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MODELLING OF THE LIQUID FLOW IN THE MICROREACTOR

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МОДЕЛЮВАННЯ ПОТОКУ РІДИНИ В МІКРОРЕАКТОРІ

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МОДЕЛИРОВАНИЕ ПОТОКА ЖИДКОСТИ В МИКРОРЕАКТОРЕ

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Microstructured reactors (MSR) open a new perspective to chemical technology and reaction engineering offering a better process control. Computational fluid dynamic simulations provide insight into liquid-phase systems. In the present work, processes and products implemented for commercial production with the help of MSR is presented. The practical examples confirmed an economic potential of microreactors scaling-up strategy.

Keywords: *microstructured reactor; computational fluid dynamics; liquid-phase system; microchannel*

Мікроструктурні реактори (МСР) відкривають нові перспективи для хімічної технології за рахунок широких можливостей управляння виробничим процесом. Моделювання динаміки руху потоків рідини в ректорі дозволить повноцінно описати рідинні системи. В даній роботі представлено огляд процесів та продуктів, реалізованих з допомогою МСР в комерційних цілях. Економічний потенціал впровадження мікрореакторів у масштабне виробництво підтверджено практичними прикладами.

Ключові слова: *мікростурний реактор; розрахункова гідродинаміка; рідкофазна система; мікроканал*

Микроструктурные реакторы (МСР) открывают новые перспективы для химической технологии за счет широких возможностей управления производственным процессом. Моделирование динамики движения потоков жидкости в ректоре позволит полноценно описать жидкостные системы. В данной работе представлен обзор процессов и продуктов, реализуемых с помощью МСР в коммерческих целях. Экономический потенциал внедрения микрореакторов в масштабное производство подтверждено практическими примерами.

Ключевые слова: *микростурний реактор; расчетная гидродинамика; жидкофазная система; микроканал*

Introduction

Microreactors as a novel concept in chemical technology enable the introduction of new reaction procedures in chemistry, molecular biology and pharmaceutical chemistry [1]. Potential advantages of microstructured reactors (MSR) allow successfully use them to liquid-phase processes such as solvent extraction, reactive extraction, nitration, polymerization, and phase transfer catalysis [2]. These processes are limited by heat and mass transfer. Microreactors offer several opportunities to optimize the reaction systems due to high specific interfacial area improving heat and mass transfer. Apart from this features, the smaller working volumes, continuous mode of operation, efficient operation, low wastage of chemicals and intrinsic safety are some of the important advantages of the microreactors. More details about the reaction transformation, parameters of the process, the definition of characteristics of the input and output products, etc. can be obtained by modelling.

Computational modeling is the important tool for the investigation of microreactor systems. Detailed simulation studies conducted by various researchers have provided important insights to the reaction behavior in the microsystem environment [3]. Comparison of performances in theoretical and practical experiments has been presented in the literature for different types of reactions in a laboratory or industrial scale [4] [5].

As for liquid reactions, their modeling has been presented only in a few studies and related to certain processes. Thus, the performance of flow distribution in a capillary microstructured reactor has been investigated in [2] by means of CFD simulations. However, the topic of the modelling has been numbering-up of the MSR, but not the receiving of information about the reaction transformation. In another paper has been discussed a volume of fluid (VOF) based CFD methodology to investigate the slug flow generation in a T-type mixing element considering the wall film [6]. The simulations carried out for different channel dimensions showed the range of changing for the channel diameter to achieve a slug flow generation in the microstructured reactor. But the variation of input materials ratio and characteristics of operation conditions on the slug size ought to be researched.

So, the literature shows a very few studies addressing the physicochemical mechanism of liquid-liquid processes which is not enough for the forming of a holistic picture of the fluid-phase reactions in a microvolume of the MSR.

The purpose of this article is to analyze the approaches to modeling the liquid-liquid reactions; to study the simulation results of various numerical methods and to review the appropriate software environments; to evaluate the potential benefits of microdevices for commercial application.

Mass transfer in liquid–liquid systems

Various experimental techniques for flow characterization, visualization and sensing are described in the literature [6] [7]. The observed flow pattern is the result of a complex interplay between interfacial, gravitational, viscous and inertia forces [8]. In practice, these forces are determined by the geometry of the flow mixer, the physical properties of the fluids and the chosen operating conditions such as the relative flow rates of the fluids. Most studies take advantage of flow regimes in which the two phases are segregated. For example, slug-flow and parallel flow as two stable flow regimes in the MSR with two immiscible fluids have been discussed in [2]. This study gives evidence that the enhanced performance is observed in the slug-flow due to two mass transport mechanisms: convection through the internal circulation within each slug and diffusion between adjacent slugs. The shear between the capillary wall and slug axis generates intense internal circulations within the slug, which in turn reduces the thickness of interfacial boundary layer and thereby augments the diffusive penetration. More detailed classification has been proposed by M. N. Kashid et al. in [7]. Authors considered such flow regimes as drop, slug, slug-drop, deformed interface, annular, parallel and dispersed flow.

Mixing is a critical issue in the design of liquid-phase microreactors. The small dimensions in microfluidic devices imply small Reynolds numbers and laminar flow so that mixing occurs by diffusion. This characteristic becomes both a challenge and an advantage for liquid-phase reaction systems. The slow mixing of co-flowing streams offers additional opportunities for phase transfer reactions and separation devices, and it can be exploited in novel fabrication schemes [9].

Thus, a precise investigation of slug size and interfacial area is required to achieve the optimal performance of microstructured flow reactors that can be used for intensification of the large number of liquid-liquid chemical reactions. A short list of reactions practically implemented in micro devices with different plate materials is presented in [10].

Microfluidic modelling and simulation of flow in microreactors

Modelling is necessary to provide in-depth understanding of the process characteristics associated with the type of reaction in the microreactor, as well as to determine the optimal operating conditions.

Simulations serve not only as a design tool, but also as a means to interpret experimental data. If all physical parameters are known, simulations should accurately reflect experimental observations, since the basic transport equations for laminar flow are well established. Thus, it is possible to carry out theoretical experiments, and develop certain recommendations for practical realization of the process.

The modelling generally aims to realize the following points [11]:

- defining the fundamental transport-kinetic equations (heat, mass, species, momentum, etc) and the appropriate initial and boundary conditions for the particular application of interest;
- specification of any constitutive equations;
- transformation of the primitive or scaled forms of the equations into a numerical scheme;
- conversion of the numerical algorithm into a computer-based code;
- development of methods for visualization and analysis of the numerical results;
- investigation of the effect of various model and system geometrical parameters on the microprocess performance;
- identifying and implementation of a scheme for microprocess component and/or system optimization.

To date, the most widespread approaches to the modelling of the fluid-phase reactions are the finite-volume method, the Navier-Stokes Equation, Computational Grids, Methods for Linear Algebraic Systems. By comparing the predictions of various codes and the methods upon which they are based, it was concluded that the volume-of-fluid approach with piecewise linear geometrical interface reconstruction produces the most consistent results, especially at the fluid–fluid interfaces [11].

Various commercially available software tools have subsequently been developed and can now be used to solve mathematical models that describe microtechnology systems. Some examples of program packages that have been used to study microfluidics include Fluent, CFD-ACE+, COMSOL Multiphysics, and CoventorWare.

Table 1

Examples of microfluidic modeling of reactions and processes in the microreactor

Modelling object	Microreactor	Simulating			Reference
		Operation condition	Model description	Software	
Knoevenagel condensation reaction	The membrane microreactor	Isothermal, steady state operation condition	The model includes the differential material balance equations for the bulk fluid in the channel and across the catalyst layer. The transport mechanisms are considered to be convection along the flow direction and diffusion along the traverse directions.	Femlab™	[3]
Selective catalytic reduction (SCR) of NOx	The microstructured reactor	Continuum flow with no-slip boundary conditions	The dynamic model consisting of a system of partial differential equations was discretized using a finite difference formulation with respect to the spatial coordinate. The resulting ordinary differential equations were solved with backward difference method.	Comsol Multiphysics 3.5	[4]
Slug flow generation	T-type microstructured reactor	Isothermal flow of two immiscible Newtonian fluids of constant density	The volume of fluid (VOF) based computational fluid dynamics (CFD) methodology was developed to investigate the slug flow generation in a T-type mixing element considering the wall film.	FLUENT (ANSYS Inc.)	[6]
Hydrodynamics and liquid phase residence time distribution (RTD)	Mesh microreactor	Dynamic liquid zone; Static liquid zone	The standard axial dispersion exchange model (ADEM) was used for the analysis of liquid phase back-mixing. Axial dispersion in the flowing liquid is incorporated to improve RTD prediction.	gPROMS©-3.0.2	[12]

So, the correct choice of the modelling method and simulation of hydrodynamics allow to create optimal conditions for the process and to obtain the desired product with minimal costs.

The commercial dimension of the introduction of microtechnology in production

In order to integrate the innovative microreaction technologies from research and development to sustainable industrial processes a joined comprehensive approach is necessary. For commercial production, the use of continuous microreactor technology must be justified by a clear cost advantage in comparison to currently applied technologies, which are often performed in batch. The financial benefits could be derived from reduction in capital expenditure (e.g. costs of reactor and other apparatus used) and/or reduction in operating costs (e.g. decreased energy demand and material input). Moreover, scaling from laboratory to production plant is performed by numbering-up approach rather than by scaling-up, that allows to increase productivity and avoid the problem of limited physical size of the equipment. Analysis performed for organic chemical synthesis revealed that the microstructured reactor gives a significant economic gain from applying microreactor technology to the actual production [8]. It was shown that improvements in space–time yield could be offset by higher capital investment costs when comparing production in continuous microreactors with conventional batch production [8].

To identify the expediency of the larger-scale manufacturing process integration into microscale the comparative analysis need to be used. Unfortunately, this is difficult since commercial experience with the technology is limited. A short list of international commercial companies using microreactors in production has been presented in our previous papers [13]. However, there are a number of research projects involving joint collaboration between universities and companies in Europe and the Far East where robust MRT systems are being developed for various commercial applications. Some examples of these projects are [11]:

- Strategic Research Project on Modular Micro Chemical Engineering (MicroChemTec, www.microchemtec.de);
- Research Association of Micro Chemical Process Technology (MCPT, www.mcpt.jp/english/elink.html),
- New Eco-efficient Industrial Process Using Microstructured Unit Components (NEPUMUC, www.nepumuc.info);
- Towards Optimised Chemical Processes and New Materials by Combinatorial Science (TOPCOMBI, www.topcombi.org);
- Integrated Multiscale Process Units with Locally Structured Elements (IMPULSE, www.impulse-project.net).

A further example for a joint approach from academia and industry is the "Blue Sky Vision" project of Novartis and the MIT aiming at a radical transformation of batch orientated pharma production to a fully continuous approach integrating quality by design, new product development processes, new equipment and new facility lay-out in a 4 years project [14]. These programs are generally concerned with using modern approaches for the design, integration and automation of MRT systems for process intensification with economical benefits.

A recent technical business analysis suggests that fine and specialty markets represent a viable market target with an economic potential of 140 MM euros within 15–20 years. A related document from the same group mentions the start-up of several production plants based on a microreactor scaling-out strategy, namely: (1) a high value-added polymer at DSM; (2) a 1000 ton/yr pigment plant at Clariant (CH); and (3) several production plants at Degussa. Additional details are not provided but must be obtained in a private client report [11].

The above examples illustrate how academia, industry and equipment suppliers work together on the development of these novel processes, micro manufacturing concepts and their industrial implementation.

Conclusions

The development of microreactors is the future direction for process engineering in terms of "smart reactors" or "intelligent" devices for chemical production. In this article the analysis of approaches to modeling the liquid-liquid reactions has been conducted; the simulation results of various numerical methods were studied and the appropriate software environment was considered; the potential benefits of microdevices for commercial application were confirmed.

In the following, we are going to simulate the process of silica surface functionalization in the flow microreactor which could be effectively used for the synthesis of hybrid organic-inorganic materials. Ultimately, clear guidance for producing functionalized silica materials could be proposed and used for the synthesis of innovative substances with prescribed properties.

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МАТЕМАТИЧНА МОДЕЛЬ АБСОРБЦІЙНОЇ КОЛОНИ ВИРОБНИЦТВА АЗОТНОЇ КИСЛОТИ

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МАТЕМАТИЧЕСКАЯ МОДЕЛЬ АБСОРБЦИОННОЙ КОЛОННЫ ПРОИЗВОДСТВА АЗОТНОЙ КИСЛОТЫ

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MATHEMATICAL MODEL OF THE ABSORPTION COLUMN NITRIC ACID PRODUCTION

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Розроблено алгоритм та програму розрахунку тарілчастої абсорбційної колони виробництва азотної кислоти, при цьому матмоделлю враховано реакції окиснення оксиду азоту до двооксиду азоту і його димерізації у вільному просторі між тарілками, утворення кислоти у шарі рідини на тарілці. Створено програму розрахунку в середовищі Visual Basic for Applications, що дозволяє варіювати технологічними і конструктивними параметрами.

Ключові слова: *азотна кислота, абсорбційна колона, швидкість окиснення і абсорбції, рівноважний склад, математична модель*

Разработаны алгоритм и программа расчета тарелчатой абсорбционной колонны производства азотной кислоты, при этом матмоделью учтены реакции окисления оксида азота до диоксида азота и его димеризации в свободном пространстве между тарелками, кислотообразование в слое жидкости на тарелке. Создана программа расчета в среде Visual Basic for Applications, что позволяет варьировать технологическими и конструктивными параметрами.