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Modern State and Perspectives of Microtechnique Application in Chemical Industry

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Abstract—A brief review of application of microtechnique, design and technologies of its manufacturing, methods of process intensification, and use for diagnostic purposes is presented. The main physical factors promoting heat- and mass-transfer intensification are described.

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INTRODUCTION

The vigorous progress of nanotechnologies in 1990s generated increasing demand for quite a small-scale equipment, specifically micro- and minitechniques. The advent of microdevices dates back to 1970s and is associated with the development of microelectromechanical systems (MEMS). At present it is safe to declare the appearance of a new type of equipment for many industries – microsystem technique. According to the definition in [1], the microsystem technique is a complex of scientific technical and engineering tools for creation in the bulk and/or surface of a solid body of an ordered ensemble of micron- or submicron-sized domains of materials with a preset composition, structure, and topology and serving for fulfilling the functions of receipt, transformation, storage, processing, and translation of information, energy, motion, as well as generation of control actions in the required regimes and operation conditions.

The principal element of a microsystem is a functional microdevice inseparately linked to the system constructively, electrically, and mechanically and providing fulfillment of a preset function.

In terms of the operation principle and fulfilled function, the following types of functional microdevices are recognized [1]: electromechanical; optoelectromechanical; thermophysical; fluidic; biotechnical; microengines; microdrives; and microactuators.

Functional characteristics of chemical engineering are fulfilled by thermophysical, fluidic, and biotechnical microdevices.

The function of thermophysical microdevices in chemical engineering is to accumulate thermal energy in microvolumes and transform it, sometimes reversibly, into other forms of energy.

Fluidic microdevices function to localize, transfer, separate, and store micro and nano quantities of fluids or gases, and also provide their physicochemical transformation under the action of external electrical, magnetic, optical, mechanical, thermal, and chemical factors.

Biotechnical microdevices fulfill actuation functions due to integration with biological objects and substances.

Along with a functional device, microsystems include micro hangers, microarms (single- and double-support), microdrives, microtransmissions, microreducers, microplungers, microtorsions, microgears, microlevers, microclips, microtweezers, microsprings, microfly wheels, microvalves (microdumpers), micro - nozzles, microthrottles, micropumps, microreactors, microchannels, etc.

The elements of microsystemic technique most important in terms of chemical engineering are the following.

Microvalve (microdumper) controls fluid, steam, and gas flow rates by varying the passage cross section.

Micropump fulfills the function of controlled forced transfer of microvolumes of fluids, steam, or gases under the action of energy imparted to them.

Microreactor is a component of a microsystem, where controlled chemical reactions occur.

Microchannel serves for controlled transfer of fluids in microvolumes.

Vigorous progress of microsystem technique dates back to 1990s. Thus, drives 5 and 3 mm in diameter were developed in 1997 for application in medical practice and microrobots (for example, in micro-helicopters), and at present microengines and micro-reducers (including multistep ones with gear ratios of up to 80) 1.9 mm in diameter have been developed [2]. In these devices, the gear wheels of separate steps are no larger than 0.5 mm in diameter, and their gear modulus is 30−40 μm. The scaling effect in MEMS is associated with close characteristic dimensions of structural components of material of details, details themselves, and water layers adsorbed on their surface [2]. For example, the gear modulus of super-miniaturized gear wheels compares in size with the size of supramolecular structures and reinforcing phases of polymer composites, used for fabrication of these details.

As noted in [1], the dominating forces in microsystems, due to their small size (micrometers and smaller), are surface forces proportional to the second degree of size (capillary, electrostatic, and viscous friction forces), rather than volume forces (inertia and gravity forces) proportional to the third degree of size. Moreover, the volume and surface properties of micro-objects differ from those of macroobjects. For example, the strength and friction parameters of micro-objects differ from those in the macroworld, and, therefore, the changed properties of microobjects and efficiency of action on them are thoroughly accounted for in designing microdevices.

More and more R&D effort in the field of micro-systems focuses on microelectronic sensor systems [3].

Mini- and Microtechnique in Chemical Engineering

Over the past two decades a high emphasis has been placed on development of mini and microtechnique for chemical engineering applications [4–6]. The greatest progress has been reached in micro-pumps, microvalves, micromixers (for liquid−liquid systems), micro eat exchangers, microextractors, and microreactors.

Let us first of all focus on the terms “mini technique” and “microtechnique.”

The characteristic cross-section of microchannels varies from 10 μm to 1−3 mm (rarely up to 4−5 mm). Some authors suggest to differentiate between the micro and mini scales, but still there is no clear and substantiated criterion of the borderline between the scales. Analysis of numerous publications allowed the lower channel cross-section limit to be set at ~10 μm. Further decrease in size not only increases the hydraulic resistance and decreases the device performance, but also gives rise to scaling effects associated with the enhancement of viscous and surface forces, as well as with a change of media properties in the submicron region. Moreover, the fabrication technologies of microchannels (etching, micromechanical processing, laser ablation, selective laser melting), too, have their natural limita-tions. The surface roughness of microchannels spans the range from tens to a few micrometers [13], which compares with the cross-section of the channels. The fabrication cost considerably increases with decreasing size of the device. Thus, the cross-section of 10 μm has become a kind of the lower limit. At the same time, the development of nanodevices has recently been reported in the scientific literature [14, 15] (their review can form the subject of a separate paper).

Let us now pass to consideration of certain com-ponents of microtechnique for chemical engineering.

The operation of mini and micromixers is based on the following physical principles [4]:

– for active mixing (use of an external power source): ultrasound; acoustic oscillations; electrokinetic instability; periodic flow pulsations; electrically induced droplet coalescence; piezoelectric membrane oscillations; mag-netohydrodynamic action; microim-pellers; integrated microvalves and micropumps;

– for passive mixing (use of the fluid pumping power): interdigital multilamellae flow; split-and recombine principle; chaotic mixing by eddy formation and folding; nozzle injection in flow; jet collision; special methods, for example, the Coandă effect.[1]

– German companies developed glass modular micro mixers with performances varying from 10 to 1000 l/h (mikroglas chemtech, Mainz) and stainless-

[1] The tendency of a fluid jet flowing from the nozzle to deflect toward the wall (under certain conditions, the jet can adhere to the wall). This phenomenon is explained by the fact that the side wall prevents free air inlet at one side of the jet, thus creating conditions for vortex and low-pressure zone formation.

steel modular micromixers with performances varying from 100 to 10000 l/h (IMM, Mainz). Both types of micromixers operate by the principle of splitting the fluid stream into thin lamellae and their subsequent recombining. Efficient mixing is reached due to shorter diffusion distances and higher shear strains. The Research Center Karlsruhe (Forschungszentrum Karlsruhe, FZK) developed a micromixer with distributed tangential component injection, as well as a line of micromixers analogous to static macro-scale mixers.

Micro heat exchangers and technologies of their fabrication from metals, ceramics, and glass were first developed in 1980s at the FZK and later in Ilmenau (Germany) [13].

Micro heat exchangers are able to transfer energy from one liquid medium to another (cross-flow heat exchangers), as well as from electrical microheaters to liquids and gases. In the first case, the apparatus represents a stack of pressure-welded plates which have longitudinal microchannels (100×100 μm^2) on one side. Thus formed block contains two networks of channels, which are at the right angle to each other. The block is mounted into a cage with Swagelok gaskets providing hermetic connection to metal pipes. Figure 1 shows a photograph of a $20\times20\times20$-mm^3 micro heat exchanger capable of transferring the thermal power of up to 50 kW.

The technical characteristics of FZK cross-flow micro heat exchangers are as follows:

– channel dimensions: 100×70 μm^2, 200×100 μm^2, 200×200 μm^2, etc;

– specific internal surface area up to 30000 m^2/m^3;

– heat transfer coefficient up to 20000 W m^{-2} K^{-1};

– working pressure ≥ 100 bar;

– leakage (by He) 10^{-8} mbar l^{-1} s^{-1};

– thermal stability up to 850°C;

– materials: stainless steel (DIN 1.4301, 1.4435), hastelloy, etc.

The other type of micro heat exchangers constitutes a solid body with microchannels and holes for tubular thermoelectric heaters (the FZK micro heat exchanger can accommodate up to 15 such heaters 1 kW each).

The technical characteristics of micro heat exchangers with thermoelectric heaters are as follows:

– production of hot water (45°C) at the input power of 14 kW and the flow rate of ~6 l/min;

Fig. 1. General view of the micro heat exchanger $20\times 20\times 20$ mm^3 in dimensions (Ehrfeld Mikrotechnik, Germany).

– complete water evaporation at the flow rate of 5 l/h;

– heating of air stream within 1 ms from 25°C to 850°C at the input power of 400 W and the volume flow rate of 2000 l/h;

– heat transfer coefficient (for water) 17500 W m^{-2} K^{-1};

– efficiency > 90%;

– maximum electric power 15 kW;

– pressure drop 100 mbar at the water flow rate of 5 l/h;

– channel dimensions $95\times30\times35$ mm^3.

The central element in a micro-scale chemical engineering system is the microreactor.

The idea of microreactors was first implemented in mid-1970s by the development of catalytic converters for single-phase systems (purification of motor vehicle exhaust gases, selective catalytic reduction of NO_x, catalytic combustion systems in power engineering).

Horvath et al. [7] are likely to be the first to assess process intensification in microreactors in their research on a biochemical reaction in slug flow (enzymes were immobilized on the channel walls). Application of monolithic catalysts in heterogeneous catalytic processes in the gas-solid surface system was studied in 1980s. The pioneering research at the Chalmers University of Technology (Sweden) related to hydrogenation of nitroaromatic compounds [8, 9], 2-ethylhexenal [10], anthraquinone [11], and thiophene and dibenzothiophene [12].

At present microreactors are finding growing application in chemistry, petrochemistry, and bioengineering [16]. The fields of the most active chemical and biochemical application of micro-

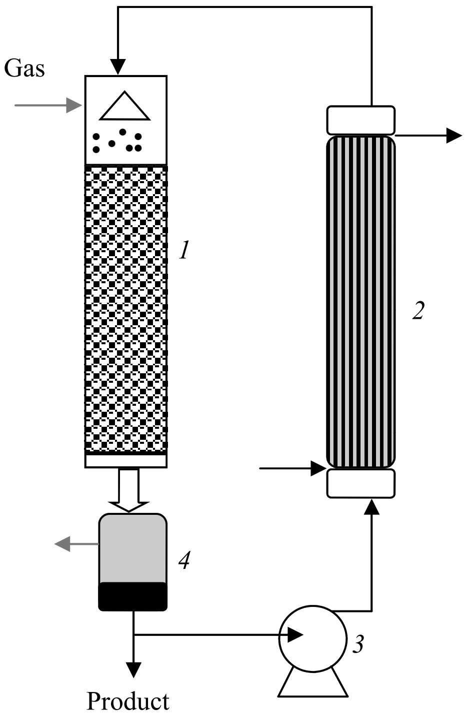

Fig. 2. Process scheme in a gas–liquid monolithic microreactor [16]: (*1*) monolith; (*2*) heat exchanger; (*3*) pump; and (*4*) gas–liquid separator.

technique include fine organic synthesis, production of hydrogen-containing gases, bioengineering processes, pharmacy, nanoparticle synthesis in microreactors, and catalyst screening.

The performance of a microreactor is fairly low. But a reactor complex comprising a great number of microreactors operating at high flow rates of media can compare in performance with traditional equipment. Moreover, mini- and microscale equipment offers essential advantages in certain characteristics. A size decrease (reaction channel length $L \sim 10^1$–10^3 mm, channel cross section $d \sim 10$–10^3 μm, wall/film thickness $d \sim 20$–50 μm) entails the following effects:

(1) high heat transfer coefficients, up to 20 kW $m^{-2} K^{-1}$;

(2) narrow residence time range, which ensures high reaction selectivity; when necessary, say, at a small volume of reaction chamber, extremely short residence times can be reached ($\leq 10^{-3}$ s);

(3) low hydraulic resistance due to a low channel length and a laminar flow regime;

(4) increased specific surface area (10000–50000 m^2/m^3 against $\geq$1000 m^2/m^3 in usual reactors);

(5) highly enhanced transverse temperature and concentration gradients (due to a smaller channel cross sections);

(6) intensified mass transfer in heterogeneous media (circular mixing in Taylor flow);

(7) sharply reduced dimensions of devices, reduced metal consumption;

(8) reduced risks of small-scale experiments with toxic and explosive materials.

The shorter residence time makes it possible to (1) en-hance reaction selectivity and process safety and (2) pass to a continuous process.

The paralleling of flows in mini- and microdevices makes it possible to (1) enhance process flexibility; (2) facilitate research; and (3) use the modular principle; moreover, the problems of scaling are avoided.

Mini and microdevices can make serious competition to normal chemical equipment in certain laboratory and industrial applications.

Example applications of monolithic reactors [17]

Reaction	Active component/support	Fluid and gas flow directions
Hydrogenation of anthraquinone	Silica	Downward
Hydrogenation of α-methylstyrene	1.8 wt % Pd / γ-Al_2O_3	″
Oxidation of cyclohexanone	Carbon	″
Oxidation of glucose and cellulose	0.26 wt % Pt / Al_2O_3	Upward
Hydrogenation of but-2-en-1,4-diol	1.0 wt % Pd / α-Al_2O_3	Downward
Hydrogenation of nitroaromatic compounds	Co–Mo / γ-Al_2O_3	″
Hydrogenation of vegetable oils	2.0 wt % Pd	″
Biological decomposition of quinoline	*Burkholderia pickttii*	Upward

(1) Laboratory measurements in microdevices feature a higher precision. For example, when sampling is performed continuously, one of the problems is to preserve identity of the sample (the problem of longitudinal mixing). The use of an inert gas (or fluid) to separate fluid slugs in the capillary tube from one another (Taylor flow) virtually excludes mixing and favors sample identity [21].

(2) Production of substances and materials (including nanomaterials) in microdevices allows fine dosing of reagents, as well as fast and efficient mixing in small volumes [22].

(3) Microtechnique can be mounted in mobile devices (reduced mass-dimensional parameters).

(4) Microdevices in the large-scale chemistry can serve for improving certain parameters: provide better mixing, enhance heat- and mass-transfer efficiency, increase reaction selectivity and yield, and decrease process time [4–6]. Therewith, the high performance is reached due to very high flow rates of media in mini- and microchannels (≥100 m/s), as well as a large number of parallel channels [17, 19]. Note that the laminar flow in microchannels is preserved even at such high flow rates (!), thus ensuring very low mechanical energy losses of the fluid.

Quite a promising alternative to conventional slurry- or fixed-bed catalytic reactors are so-called structured reactors with a monolithic catalyst [16, 17] (Fig. 2, see table).

To illustrate the efficiency of certain microreactors, we would like to present below the specific yields of the product of direct fluorination of toluene, mol $m^{-3} h^{-1}$: falling-film microreactor (FFMR) ~35000, microbubble column (MBC) ~120000 (see Fig. 3), and laboratory bubble column (LBC) ~20 [18]. Thus, the specific product yields in the above microreactors are 2−3 orders of magnitude higher than in reactors of other types.

Problems of Chemical Microtechnique

Even though a number of microreactors for work with microparticles (for example, fixed-bed catalytic microreactors or microjet reactors for nanoparticle production by precipitation with gas purging of the suspension have been developed) microdevices in general are hardly suitable for processing fluids and gases with solid inclusions in view of the risk of rapid clogging.

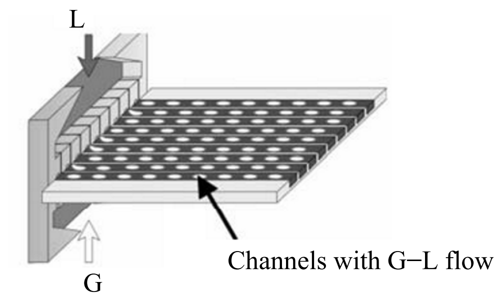

Fig. 3. Scheme of a multichannel gas-liquid column [19]: (L) liquid and (G) gas.

The performance of microdevices can be much deteriorated by the pulsation of flow, which occurs when the fluid is supplied by conventional pumps. At present pumps with reduced flow pulsation have been developed, and attempted use of electroosmotic pumps has been reported.

The problem of uniform phase distribution among a great number of microchannels (this number can reach a few tens of thousands) has not yet been solved, as evidenced by high-speed tomography (Helmholtz-Zentrum Dresden-Rossendorf).

Obviously, processing extra viscous media in microdevices will enhance pressure drop (linearly) and power consumption (quadratically). At the same time, many processes occur at high temperatures, when fluids are much less viscous, and, therefore, this limitation is rarely of primary importance.

Microreactors are best suited for comparatively low-performance technologies (≤5000 l/h) and residence times no longer than 5–20 min (longer residence times adversely affect performance, entail the demand for longer channels, and enhance pressure drop).

At the same time, the sharp growth of the number of research works and patents in the field of chemical mini and microtechnique is a serious indicator to predict an escalating demand for this high-performance and power-saving equipment in the near future.

The present issue of the Journal highlights the theoretical and applied aspects of chemical microtechnique. The increased interest of researchers to microsystem technique and its application in various industries, and, in particular, chemical engineering, manifests itself in the diversity of subjects the papers in this issue deal with. These are the organic syntheses and direct synthesis of hydrogen peroxide in microreactors, microscale distillation, application of microchip-based systems for molecular genetic analysis, study of chemical kinetics, thermal lens detection, modeling hydrodynamics and mass transfer, and intensification of heterogeneous processes in microreactors.

CONCLUSIONS

Microtechnique, which was considered a fairly specific field of science and technics as little as two decades ago, is presently finding expanding application. Microdevices offer essential advantages over traditional equipment, primarily in small-scale manufacturing industries, but, they are not free of certain limitations. Apparently, we can expect ever-growing use of microtechnique in research, fine organic synthesis, pharmaceutics, and especially express analysis.

In Russia this quite an important problem is studied in only a few institutions, including Boreskov Institute of Catalysis, Institute of Analytical Instrumentation of the Russian Academy of Sciences, St. Petersburg State Technological Institute (Technical University).

The goal of the present issue of the Journal is to attract attention of interested organizations both in collaborative research and in gradual commercialization of this up-to-date and perspective equipment.

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