Novosibirsk State Technical University

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BORESKOV INSTITUTE OF CATALYSIS

MODELLING METHANOL TO FORMALDEHYDE OXIDATION PROCESS IN THE ENVIRONMENTALLY SAFE MICROSTRUCTURED SLIT-TYPE REACTOR

Sheboltasov A. G.,
Vernikovskaya N. V.,
Chumachenko V. A.

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Introduction

Microsized reactors can provide significant advantages to chemical technology by ensuring reaction conditions that may otherwise be difficult to achieve, e.g.:

- The production capacity with microsized reactors is rather easy to increase by increasing the number of reactors instead of scaling up.
- Microsized reactors are suitable for high-temperature oxidation in explosive regimes, because they provide safe operation due to extremely small reactor volumes, well-tuned reaction conditions, reliable control of reaction temperature, and efficient heat transfer due to large surface-to-volume ratios.
- The improvements in selectivity can be achieved by accurate setting of the gas residence time and avoiding hotspots in the reactor.

Formaldehyde is one of the basic chemicals. It is widely used to produce phenol-formaldehyde resins, urea-formaldehyde resins and concentrates, glues and many others. In industry, formaldehyde is produced by oxidation of methanol using Ag-containing or Fe-Mo catalysts.

TUBULAR REACTOR (CONVENTIONAL)		MICROCHANNEL REACTOR [1]
0.56-0.65 kg/l/h	Specific formaldehyde productivity	7.9 kg/l/h
5.8-8.4 vol. %	Maximum methanol concentration	12 vol. %

The main disadvantages of microsized reactors with random packing:

- improper flow distribution at the inlet can result in a broad RTD in separate channels
- it is difficult to load the catalyst evenly in each channel, it leads to spatial inhomogeneity in the channels

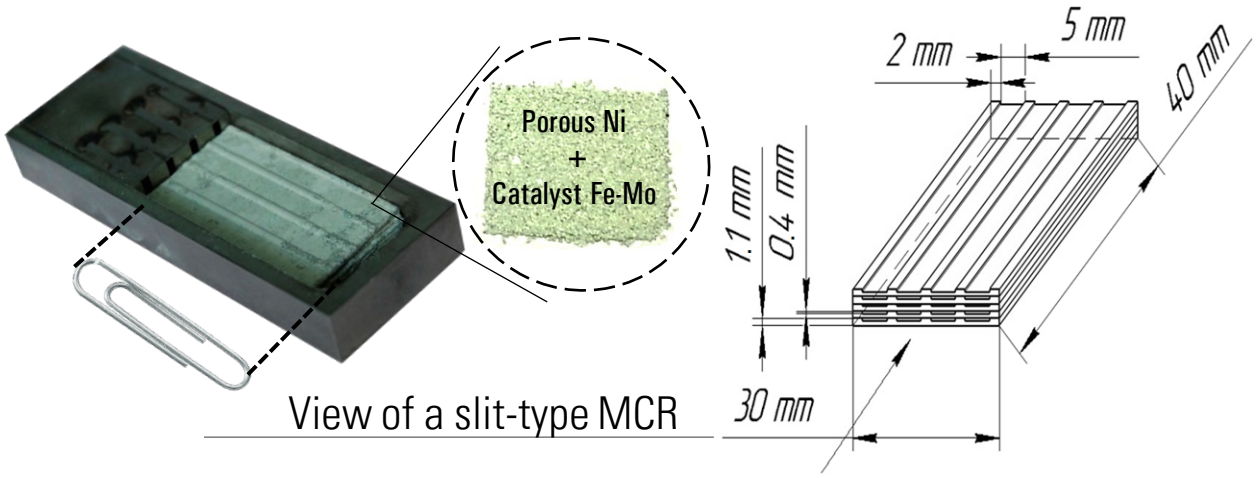
GOAL

The goal of the present work is to provide a physically realistic 3D model of the microstructured slit-type catalytic reactor for methanol to formaldehyde oxidation process (MTF). The influence of the process parameters on the spatial temperature distribution and on the methanol conversion and formaldehyde yield is evaluated. The model has been verified by experimental MTF processing in the catalytic slit-type reactor with 20 channels.

[1] V.A. Chumachenko, E.V. Ovchinnikova, A.G. Gribovskii, L.L. Makarshin, Catalysis in Industry. 2016. V.8. N3. P.199-204; E.V. Ovchinnikova, N.V. Vernikovskaya, A.G. Gribovskii, V.A. Chumachenko, Chem. Eng. J. 2021, 409, 13.

Physical object

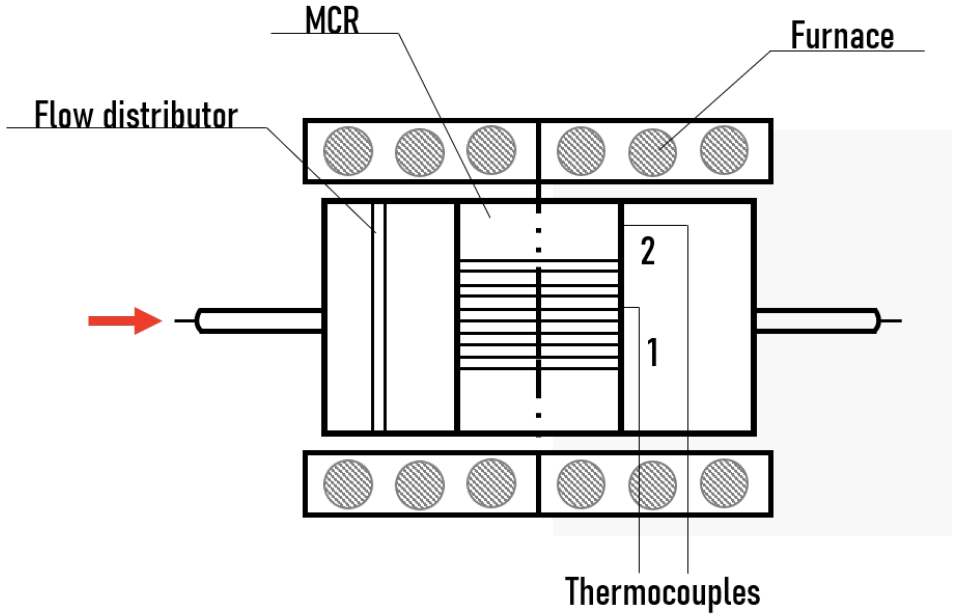
MCR



View of a slit-type MCR

The slit-type MCR consists of 5 porous nickel plates 40 mm long, 30 mm wide and 1.1 mm high. Each plate contains 4 channels 0.4 mm high and 5 mm wide. Finely dispersed particles of industrial Fe-Mo catalyst are evenly distributed within the porous matrix. The channel spacing is 2 mm.

Experimental setup



The reactor is positioned inside the furnace. Feeding device ensure perfect mixing at the inlet of the channels. Porous membrane ensures uniform flow distribution.

Thermocouples located in points **1** and **2** measure the outlet temperatures of the reactor metal part: T_m in the center, and T_{edge} at the disk edge, respectively.

Mathematical model

Domain I (Channels) | **Domain II (Catalytic plates)**

Mass balance equations:

$$u\frac{\partial y_i}{\partial z} + y_i\frac{\partial u}{\partial z} + \nabla\cdot\left(-\frac{T_0}{T}D^e\nabla y_i\right) = 0,\ i = 1,N$$

$$\frac{\partial u}{\partial z} = \sum\beta\left(y_i^c - y_i\right)$$

$$\nabla\cdot\left(-\frac{T_0}{T}D_m^e\nabla y_i^c\right) = V_{m0}\sum_{j=1}^{2}\nu_{ij}W_j = 0,\ i = 1,N$$

Energy balance equations:

$$uc_p\frac{\partial T}{\partial z} + \nabla\cdot\left(-\lambda^e\nabla T\right) = 0$$

$$\nabla\cdot\left(-\lambda^m\nabla T_m\right) = \sum_{j=1}^{2} -\Delta H_j W_j$$

Boundary conditions:

$$z = 0: \frac{T_0}{T}D^e\frac{\partial y_i}{\partial z} = u\left(y_i^{in} - y_i\right), i = 1,N; \lambda_l^e\frac{\partial T}{\partial z} = uc_p\left(T^{in} - T\right)$$

$$z = H: \frac{\partial y_i}{\partial z} = 0; \frac{\partial T}{\partial z} = 0$$

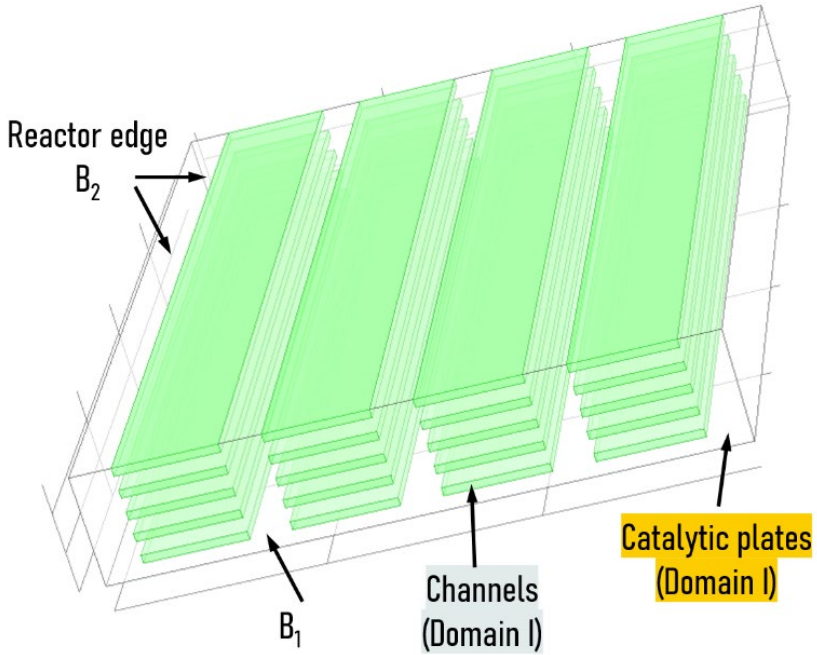
$$\text{на } B_1: D^e\nabla y_i = \beta(y_i^c - y_i), i = 1,N; \lambda^e\nabla T = \alpha(T_m - T)$$

$$z = 0: \frac{\partial T_m}{\partial z} = 0;\ z = H: \frac{\partial T_m}{\partial z} = 0$$

$$\text{на } B_1: D_m^e\nabla y_i^c = \beta\left(y_i - y_i^c\right), i = 1,N; \lambda^m\nabla T_m = \alpha(T - T_m)$$

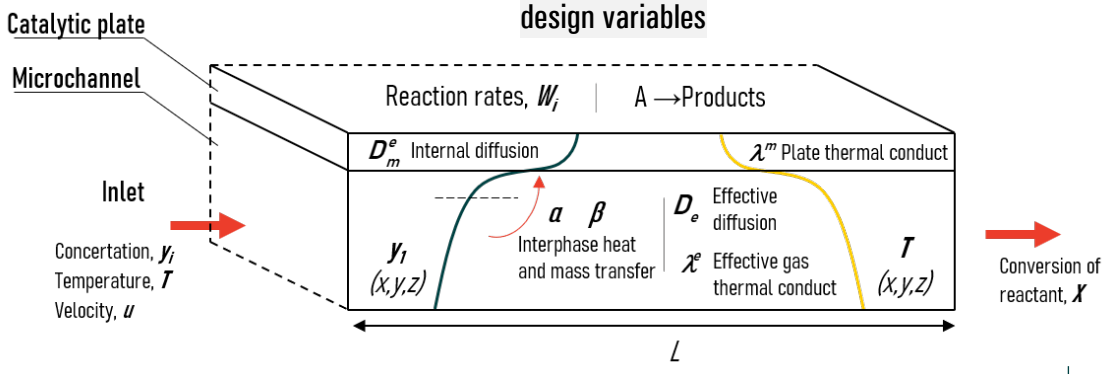
$$\text{на } B_2: T_m = T_{edge}$$

$$i = 1(CH_3OH),\ i = 2(CH_2O),\ i = 3(O_2),\ i = 4(H_2O),\ i = 5(CO),\ i = 6(N_2)$$



On the single channel scale, the model accounts for convective flow, effective axial and transversal diffusivity and conductivity.
On the reactor scale, catalytic reactions and the temperature distribution due to the finite thermal conductivity of the metal base are considered.

Schematic representation of a catalytic plate microchannel and main design variables



Reaction stoichiometry

The pattern in MCR is close to isothermal. Isothermal mode is favorable for the consecutive reactions A →B → C, if the activation energy of the target product B formation is higher than that of by-product C formation. At the maximum allowable temperature, the yield of the product B will be the highest, while selectivity to the product C will be low. Selective oxidation of methanol to formaldehyde on Fe-Mo oxide catalyst follows the above scheme; we considered MTF as a model highly exothermic process occurring in MCR.

Reaction scheme and enthalpies in MTF:

$$1.\ CH_3OH + 0{,}5O_2 \rightarrow CH_2O + H_2O,\ (-\Delta H_1) = 159\ kJ/mol,$$

$$2.\ CH_2O + 0{,}5O_2 \rightarrow CO + H_2O,\ (-\Delta H_2) = 230\ kJ/mol.$$

Kinetic equations[1]:

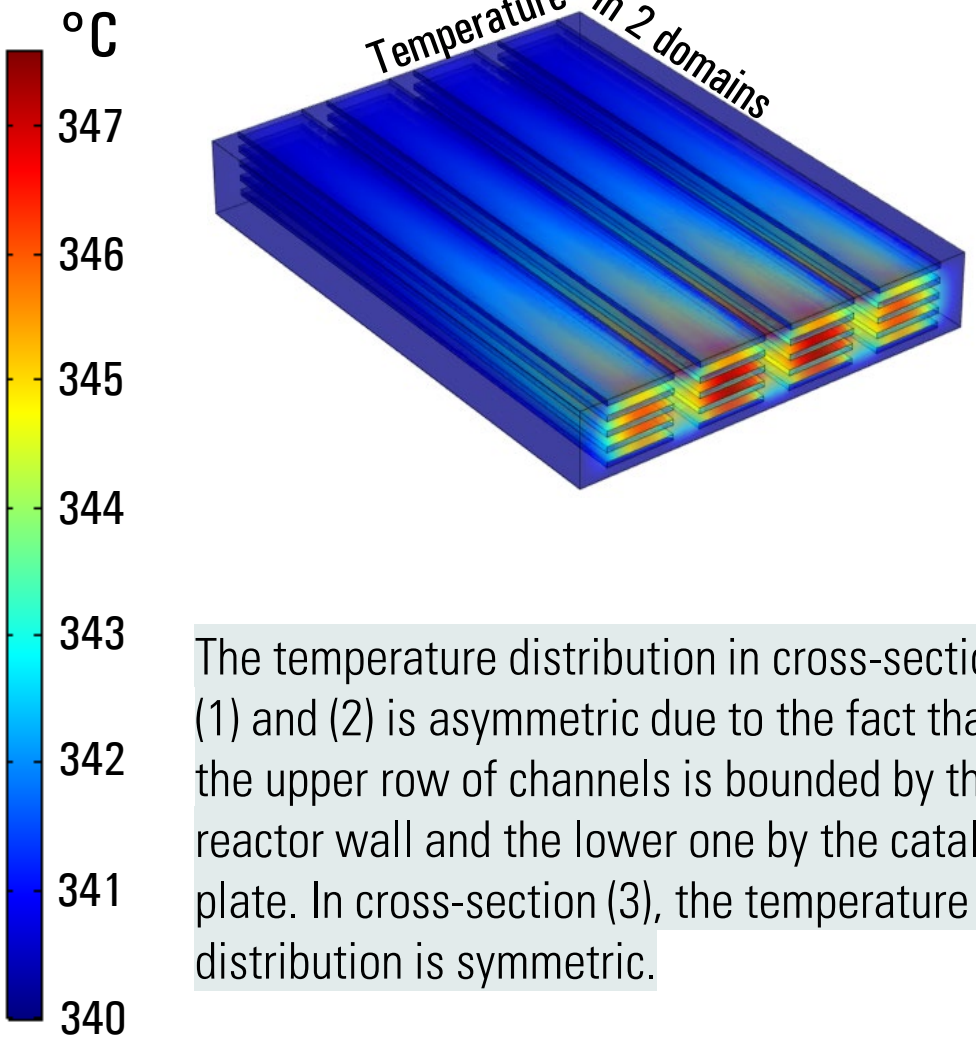
$$W_1 = \frac{K_1 C_{CH_3OH}}{1 + a_1 C_{CH_3OH} + a_2 C_{H_2O} + a_3 \frac{C_{CH_3OH}}{C_{O_2}}}$$

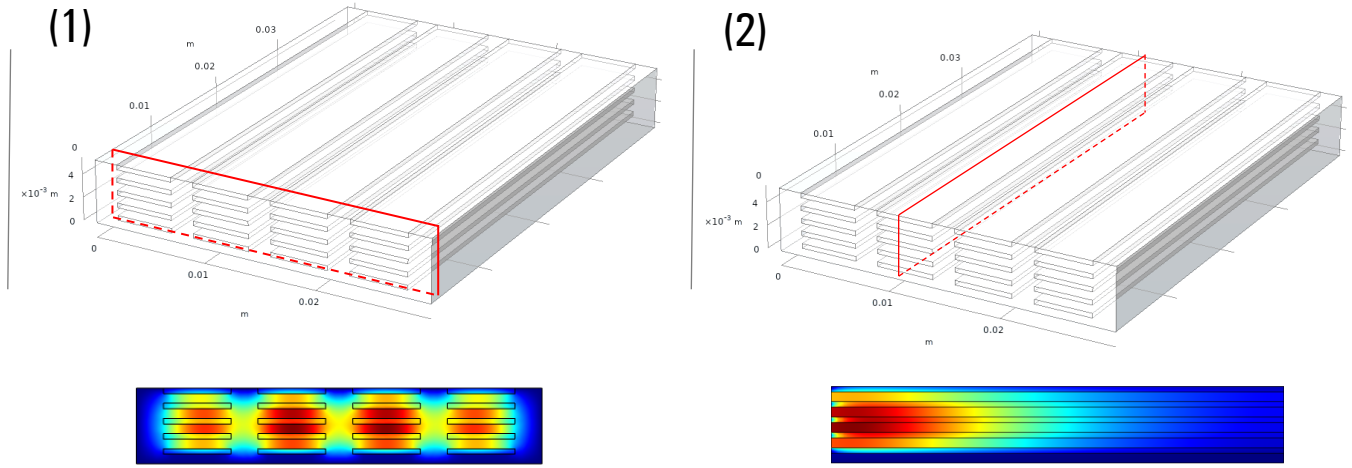
$$W_2 = \frac{K_2 C_{CH_2O}^{\alpha_1}}{1 + b_1 C_{CH_3OH} + b_2 C_{H_2O} + b_3 \frac{C_{CH_2O}}{C_{O_2}}}$$

[1] E.V. Ovchinnikova, N.V. Vernikovskaya, A.G. Gribovskii, V.A. Chumachenko, Chem. Eng. J. 2021, 409, 13.

Results

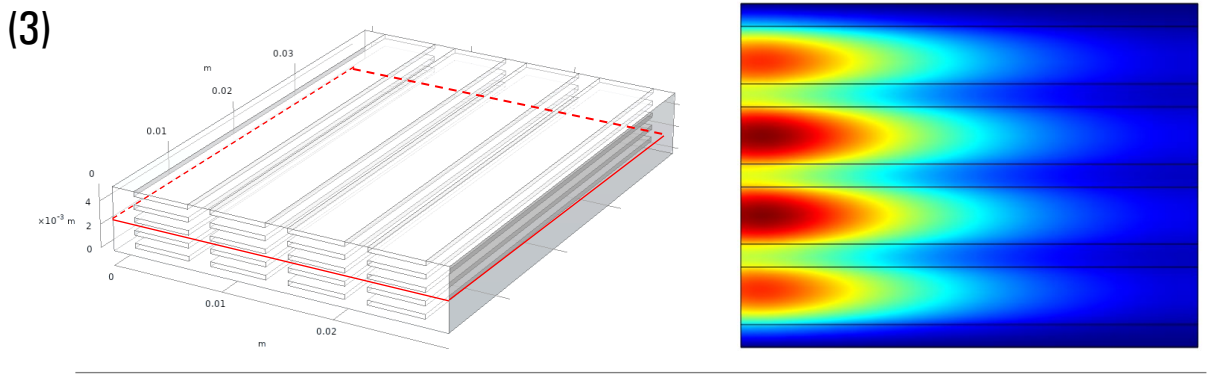
Temperature distribution in MCR





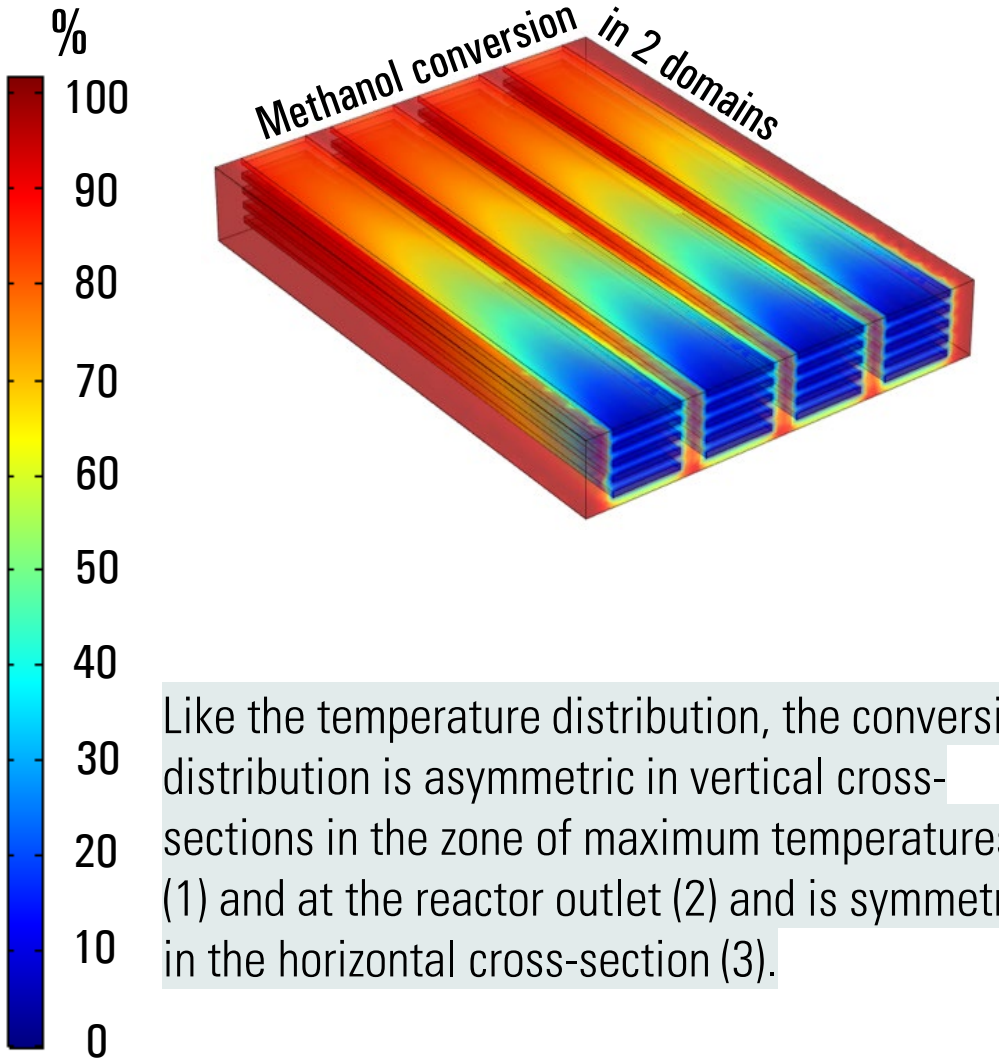
Temperature distribution in different cross-sections of MCR

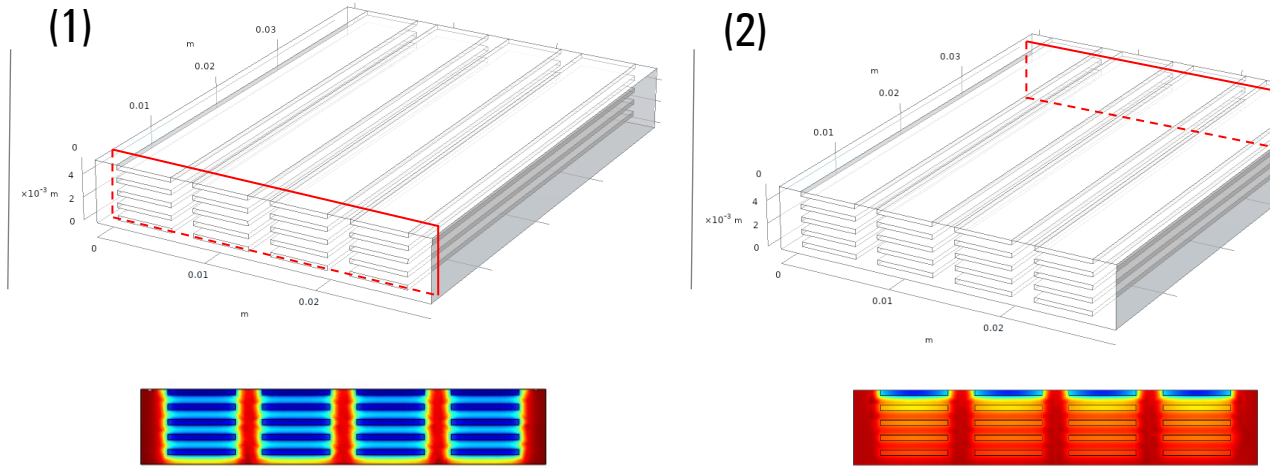
The temperature distribution in cross-sections (1) and (2) is asymmetric due to the fact that the upper row of channels is bounded by the reactor wall and the lower one by the catalyst plate. In cross-section (3), the temperature distribution is symmetric.



Results

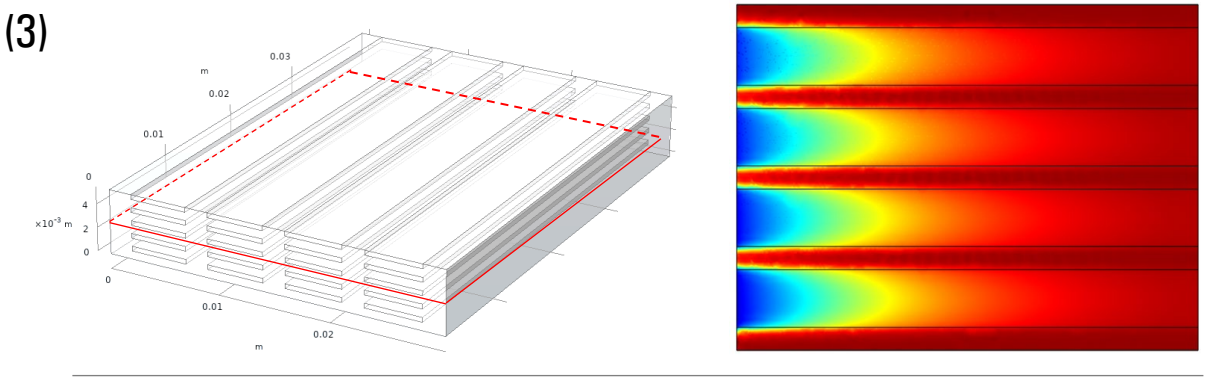
Conversion distribution in MCR





Conversion in different cross-sections of the reactor

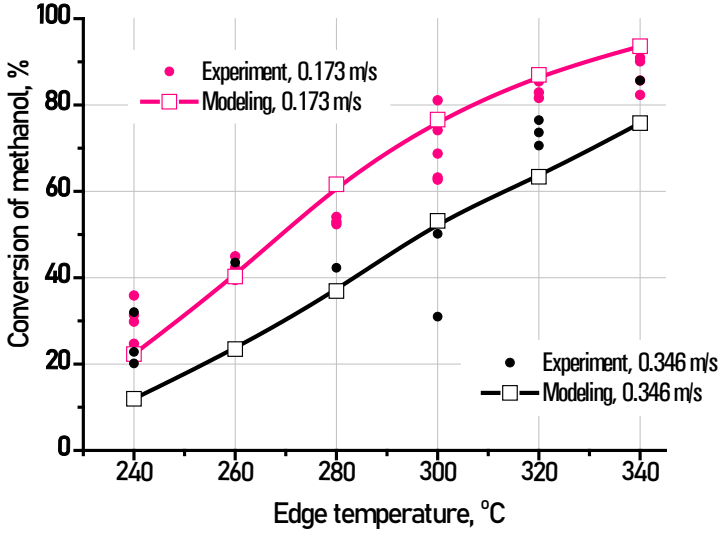
Like the temperature distribution, the conversion distribution is asymmetric in vertical cross-sections in the zone of maximum temperatures (1) and at the reactor outlet (2) and is symmetric in the horizontal cross-section (3).



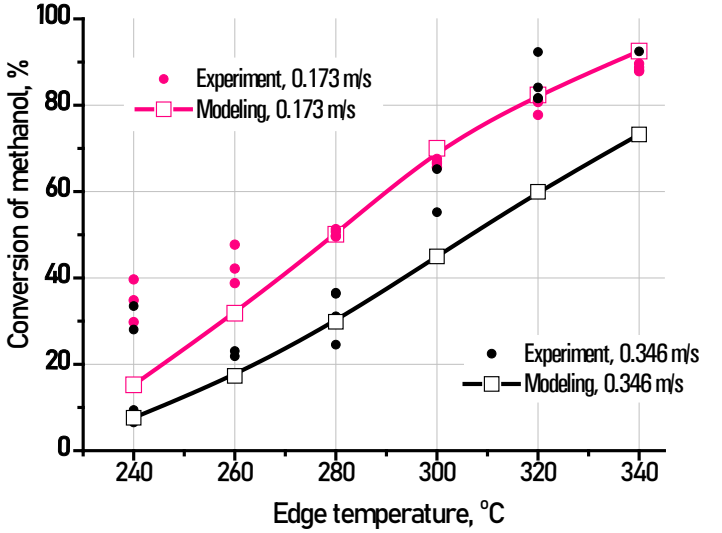
Results
Modeling and experiments

Methanol conversion at u = 0.173 and 0.346 m/s

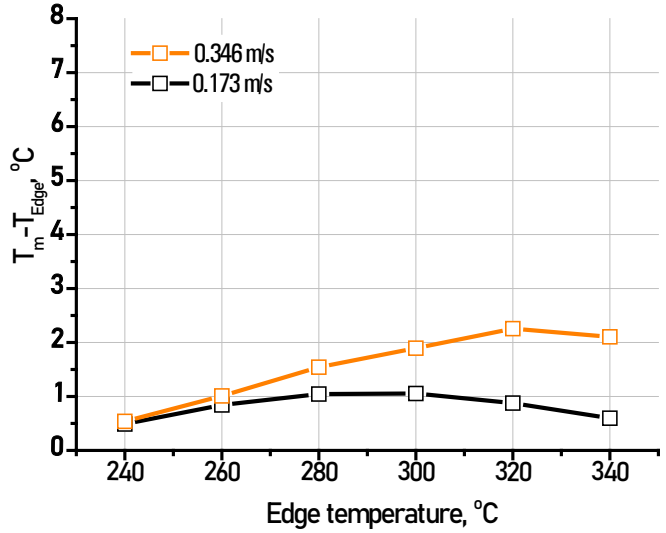
$[CH_3OH]_0$ = 6.5 %

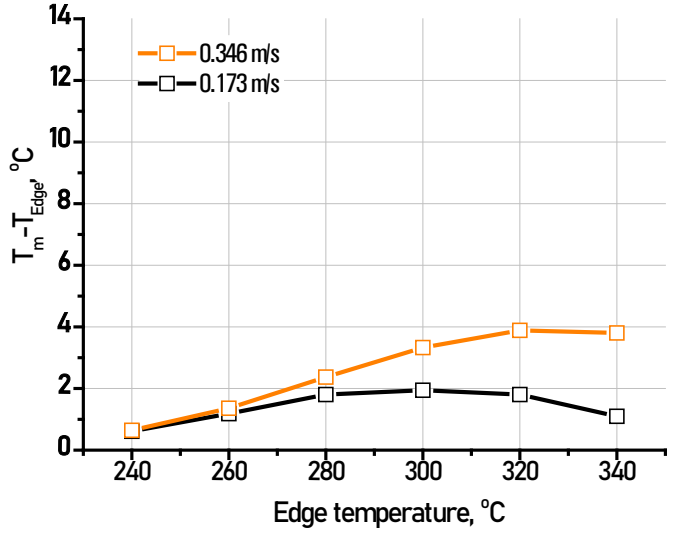


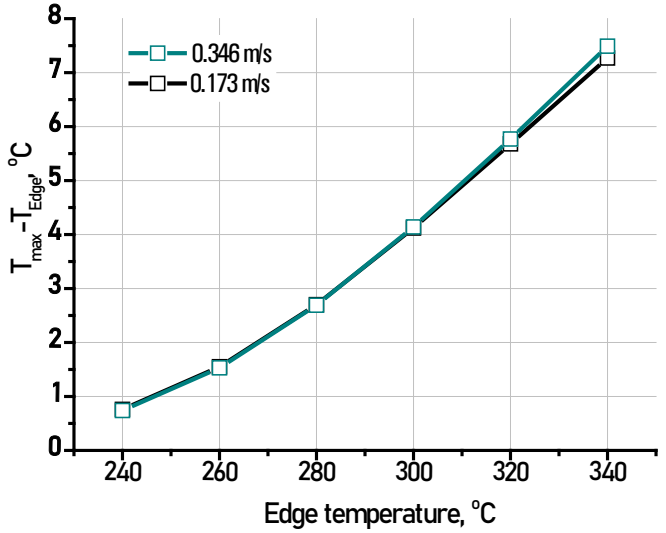
$[CH_3OH]_0$ = 12 %

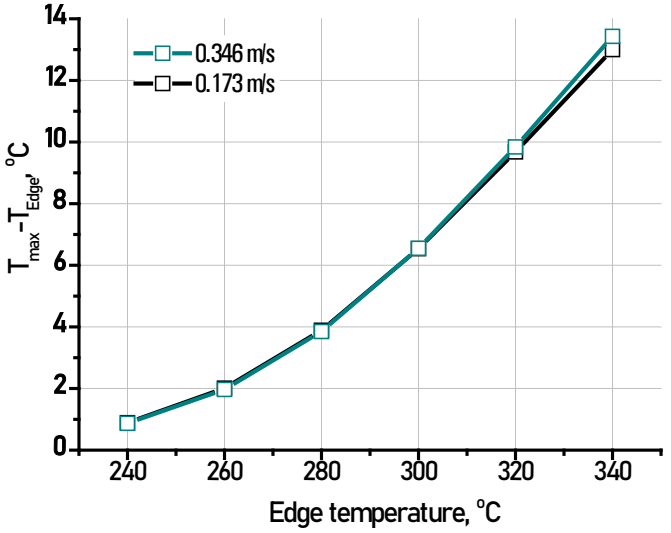


Temperature gradients at u = 0.173 and 0.346 m/s









Formaldehyde selectivity is close to 100 %

T_m – temperature of the plates at the outlet of the central channel; T_{max} – maximum temperature in the central channel, °C

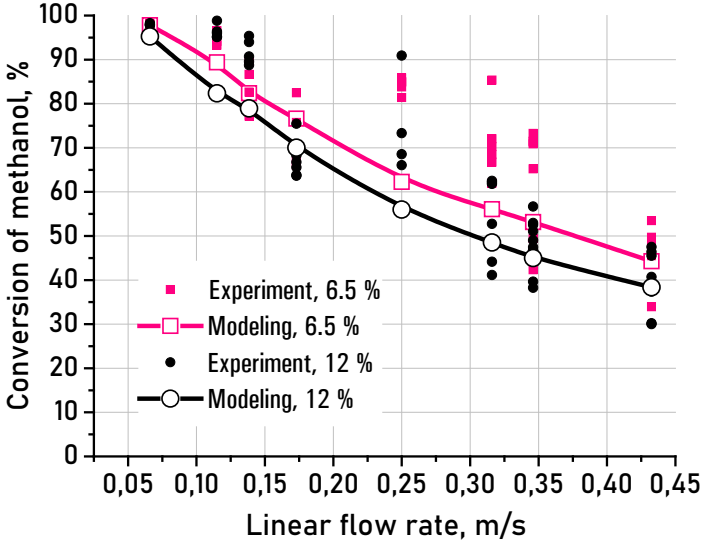
Results

Modeling and experiments

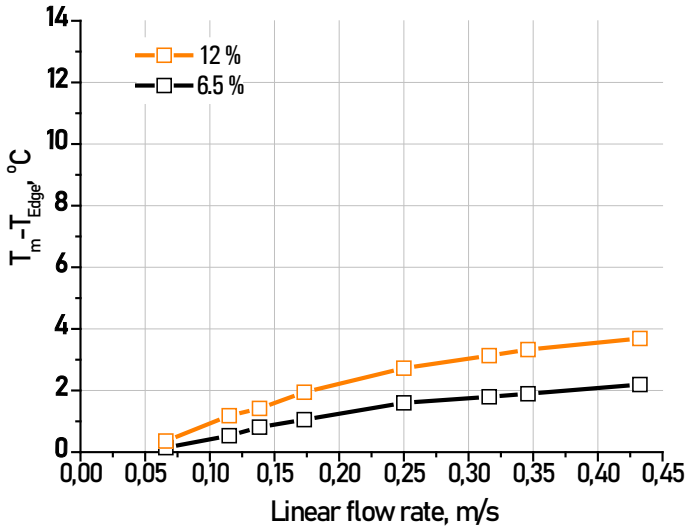
T = 300 °C

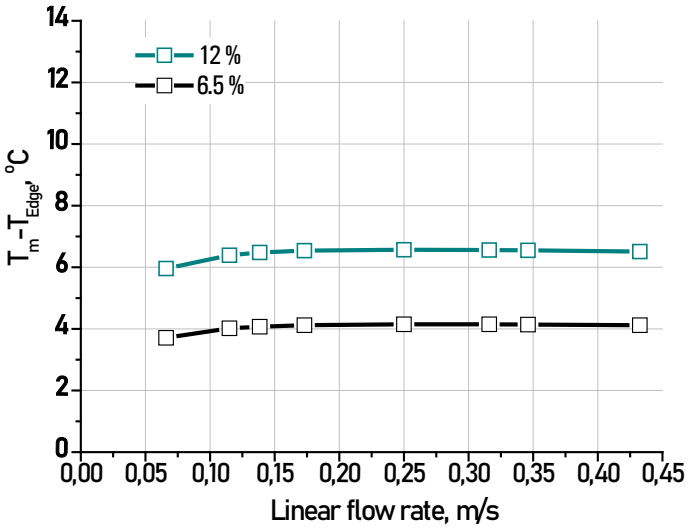
$[CH_3OH]_0$ = 6.5 and 12 %

Methanol conversion at u = 0.066...0.432 m/s



Temperature gradients at u = 0.066...0.432 m/s





An increase in the edge temperature and methanol concentration is accompanied by the increase in reaction rate and the heat released. This leads to an increase in the temperature gradient relative to the edge temperature both at the outlet from the central channel and at the hot spot (Slide 8).

As the linear velocity increases, the temperature gradients between the edge temperature and the temperature at the outlet of the central channel and at the hot spot increase, mainly due to more heat release (Slide 9).

Conclusion

A new model of the slit-type microchannel reactors for conducting highly exothermic catalytic reactions has been developed. The three-dimensional model of the reactor involves two interconnected computational domains.

The good agreement between simulated and observed results obtained with changes in methanol concentration, linear velocity and reactor edge temperature demonstrates the model's ability to provide accurate determination of temperature, conversion and yield for each specific channel.

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Thank you for your attention!

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