European Roadmap of Process Intensification

- Technology Report -

TECHNOLOGY:
Gas – Solid – Solid Trickle Flow Reactors

TECHNOLOGY CODE: 2.2.3.3

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Table of contents

1. Technology

1.1 Description of technology / working principle

Gas – solid – solid trickle flow reactors (GSSTFR) are multiphase systems where gas flows counter-currently (or co-currently) to the stream of fine solid particles, through the second solids phase – packed bed. In literature those systems are named “gas – flowing solids – fixed bed contactors”, “raining packed bed contactors”, “solids trickle flow contactors” or similar.
The concept of contacting flowing solids and gas in fixed beds was patented nearly sixty years ago (Directie van de Staatsmijnen, 1948). First studies were carried out by Kaveckii and Plankovskii (1962). Subsequent research was devoted to experimental evaluation and mathematical modeling of two basic design parameters: pressure drop and flowing solids holdup. Further investigations included heat and mass transfer, as well as potential applications. Several advantages of this type of columns over the other gas – flowing solids systems were reported: low pressure drop, high heat and mass transfer rates, low axial mixing in both flowing phases, simple construction and operational flexibility.
In addition to their favorable characteristics, these columns can operate as multifunctional systems, where different processes are integrated in a single unit. The example for this kind of process intensification could be catalytic chemical reactors with adsorption *in situ.* The other example would be a heterogeneous chemical reactor with simultaneous heat transfer in a bed of catalyst. Westerterp et al. (1986, 1987, 1988) were first to propose this concept for methanol synthesis, where fine solids acted as regenerative adsorbent. According to their experimental data in mini-plant and full-scale model simulations, GSSTF principle for methanol synthesis would have a lot of potential for savings in energy, raw materials, etc.

1.2 Types and “versions”

Several types of gas – solid – solid trickle flow systems can be distinguished:

Type 1. Heterogeneous catalytic reactions with adsorption *in situ*:
This type of multifunctional reactors could be used for equilibrium catalytic reactions. In order to overcome the equilibrium negative effects, the reaction product is removed from the reaction zone by selective adsorbent. Fine adsorbent solids are trickling counter-currently to the gaseous reactant mixture inside of the fixed bed of catalyst. When the product is removed from the system, the driving force for forward reaction remains high. This could lead to the complete conversion of reactants, despite the thermodynamic limitations. The effects of increased conversion could benefit in energy and material savings.

Type 2. Heterogeneous catalytic reactions with heat transfer *in situ*:
This concept can be applied for highly endothermic or exothermic heterogeneous chemical reactions, where input or output of heat in the reaction zone is needed. For chemical reactors with fixed bed of catalyst, the heat supply / removal can be provided by flowing solid particles which act as a heat carrier. The phases flow co-currently; the gaseous mixture of reactants is introduced at the top of the column together with flowing solids, at the same temperature. Due to higher heat capacity of solids than the gaseous mixture, the temperature gradient along the reactor is small. Moreover, moving particles have a strong influence on the rate of heat and mass transfer rates in a catalyst bed.

Type 3. Heterogeneous reactions with flowing catalyst-adsorbent

This type is appropriate for equilibrium catalytic reactions where catalyst particles are flowing counter-currently to the gas. Catalysts particles also need to have a strong adsorbing capacity for the product. Thus, flowing solids are selectively adsorbing the reaction product immediately after it is formed on the surface. Because the product is removed from the reaction zone, forward reaction is favorable, providing higher conversion. In this case, fixed bed is inert, acting only as a distributor of the flowing particles and gas. Therefore, there is no limitation in geometry of the bed, so structuralized packing can be used. Regularly stacked packings can improve solids flow pattern and enable better conditions for heat and mass transfer.

Type 4. Additional – heat recuperation, adsorption, drying, etc.
Gas – solid – solid trickle flow principle can be used in various processes apart from chemical reaction: heat recovery, gas purification, drying. Because of their advantageous characteristics (listed above) these contactors can be used in chemical plants for optimization of energy utilization or gas pollutant control. In all those cases, gas and flowing solids are active phases, while the packing is inert. Thus, the use of structuralized packing is recommended, for the reasons described above.

1.3 Potency for Process Intensification: possible benefits

Table 1: Documented and expected benefits resulting from technology application

Benefit	Magnitude	Remarks
Energy savings	Up to 50% on cooling water; Up to 70% in recirculation energy *	For equilibrium catalytic reactors (*Type 1*), higher conversions (see further) result in minimization or even elimination of recycle loop (recycle rations in conventional systems are from 4 to 9). This could lead to savings in: • Energy for recirculation of the reactants; • Cooling water for the separation of reactants from products; • Feed-gas compression energy due to lower pressure drop in the reactor and raw material savings (see further).
Investment savings	No data available	For *Type 1* investments savings can result from: • Elimination of the compressor and the heat exchanger in recycle loop (see above); • Smaller condenser (after the reactor) because the pure product is condensed (see further about conversion); • Length of the reactor decreases because less catalyst bed is needed (see further); • Diameter of the reactor can be reduced, due to elimination of recycle stream. For *Type 2* cost savings can be established in: • Simpler constructions of the reactor since no additional internal heating system is needed (flowing solids are heat carriers).
Increased conversions	Up to 100% **	For equilibrium catalytic reactions (*Type 1 and Type 3*) removal of product from reaction zone increases conversion; even compete conversions of reactants in a single pass can be achieved (in conventional reactors equilibrium limitations allow much lower conversions).
Catalyst savings	From 40 to 70% *	For *Type 1*, higher specific reaction rates can be achieved (see above), thus less catalyst is needed. Percents vary for different reactions and designs of reactors.

Raw material savings	From 5 to 12% *	For *Type 1* consumption of raw materials can be decreased as no reactants are lost when gasses are purged in recycle loop (complete conversion).
Increased safety	No data available	Safety of systems can be increased due to: • Lower pressure used in equilibrium catalytic reactors, • Less equipment use (see above).

* Reported for methanol synthesis in GSSTFR and compared to conventional, but optimized process (Lurgi); based on model simulations for capacity of 1,000 t/d.

** Reported for methanol synthesis, both experimentally in mini-plant and theoretically by the model.

1.4 Stage of development

Despite the favorable properties and potential for commercial benefits, the development of GSSFTR is still in an early stage. Several university groups (see 4.3) developed ‘small pilot’ systems, whose capacities placed them more in the class of laboratory-scale equipment. Some university groups experimentally examined the possibilities of GSSFTR *Type 1, 2* and *3* for particular applications (see 2.4), while the others investigated only transport phenomena. Nevertheless, the development of commercial scale units was carried out only for the *Type 4*, specifically for the GSSFT heat exchangers (see 2.2), which are not the major representatives of the Technology described. According to the available information, there aren’t any companies working on the development of gas – solid – solid trickle flow reactors on commercial scale.

2. Applications

2.1 Existing technology (currently used)

The annual world production of bulk chemicals like ammonia and methanol is extremely large. Those substances are being converted from raw materials in well known conventional processes, which have not been changed fundamentally in the past century. The nature of these equilibrium catalytic reactions demands high energy consumption and strict safety procedures. Low conversion of reactants per one pass, high recycle rates, large energy demand in separation and recycle sections, operation under high pressure and temperature, are all common and non-desirable characteristics of classical processes. Despite of the high energy integration and optimization in modern plants, the specific energy has not been reduced radically.
In the other example, dehydrogenation of hydrocarbons is a frequently operating process in petrochemical industry. These catalytic reactions are endothermic, thus internal heating is required. Large number of developments is dedicated to optimization of heat supply for these heterogeneous catalytic reactors. Even though good design of classical processes was achieved, so far no breakthrough in heat supply has been announced.

2.2 Known commercial applications

There are no commercial applications reported for gas – solid – solid trickle flow reactors, for Technology *Types 1, 2* and *3* (see 1.2). There are commercial realizations only for the Technology *Type 4*, which represents additional equipment besides the chemical reactors. One of the examples is heat exchangers presented 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
Large volume chemicals	Saint Gobain and Tunzini Nessi Enterprises d'Equipment - SATURNE	Two GSSTF heat exchangers recuperating the heat from fluidized bed combustion zone for the reclamation of used foundry sand	Sand flow rate: 3-4 t/h; unit inside diameter: 1.6 m	1979	• Complete heat recovery with one unit before and one after the combustion zone; • No need for supplemental fuel consumption when sand contains >1% of organic binders; • No organic pollutants from the process.

2.3 Known demonstration projects

No demonstration projects on gas – solid – solid trickle flow reactors are known.

2.4 Potential applications discussed in literature

Potential applications presented in the open literature are grouped under technology types:

Type 1. The main examples of products which are synthesized in heterogeneous catalytic equilibrium reactions, and could benefit from process intensification described here, are methanol and ammonia. The ammonia synthesis under GSSTF concept has not been researched so far, though principles have been patented (US4731387, see 4.2). The methanol synthesis had been investigated experimentally and theoretically in the group of Prof. Westerterp at Twente University of Technology, Netherlands (see 4.1). The small-scale system consisted of three tubular packed bed reactors in series with intermediate cooling. Recently, researches from University of Santander, Colombia, have proposed the use of GSSFTR principle for catalytic partial oxidation of methane to methanol. They have simulated the reactor in order to allocate the optimal conditions and constructions, still no experimental research was reported (see 4.1). This principle could be applied on a variety of equilibrium reactions with fixed bed of catalyst, for what new research would have to be established.

Type 2. Heat supply by flowing particles for endothermic catalytic reactions has been proposed for dehydrogenation of hydrocarbons. Research group in Boreskov Institute of Catalysis, Russia, has patented this intensified process for particular hydrocarbon applications (RU2178399, see 4.2). Research papers on applications from Boreskov Institute have not been published, apart from fundamental studies of particles flow through porous media (see 4.1). The presented concept can be easily applied on various processes with fixed beds, with necessary internal heating or cooling.

Type 3. Several applications of processes with catalyst-adsorbent particles trickling through regularly stacked beds were discussed in the literature. Verver and Van Swaaij (1987) from Twente University of Technology studied the catalytic oxidation of hydrogen sulfide to sulfur in gas – solid – solid trickle flow reactor. Flowing solids were NaX and NaY zeolites which acted both as catalysts and adsorbents (see 4.1). Kiel and Van Swaaij (1992) investigated removal of sulfur oxides and nitrogen oxides from flue gases in a GSSTF reactor. Silica supported copper oxide particles acted as adsorbents and catalysts for the selective catalyst reduction of NOx (see 4.1). Other processes with combined reaction and adsorption for environmental applications could be considered.

Type 4. In a number of chemical processes heat recovery can be realized in gas – solid – solid trickle flow contactors, where particles operate as heat carriers, flowing counter-currently to the gas through structuralized packing. For example, particles can be preheated by used gases, or feed gases can be preheated by hot particles from the main process. Large, Guigon and co-workers from Université de Technologie de Compiegne, France, investigated GSSTF heat exchangers and collaborated with companies Saint Gobain and Tunzini Nessi Equipment in development of commercial-scale equipment (see 2.1, 4.1 and 4.2). The exchangers have been used in production of glass and metal silicates, or for heat recuperation in foundry sand reclamation system. GSSTF contactors as heat exchangers, adsorbers, dryers can be efficiently exploited in a wide range of chemical processes.

3. What are the development and application issues?

3.1 Technology development issues

Table 4. Technology development issues

Issue	Description	How and by whom should be addressed?
Pilot-plant scale development	New developments of GSSTF reactors are needed on a pilot-plant scale, as the existing systems are too small to be representative for commercial issues. Experiments from pilot-plant for particular applications would be the basic source of data for the scale-up.	R&D projects carried out at universities, in collaboration with companies from the interest sectors.
Modeling and simulation	Fundamentals of multiphase flow dynamics and flow pattern are fairly well described by mathematical models from open literature, while there is a need for model improvements in heat and mass transfer subjects. Integrated models and simulations of whole processes for potential products should be generated with a help of innovative computer tools.	R&D projects carried out at universities, in collaboration with companies from the interest sectors.
Scale-up and design concepts	Scale-up issues were not discussed so far, so new R&D projects regarding the matter should be launched. New design concepts should be considered, especially for the solutions of flowing solids recycle loops.	R&D projects carried out at universities, in collaboration with companies from the interest sectors.
Design of packing/catalyst	Designs of structuralized packing with catalytic activity, which would enable preferable solids	R&D projects carried out at universities, in

	flow pattern and low pressure drop, should be involved in overall design.	collaboration with companies manufacturing the catalysts.
Adsorbent selection	Accurate adsorbent selection, even targeted adsorbent design, which would well facilitate the process requirements, is a development task (for *Types 1* and *3*).	R&D projects carried out at universities, in collaboration with companies manufacturing the adsorbents.
Control systems	Complex dynamics of these multiphase and multifunctional reactors need to be researched more in order to develop reliable and predictive control systems.	R&D projects carried out at universities, in collaboration with companies from the interest sectors and process control sector.

3.2 Challenges in developing processes based on the technology

Table 5. Challenges in developing processes based on the technology

Challenge	**Description**	**How and by whom should the challenge be addressed?**
Flowing solids handling	Design of efficient system for continuous regeneration and recycling of flowing solids under high pressure and temperature is one of the major challenges. Large investment costs for vessels and other transport equipment in this section can place the whole concept in the profit range of the conventional plants. For this reason optimal (or new conceptual) design and handling of flowing solids system is of primary concern.	R&D projects on engineering, design and scale-up (pos. 1, 2 and 3 in Table 4)
Adsorption conditions	Conditions of high temperature which are usual for processes under consideration (*Types 1* and *3*), are not favorable for the adsorption processes. Therefore, selection of a proper adsorbent or/and catalyst could sometimes be a challenging task, which has to be performed carefully.	
Adsorbent / heat carrier regeneration and reuse	Described GSSTFR technology can be fully profitable if the flowing solids, which act as adsorbents (*Type 1* and *3*) or heat carriers (*Types 2* and *4*), are reused in processes. Continuous regeneration of solids often implies frequent thermal and mechanical shocks which can degrade the particles. Improvement and new materials design of robust solids which would keep desirable activity for many recycle loops, is particularly challenging task for engineering of materials.	R&D projects on material improvements, design and testing. Collaboration between different university groups and manufacturing companies (pos. 5 in Table 4)
Control	Solids flow rate is very important operational parameter of GSSTFR. Small disturbance of it may cause serious impact on reactor performance. Therefore, attention has to be paid on proper solids flow control. Uniform distribution of particles in fixed bed can be a challenge for control system as well.	R&D projects on process dynamics and control (pos. 6 in Table 4)

4. Where can information be found?

4.1 Key publications

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Kaveckii, G. D., Planovskii, A. N., 1962, Flow Study of Solids in Up Flowing Gas in Packed Columns (In Russian), Khim. Teknol. Topl. Masel. 11, 8-12	Research paper	First paper in the field
Roes, A. W. M., van Swaaij, W. P. M., 1979, Axial Dispersion of Gas and Solid Phases in a Gas – Solid Packed Column at Trickle Flow, Chem. Eng. J., 18, 13-28	Research paper	Flow dynamics and flow pattern
Le Lan, A., Niogret, J., Large, J. F., McBridge, J. A., 1984, Use of RPBE in an Efficient Foundry Sand Reclamation Unit, AIChE Symposium Series, 80 (236), 110-115	Research paper	Applications – *Type 4*
Guigon, P., Large J. F., Molodstof, Y., 1986, Hydrodynamics of Raining Packed Bed Heat Exchangers, In *Encyclopedia of Fluid Mechanics*, Cheremissinoff, N. (ed.), Gulf Publishing Co., Houston, 1185-1214	Book chapter	Review – Flow dynamics
Verver, A. B., van Swaaij, W. P. M., 1987, The Gas Solid Trickle Flow Reactor for the Catalytic Oxidation of Hydrogen Sulphide: A Trickle-Phase Model, Chem. Eng. Sci., 42, 435-445	Research paper	Applications – *Type 3*
Westerterp, K. R., Kuczynski, M., 1987, A Model for a Counter-current Gas-Solid-Solid Trickle Flow Reactor for Equilibrium Reactions. The Methanol Synthesis, Chem. Eng. Sci., 42, 1871-1885	Research paper	Applications – *Type 1*, modeling
Kuczynski, M., Oyevaar, M. H., Pieters, R. T., Westerterp, K. R., 1987, Methanol Synthesis in a Countercurrent Gas-Solid-Solid Trickle Flow Reactor. An Experimental study. Chem. Eng. Sci., 42, 1887-1898	Research paper	Applications – *Type 1*, experimental
Westerterp, K. R., Bodewes, T. N., Vrijiland, M. S., Kuczynski, M. A., 1988, Two New Methanol Converters. Hydrocarbon Processing, Int. Ed. 67 (11), 69-73	Research paper	Applications – *Type 1*, economical evaluation
Kiel, J. H. A., Prins, W., Van Swaaij, W. P. M., 1992, Modelling of Non-Catalytic Reactions in a Gas-Solid Trickle Flow Reactor: Dry, Regenerative Flue Gas Desulphurization Using a Silica-Supported Copper Oxide Sorbent, Chem. Eng. Sci. 47, 4271-4286	Research paper	Applications – *Type 3,* modeling
Nikačević N. M., Duduković A. P., 2005 , Solids Residence Time Distribution in Gas-Flowing Solids-Fixed Bed Contactors, Ind. Eng. Chem. Res., 44 (16), 6509- 6517	Research paper	Flow pattern and contacting
Duduković A. P., Nikačević N. M., 2005, Gas-Flowing Solids-Fixed Bed Contactors, In *Finely Dispersed Particles: Micro-, Nano-, and Atto-Engineering,* Aleksandar Spasić, Jyh-Ping Hsu (eds.), CRC Taylor and Francis Inc., New York,	Book chapter	Comprehensive review – Flow dynamics, heat and mass transfer, potential

567-600		applications
Matveev, A. V., Barysheva, L. V., Koptyug, I. V., Khanaev, V. M., Noskov, A. S., 2006, Investigation of fine granular material flow through a packed bed, Chem. Eng. Sci., 61 (8), 2394-2405	Research paper	Recent paper – Flow studies by NMR technique
Wen, D., Ngoc Cong, T., He, Y., Chen, H., Ding, Y., 2007, Heat transfer of gas-solid two-phase mixtures flowing through a packed bed, Chem. Eng. Sci., 62 (16), 4241-4249	Research paper	Recent paper – heat transfer experiments
Dallos, C. G., Kafarov, V., Filho, R. M., 2007, A two dimensional steady-state model of the gas-solid-solid reactor. Example of the partial oxidation of methane to methanol, Chem. Eng. J., 134 (1-3), 209-217	Research paper	Recent paper – simulations, *Type 1*

4.2 Relevant patents and patent holders

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
FR978287: Procédé pour augmenter la concentration des particules solides dans un courant de milieu gazeux (LU29320, BE486551)	DIRECTIE STAATSMIJNEN	First patent – general principles
FR1469109: Method of making silica bonded to sodium metasilicate (US3503790, NL6617478, LU52679, ES334951, DE1596383)	SAINT GOBAIN	Products: glass and metal silicates *Types 2, 4*
FR2452689: Method of recuperating heat from a current of warm gas and apparatus for carrying out the method (EP0016713, US4369834, JP56000990, ES8100835)	SAINT GOBAIN, TUNZINI NESSI EQUIP.	*Type 4*
US4731387: Process for carrying out a chemical equilibrium reaction (EP0218285, JP62084031)	SHELL OIL CO.	Products: methanol, ammonia *Types 1, 2*
RU2178399: Method of catalytic dehydrogenation of hydrocarbons	BORESKOVA INST. KATALIZA	Products: hydrocarbons *Type 2*

4.3 Institutes/companies working on the technology

Table 8. Institutes and companies working on the technology

Institute/Company	Country	Remarks
Twente University of Technology (K. R. Westerterp, W. P. M. Van Swaaij, …)	Netherlands	Wide range of research, fundamentals and applications, *Types 1* and *3* (non-active, no publications since 1993).
Université de Technologie de Compiegne (J. F. Large, P. Guigon, …)	France	Focused on fundamentals and applications in heat transfer, *Type 4* (non-active, no

		publications since 1994).
Boreskov Institute of Catalysis (A. S. Noskov, L. V. Barysheva, …)	Russia	Focused on particle flow analysis and applications in *Type 2.*
University of Belgrade (A. P. Duduković, N. M. Nikačević, …)	Serbia	Focused on flow pattern and flow dynamics
University of Novi Sad (D. Dj. Petrović, Z. J. Predojević, …)	Serbia	Focused on flow dynamics
University of Leeds (Y. Ding, Y. He, …)	UK	Focused on heat transfer and flow dynamics
University of Santander (C. G. Dallos, V. Kafarov)	Colombia	Recently started, simulations, *Type 1*

5. Stakeholders

5.1 Suppliers and developers

No suppliers or developers of commercial-scale gas – solid – solid trickle flow reactors are known.

5.2 End users

Potential end users are companies working in the large-volume chemicals sector, as well as in the petrochemical sector.

6. Expert's brief final judgment on the technology

Gas – solid – solid trickle flow reactors exhibit different potential for process intensification in a production of bulk chemicals and petrochemicals. As the production rates of targeted chemicals are enormous, even minor improvements according to described concept can lead to a great energy savings and cost benefits on the global level. The development of GSSTF reactors remains in an early stage, and new R&D projects are needed to include the complete scale-up process and engineering, with a special attention to the design of optimal solids recycle system. A list of potential applications should be extended, with consideration to new products, along with the ones described in literature. Furthermore, interdisciplinary projects involving materials engineering should be initiated for the improvement or development of novel adsorbents (and structuralized catalyst packing) which would attain particular conditions in reactors and properties for continuous solids reuse.