulting in some bypass of the inlet mixture directly to the outlet pipeline, that leads to the decrease in conversion.

Comparison with competitive technologies

The basic conventional technology, which is commonly used for the similar purposes, is the steady-state reactor. There exist a great variety of different steady-state reactors and process flow-sheets, but the typical process for the application area, which is most tightly connected with RFRs (processing of gases with low inlet temperature and low or moderate initial concentrations of reagents), includes a fixed bed (most often - catalytic) reactor, recuperative heat-exchanger and additional heater, used for the reactor start-up and, if necessary, for the supply of additional energy during the operation (Fig. 11).

Such technology is relatively simple, efficient and has huge experience of commercial application in different areas. At the same time, processing of gases with low concentrations of reagents may require a rather large surface area in the heat

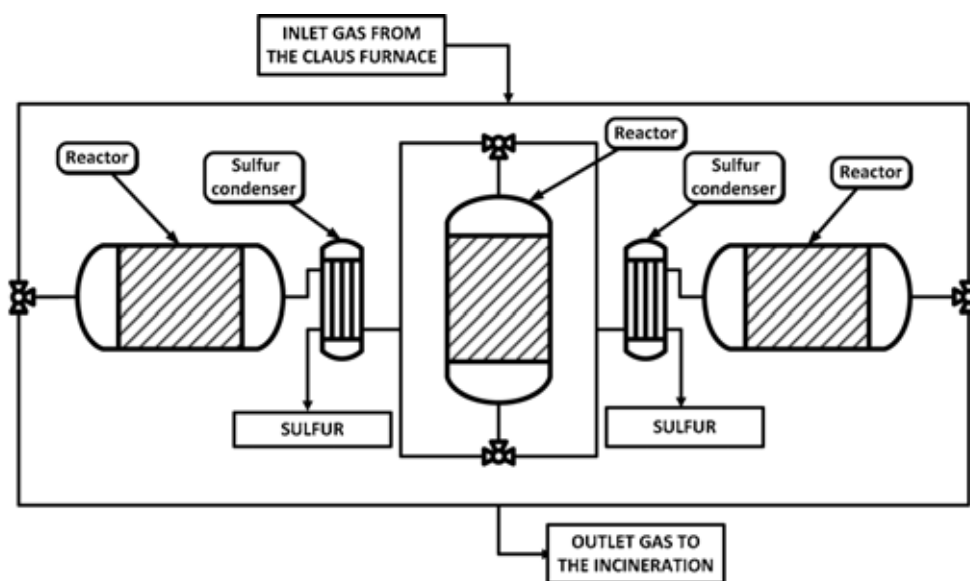


Fig. 9. "Double" reverse-flow process configuration with two flow reversal contours.

exchanger (both due to the low heat-exchange coefficient for gas-gas heat transfer and to the low temperature gradients in the heat-exchanger in case of lean gaseous feedstock) resulting in

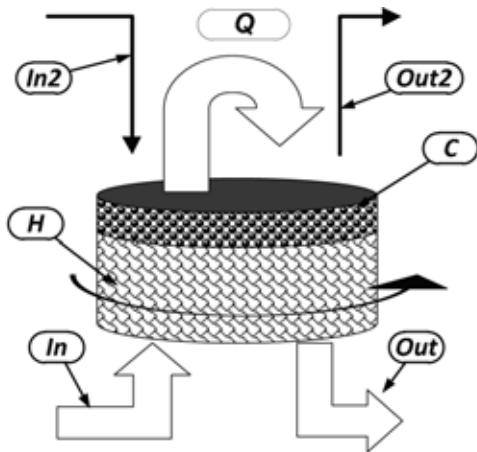


Fig. 10. Rotating catalytic RFR with possible central heat and side stream addition/withdrawal. *In*, *Out* - basic inlet and outlet gas streams respectively, *In2/Out2* - alternative points streams feeding/withdrawal respectively, *C* - packed bed of solid catalyst, *H* - packed bed of the heat regenerative material, *Q* - heat exchanger.

unreasonably high capital cost of the technology in general. Inefficiency of recuperative heat-exchange in such case may also lead to the need in additional energy supply during the operation and, thus, to increase of energy consumption of the technology. Additionally, heat exchange between inlet and outlet streams creates the positive energy feedback, leading to process operation instabilities and complicating the process control very much in case of oscillation of the inlet gas parameters (inlet gas flow rate, temperature and composition), which are quite typical for treatment of waste gases.

Compared to the steady-state reactor the following advantages of the RFR can be formulated as:

Decrease of energy consumption

The regenerative heat exchange provides an efficient utilization of the target reaction heat, therefore making possible to autothermally (i.e. without supply of external energy/fuel) process the reaction mixtures with adiabatic heat rise of $\sim 30^{\circ}\text{C}$ and higher, as well as to process more lean mixtures with minimized energy consumption. Decrease of energy consumption at processing of lean gases, compared to the steady-state process

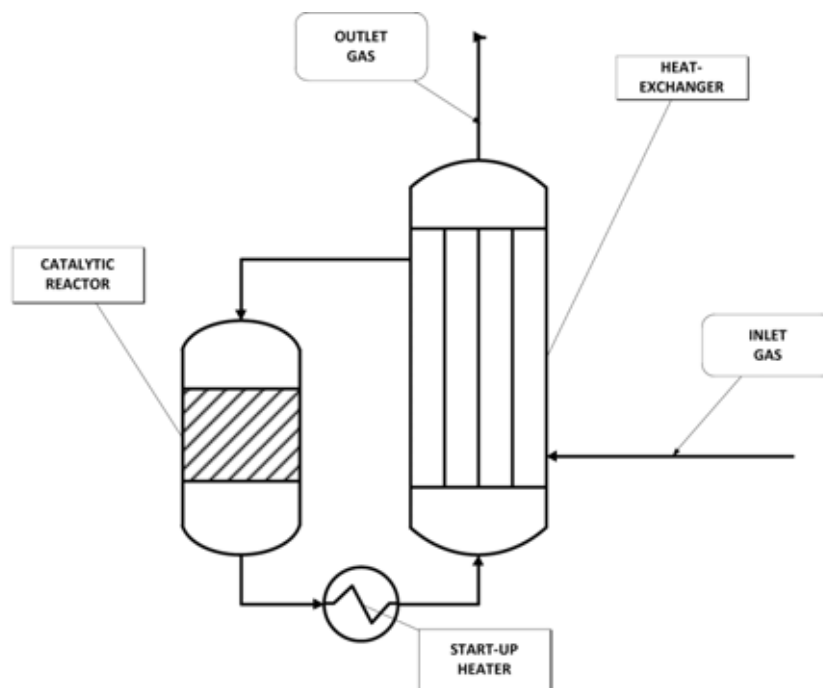


Fig. 11. Flow sheet of the conventional steady-state process.

may reach 100-130 KJ per st.m³ of inlet gas or by 30-90% of the overall energy consumption.

Decrease of capital costs

Decrease of capital costs is provided mostly by elimination or minimization of the expensive recuperative heat exchangers. The value of capital cost saving may reach 30-40% compared to the steady-state process.

High process stability under variation of external conditions

Surprisingly, reverse-flow processes are much more stable in operation and much easier to control than steady-state processes in case of significant oscillation of reaction gas parameters (gas flow rate, inlet temperature, composition) in time, which is quite a typical situation at processing of various waste gases.

High thermal efficiency of reaction heat utilization. Possibility to produce high-potential heat from lean fuel mixtures

Super-adiabatic heat accumulation in the moving heat waves open the way to achieve maximum temperatures much higher than adiabatic ones, therefore the heat of reaction may be efficiently utilized in form of a high-potential heat (e.g. high pressure steam) even from lean fuel mixtures. For example, it is possible to achieve maximum reaction gas temperatures up to 700-900°C from gaseous feedstock with typical adiabatic heat rise as low as 100-400°C, with possibility to utilize this heat in form of hot water or steam with thermal efficiency up to 80-90%.

There is also the widespread opinion that RFR may provide the increased product output in the equilibrium limited exothermic reactions due to the specific temperature distribution along the reactor - decrease of the catalyst temperature to the reactor outlet (see Fig. 4). Such decrease is theoretically favorable for shifting the equilibrium and raising the equilibrium conversion. Actually, only in the first half of the process cycle the temperature profile in the reactor is thermodynamically advantageous (see Fig. 3), while in the second half of the cycle the outlet temperature is even greater than the adiabatic one with consequent loss of equilibrium conversion. Another problem is that reaction rate sharply rises

with temperature, so the high maximum temperature in the reverse-flow reactor may impose the more significant negative influence on the equilibrium conversion than the low outlet temperature and, thus, the observed conversion may be even lower than in the steady-state process. In some cases the specific reasons may exist for the improvement of thermodynamically limited conversion in the reverse-flow regime [38], but in general, this declared advantage of the RFRs does not look evident.

The catalyst lifetime in the RFRs is sometimes intuitively estimated as decreased compared to steady-state process due to possible negative influence of periodical temperature oscillations. Actually, commercial experience with reverse-flow reactors does not show any specific influence of non-stationary conditions and the observed catalyst lifetime does not differ from the conventional one. Moreover, this is directly confirmed by special experimental studies [53].

Notably, the reverse-flow processes may be performed using the conventional catalysts (appropriate for each specific application), thus imposing no specific requirements for the applied catalysts in terms of their composition and texture. From the other side, the important properties of the RFRs (e.g., maximum temperature in the catalyst beds) depend on the characteristics of the heat waves, which in turn, depend on the size and shape of the catalyst particles. This feature may be used for reverse-flow process optimization [16].

The main drawback of the reverse-flow reactor in comparison with steady-state one is the conversion losses during the flow reversal procedure resulting from a possible reaction mixture bypassing the reactor during valves switching and with replacement of unreacted mixture from pipelines, reactor void volume and inlet heat regenerative bed (before the catalyst bed) into the outlet stream immediately after flow switching. Losses from valve leakage may be minimized by application of quality valves with low duration of the switching, while the losses from mixture replacement require the changes in the reactor design (minimization of void volumes) and the improvements in the process flow sheet, e.g., by application of various purging circuits and intermediate vessels for gas storage during switching under appropriate control strategy [93-98].

Additional complications may be caused by reversible adsorption of reacting species in the low-temperature inlet part of the catalyst and inert beds in the end of the process cycle. After the flow switching this inlet part becomes an outlet with temperature gradually rising with time, leading to the desorption of unreacted species into the outlet flow [23, 34, 40, 62, 80]. If it is possible to feed the adsorbing components separately from the other reaction mixture (like reducing ammonia in de-NO_x process), then it is reasonable to apply multi-bed reactors with feeding of this component between the beds [31, 99-102]. Optimization of

the control strategy may also help to resolve the problem [80].

Sometimes RFRs are compared with the other types of unsteady-state reactors with moving heat waves, but not directly applying the flow reversals technique. The examples of such processes are given in Fig. 12.

The process shown in Fig. 12a is called “simulated moving bed reactor” - SMBR (sometimes also called in literature “loop reactor” or “con-current/counter-current loop reactor”) is based on the continuous movement of the reaction heat wave around the circle of reactors with periodic changing

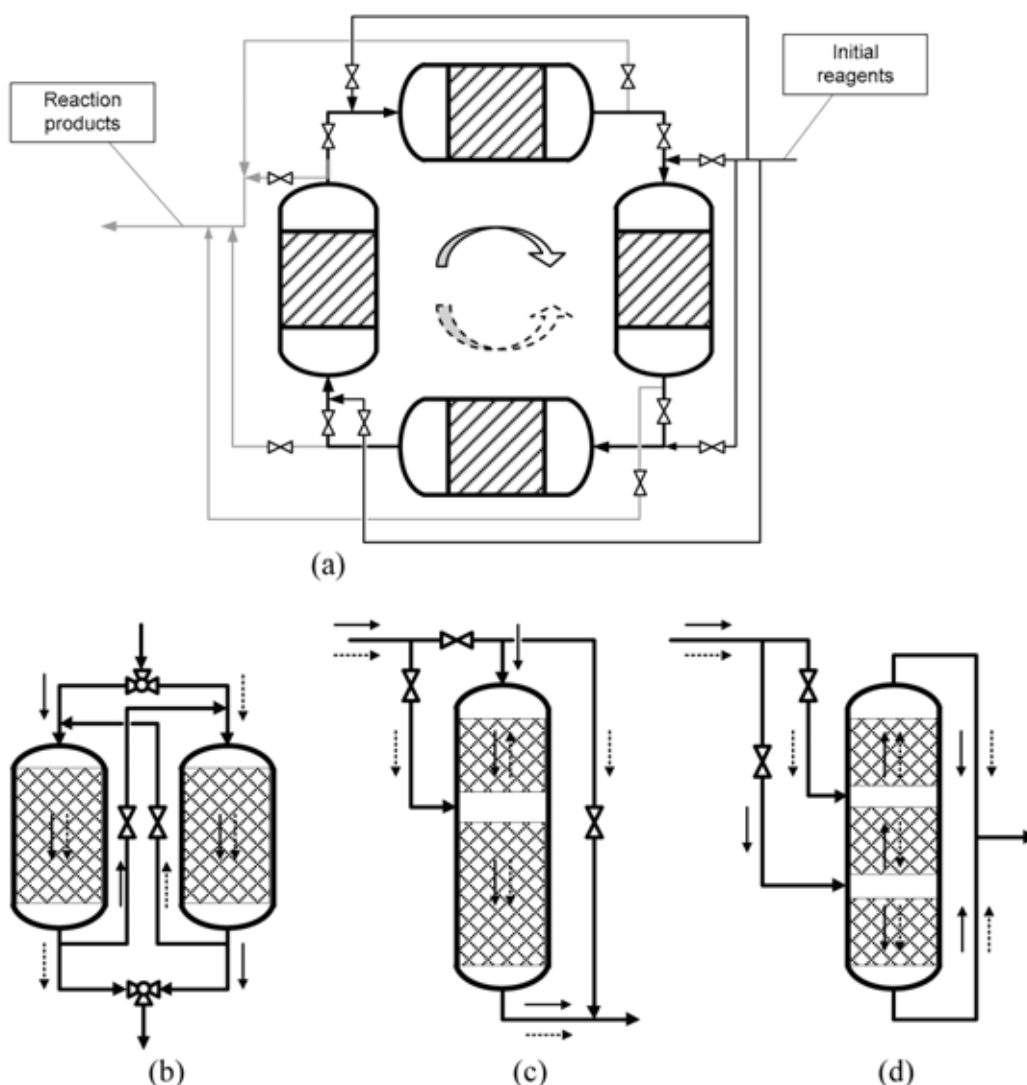


Fig. 12. Examples of unsteady-state reactors with moving heat waves, not directly applying the reverse-flow technique.

of the points of inlet mixture feeding and outlet mixture withdrawal [103, 104]. Such changing may be arranged con-currently or counter-currently to the direction of the gas flow in reactors. There are also some other flow-sheets with moving heat waves which (completely or particularly) do not apply the reverse-flow technique [26, 88] (Fig. 12 b-d).

Actually, there is no data on industrial application of such processes and they are usually used for theoretical comparison with RFRs. This general comparison demonstrates [32, 66, 105] that reverse-flow processes are more efficient in terms of heat regeneration, conversion, process stability, energy consumption and capital costs. At the same time, the non-reversal unsteady-state processes may be characterized with minimized conversion losses during flow switching. Moreover, its decreased heat regeneration efficiency may be useful for treatment of the concentrated feedstocks.

Current reverse-flow technology status

Reverse-flow reactors are applied at the commercial scale since early 1980s so the general stage of development may be characterized as commercial level.

At the same time, the potential of the reverse-flow approach is far from depletion. There are numerous new application areas and promising directions for development of new modifications of reverse-flow reactors. The stage of developments within these particular areas may differ from theoretical concept to pilot or semi-commercial level.

Such a wide range of development status reflects the fact that reverse-flow operation of chemical reactors is more a global engineering approach - a basement for creation of various chemical technologies than one specific technology.

Interestingly, though the reverse-flow reactors are under active development for more than 30 years (and it is a significant time in relation to the history of chemical reaction engineering branch which has been around for not too much more than a century), the reverse-flow approach is often considered in R&D and commercial practice as still a new approach. To some extent, it may be a result of conflict between stationary and non-stationary paradigms in engineering. It seems that

people normally tend to perceive the steady-state approaches as conventional by default, while dynamic methods are more easily accepted as new or non-traditional.

Known commercial applications

The main advantages of the reverse-flow reactors, as mentioned above, are the possibility to process lean feedstock with minimum energy consumption and the high operation stability under oscillations of external process parameters (feedstock flow rate, temperature and composition). Such conditions are generally typical for treatment of various waste gases.

The main current application area of reverse-flow reactors is incineration of volatile organic compounds (VOC) in waste gases. Such gases with relatively low VOC content (from 10-50 ppm up to 5-10 g/m³) are met in many branches of industry - chemistry and petrochemistry, painting, printing and lacquering facilities in machinery, wood processing, agriculture, paper production, food industries etc. The range of VOCs includes practically all classes of organic compounds (hydrocarbons, spirits, acids, ethers, sulfur- and halogen-containing compounds, dioxins etc.).

Both catalytic and non-catalytic reverse-flow reactors (called also as regenerative catalytic oxidizers and regenerative thermal oxidizers respectively) are applied in this area. The number of industrial installations here is measured in hundreds. The range of capacities (in respect to the flow rate of waste gases) varies from 500 to 800,000 m³/hour.

Another significant area of reverse-flow reactor application is oxidation of SO₂ in production of sulfuric acid. The most attractive area here is processing of waste gases from non-ferrous smelters, characterized with relatively low SO₂ content (1-4% vol.) and expressed oscillations of gas flow rate, composition and temperature, providing the maximum advantages for the reverse-flow technology over the conventional steady-state one. About 15 installations with maximum unit capacity (in respect to the waste gas flow rate) upto 110 thousands m³/hour (see Fig. 13) has been in industrial operation since 1982.

One industrial application is known for the reverse-flow reactor for NO_x reduction by ammonia.



Fig. 13. Reverse-flow reactor for oxidation of SO₂ at Pechenga Nickel Smelter (Nickel town, Russia).

Examples of the commercial reverse-flow reactors are given in Table 1.

Potential future applications of the reverse-flow reactors

The reverse-flow reactors may be applied to a wide range of other gas-phase exothermic reactions. The following potential applications are reported in literature:

Reverse-flow operation approach was considered for the methanol [26, 33, 43, 106, 107] and ammonia [26, 29, 33, 108] synthesis:

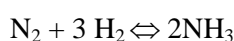
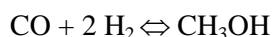
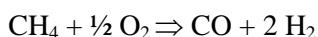


Table 1. Examples of industrial-scale applications of the reverse-flow reactors.

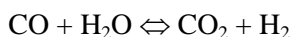
Sector	Company - Process/Product name/type	Short characteristic of application	Production capacity, st.m ³ /h	Startup date	Reported effects
Plastic component painting	Plastic injection molding company in Wisconsin, USA – <i>Anguil RTO</i> supplied by Anguil Co.	Waste gas purification from organic solvent vapors	62`800	2010	<ul style="list-style-type: none"> • Decreased capital cost • Decreased additional energy consumption • High VOC removal efficiency • Stable operation
Petro-chemicals	Formosa Chemical &FibreCorp., Taiwan – “ <i>Dynacycle™</i> ” - supplied by WATERLEAU Co. under license from MatrosTech.	Catalytic cumene incineration in waste gases	35`000	2003	<ul style="list-style-type: none"> • Decreased capital cost • No additional energy consumption • High VOC removal efficiency • No NO_x formation
Non-ferrous metallurgy	Pechenga Nickel Combine, Russia – “ <i>Reverse-Process</i> ” (developed and licensed by Boreskov Institute of Catalysis)	Treatment of waste gases from non-ferrous smelter with SO ₂ content 1.5-3.0% vol.	100`000	1987	<ul style="list-style-type: none"> • Unique stability under oscillations of the gas flow rate, composition and temperature • Decreased capital cost • No additional energy consumption • High SO₂ removal efficiency
Basic chemicals	ByiskOleum Plant, Russia – “ <i>Reverse-NO_x</i> ” (developed and licensed by Boreskov Institute of Catalysis)	Reduction of NO _x by ammonia in the waste gases from weak nitric acid production	10`000	1989	<ul style="list-style-type: none"> • Decreased capital cost • No additional energy consumption • High de-NO_x efficiency (>99%) • No ammonia slip

Application of the reverse-flow reactors for these processes may lead to decrease of capital costs and looks especially attractive for processing of purge gases at conventional ammonia and methanol plants.

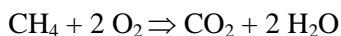
These plants may also use the RFRs for partial oxidation of the natural gas to syngas [109, 54, 55]:



or for performance of the water-gas shift reaction [56]:

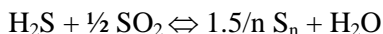


Reverse-flow reactor looks advantageous in application to the deep oxidation of methane [26, 33, 67-77] as well:



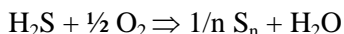
This process may be applied for efficient energy production from non-fossil methane, contained in landfill gas, biogas and coal mine waste gases with significant CO₂ sequestration effect.

Claus reverse-flow process may be applied for the production of elemental sulfur from H₂S/SO₂-containing gases by Claus reaction [17, 110]:



The simulation studies [22, 38] show that the RFRs in different configurations may significantly decrease capital costs and increase degree of sulfur recovery from sulfur-containing gases in oil and natural gas processing. Reverse-flow process may be efficiently used here for replacement of the basic catalytic stage of the Claus process as well as for replacement of the basic process with tail gas cleanup facilities.

Another potential application of the reverse-flow process is selective oxidation of H₂S to sulfur [111]:



applicable for direct desulfurization of natural gas and biogas with moderate H₂S content (up to 1-2%), as well as for tail gas cleanup in Claus units.

In addition to the RFRs for oxidation of VOCs in waste gases it is also reasonable to mention the reverse-flow processes proposed for abatement of VOCs in waste water. In one version of the

process the heat regenerators are used for evaporation and condensation of waste water, while the oxidation reactions occur in the catalyst bed in the vapor phase [112]. In another version, the VOCs are initially recovered from waste water by stripping it with the hot reaction gaseous stream from the RFR and then fed back to this reactor as reagents [113].

RFR may be used for catalytic decomposition of nitrous oxide [114]:



This application is important for environmental protection purposes once N₂O is assumed to be the major ozone depletion and greenhouse agent (with a global warming potential by 298 times higher than that for CO₂).

Reverse-flow operation principles may be also used in the catalytic neutralizers for purification of automotive exhaust gases [59, 115].

Interesting reverse-flow approach which potentially may give rise to a family of novel technologies is based on the combination of endothermic reactions with exothermic ones with the RFR. For example, such an approach may be used for coupling the endothermic methane steam reforming reaction with exothermic combustion reaction for autothermal hydrogen production. [57, 61, 116-118].

Sorption enhancement in the reverse-flow reactors

The traditional paradigm in development of the RFRs is based on account of travelling of the heat waves in the adiabatic packed beds and purposeful application of the heat inertial features of the catalyst and inert heat regenerative packing. At the same time, the sorption properties of the catalysts, providing the composition inertia of the catalyst beds, may also play a very significant role. In some cases, as it was shown above, sorption-desorption phenomena must be taken into account to avoid their negative influence on the reverse-flow process efficiency.

The first positive practical example in this area, demonstrating how the correct account of adsorption and desorption effects may lead to development of the new RFR configuration is the

aforementioned reverse-flow process for selective catalytic reduction of nitrogen oxides by ammonia, where ammonia is fed between the sections of the catalyst bed [31, 99-102].

From the other hand, it is quite possible to use the sorption effects for purposeful development of the new types of the RFRs [119].

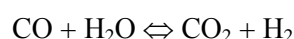
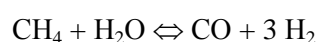
One such reactor was proposed for performance of Claus reaction under flow reversals where sorption of water helps to shift the reaction equilibrium and, thus, to increase the sulfur yield [64].

Another example of the sorption enhancement concept is adsorption-catalytic reverse-flow process for incineration of VOCs in lean gases, applying adsorptive accumulation of VOC at the catalyst surface at ambient temperature with periodical oxidation of adsorbed compounds at elevated temperatures under periodical flow reversals [35, 36, 119, 120]. Such a process may be applied for purification of lean vent gases with very low VOC content (below 100-500 mg/m³) with extremely low energy consumption.

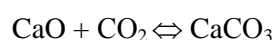
The described approach may be also used for sorption-enhanced methane steam reforming with super-adiabatic regeneration of the CO₂ scavenger under flow reversals [121, 122]. The flow-sheet of the process is shown in Fig. 14.

Both reactor chambers contain packed combined beds of methane reforming and oxidation catalyst with metal oxide CO₂ scavenger (e.g. CaO). One chamber operates in the hydrogen production mode, while another one - in regeneration mode, with periodical cyclic interchanging of these modes among the chambers.

Hydrogen production mode includes performance of steam reforming and water gas shift reactions

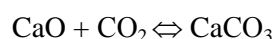


accompanied with simultaneous adsorption of product CO₂ by solid sorbent:



which helps to shift the equilibrium of hydrogen forming reaction to the right and obtain pure hydrogen in one reaction stage.

Regeneration mode includes decomposition of formed carbonate



with the supply of the heat required for both scavenger regeneration and bed preheating (for performance of endothermic steam reforming

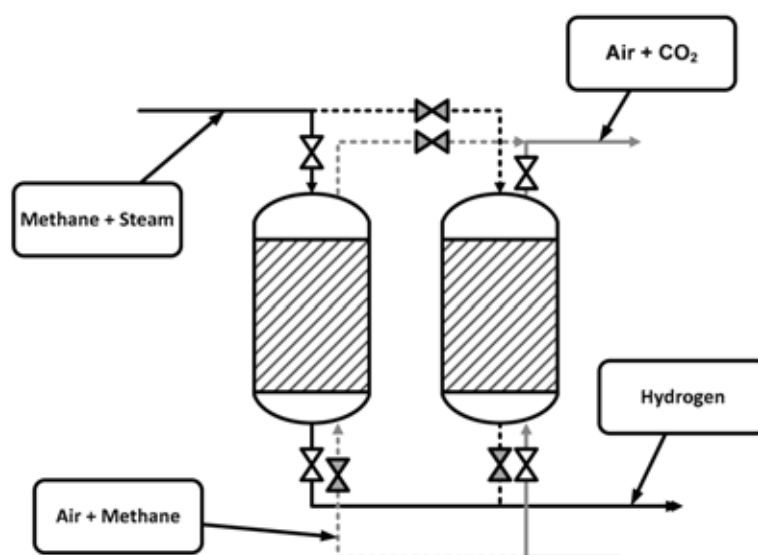
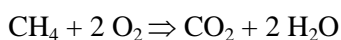


Fig. 14. Flow-sheet of the RFR with separate counter-current feeding of reagents for sorption-enhanced production of hydrogen from methane.

reaction in the further hydrogen production cycle) provided by reaction of methane combustion:



The simulation studies [122] have shown that counter-current feeding of the altering reaction mixtures, being essentially equivalent to reverse-flow operation, leads to formation of super-adiabatic heat wave in the regeneration mode, providing high maximum temperature and, thus, efficient carbonate decomposition under low consumption of methane for combustion.

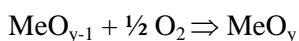
The proposed process gives the opportunity to produce CO_x -free hydrogen from methane and other organic feedstocks with minimum capital cost and energy consumption, compared both to conventional steam reforming and to other non-reverse versions of sorption-enhanced steam reforming processes.

Another possible application of this concept is the anaerobic oxidation process for selective oxidation and oxidative dehydrogenation reactions, using the lattice oxygen chemisorbed at the catalyst surface with periodical catalyst oxidation under periodical flow reversals [119, 123].

The process consists of two reaction cycles: oxide catalyst reduction by hydrocarbon with formation of the target product



and catalyst reoxidation



The reaction of hydrocarbon selective oxidation by lattice oxygen is usually slightly exothermic or even endothermic, while catalyst reoxidation is always exothermic. This makes possible to perform the hydrocarbon oxidation reaction (which selectivity is usually highly sensitive to temperature) in the packed adiabatic bed of catalyst without any heat removal with high selectivity even at processing of highly concentrated feedstock. The excessive heat emission is shifted to the reoxidation cycle, where temperature rise cannot impose the negative influence on the selectivity of the target reaction. Interestingly, the distribution of the reaction heat between the reaction cycles (and, thus, heat emission in the process cycles) may be optimized by selection of the catalysts with appropriate bonding energy of

lattice oxygen. This process may be realized in the flow sheet equivalent to one shown in Fig. 14 in two reactors with packed beds of oxide catalyst under counter-current separate feeding of hydrocarbon feedstock and air in a reverse-flow manner. Such technology may be applied, for example, for production of olefins and dienes from paraffins.

Analogous process for hydrogen production from syngas may be realized in the reverse-flow reactor with packed beds of iron oxide catalyst under counter-current altering feeding of syngas and water [124, 125]. The similar process was proposed for biogas treatment [126].

The similar two-bed RFR with periodically altering air and air+ SO_2 mixture counter-current feeding was described for SO_2 oxidation process [127]. In this case the purposeful application of absorption properties of vanadia catalyst in respect to sulfur dioxide is used for development of the new reverse-flow process, providing extremely low content of SO_2 in the outlet gases of the sulfuric acid plants [37].

The interesting example of the three-bed reverse-flow reactor with altering feeding of methane and air was proposed for production of ethylene and higher olefins from methane via intermediate bromination [128].

SUMMARY

The reverse-flow approach to operation of chemical reactors is something much more significant than just reactor design concept. Actually, it is the new direction in engineering of the chemical reactions and an excellent (and, unfortunately, rather rare) example of how the technological approach may become a self-sufficient basis for creation of a family of new technologies.

The efficiency of the reverse-flow reactors for performance of exothermic reaction with low or moderate heat effect, especially in the area of purification of waste gases with low content of admixtures, was persuasively confirmed by 30 years of successful commercial application in hundreds of installation worldwide. There are also a lot of other potential application areas for them.

Though some ideological stagnation is observed in this area during last decade, the reverse-flow concept still keeps the significant potential for

new developments and applications. In this respect, the most promising new approach is development of the sorption-enhanced reverse-flow processes, giving rise to new possibilities in performance of catalytic reactions and opening new degrees of freedom for creative chemical engineers.

ACKNOWLEDGEMENT

Author would like to express his sincere gratitude to Mrs. Maria Tione for the help with preparation of this manuscript.

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