

## A Multifuel Processor for SOFC Power Plants Created to Operate in the Arctic Region

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A mathematical model of the processes occurring in the steam reformer of methanol used in power plants based on solid oxide fuel cells (SOFC) was constructed. As a result of the numerical analysis, the concentration and temperature profiles were calculated, and the geometrical parameters of the reformer were optimized. To verify the results of the mathematical modeling, experimental studies of the parameters of the fuel processor operation were carried out. There is a good agreement between the experimental data and the theoretical model. The results described in this publication are applicable to the optimization of the technological parameters of steam reformers of methanol for SOFC power plants.

### Introduction

At present, one of the trends in the development of electric and thermal power engineering is the transition to distributed generation, when the developers of the energy system refuse from the centralized generation of high power and switch to energy production right at the place of its subsequent consumption (1-3), power is selected on the basis of local needs. Most of the territory of the Russian Federation and other northern countries is not covered by a centralized energy system (4,5), for such regions the transition to distributed generation in isolated small power systems is the only way to solve the problem of energy supply. The implementation of this approach requires the availability of highly efficient generators of electrical and thermal energy from the chemical energy of hydrocarbon fuels in a wide range of power output (from 1 kW to MWs). To date, a more efficient technology for the direct production of electricity from chemical energy of fuel than solid oxide fuel cells (SOFC) (6,7) is not known. SOFC, like other fuel cells (FC), has a number of important technical and economic advantages over traditional machine-based methods of generating electricity. Fuel cells have a high efficiency, starting from low power (units of kW), the dependence of efficiency on power is almost flat (8-10). This advantage is due to the good scalability of the technology due to the fact that power installations with different power output are created from similar basic elements. Power plants on fuel cells are practically free from moving parts, which ensures noiseless systems, as well as a high service interval and service life due to the absence of moving parts, which entails the need for a lubrication system (11-13). The systems on fuel cells are record holders in environmental cleanliness, the only emissions

are water and carbon dioxide in the case of using hydrocarbons as fuel (14–16). Emissions of CO and NO<sub>x</sub> are hundreds of times less than the values specified in the Euro-5 environmental standards (transport applications) and Tier-4 (stationary systems, primarily diesel generators used off-road) (17). Since 2003, research group in Institute of Solid State Physics RAS (Russia) has been conducting systematic research in the field of creating SOFC stacks: from search and synthesis of new electrode materials (18-20) to development of the technology for manufacture of membrane-electrode assemblies (21-23) and optimization of their total internal resistance, as well as development and the manufacture of SOFC stacks (24).

The main advantage of SOFC power plants over other types of fuel cells is the ability to use not only pure hydrogen as fuel, but also hydrocarbons: methane (25-26), propane-butane (27-28), dimethyl ether (29-30), dimethoxymethane (31), biogas (32-33) and even prepared diesel fuel (34-35). For the operation of the energy system on hydrocarbons, a reformer (fuel processor) is used as part of the power plant, which converts fuel into synthesis gas suitable for electrochemical oxidation at the SOFC anode electrode (36-38). At the same time, it is necessary to use liquid fuel stored in light and recyclable containers (plastic) at atmospheric pressure to operate the power plant at extremely low temperatures (the use of gaseous fuels makes it necessary to compress to sufficiently high pressures (>150 atm) in order to achieve significant energy consumption, which leads to the need to use durable heavy containers, the mass of which is tens of times greater than the mass of stored gaseous fuel), and not freezing in the whole working interval of temperatures and having a high yield of the target product – hydrogen. An example of such a fuel is methanol, which is 1.5 times greater than liquid hydrogen in volumetric density of H<sub>2</sub> storage (39).

The optimal conversion process in terms of fuel production (H<sub>2</sub>) for fuel cells is steam reforming of methanol. Considered two stages of the process:

- steam methanol conversion:



- shift reaction:



Decomposition reaction of methanol to formaldehyde, followed by synthesis gas, and the oxidation reaction of methanol was also considered.

In the literature, there is a fairly large number of studies on the development of catalysts for the process of steam reforming of alcohols (40-46) in order to produce synthesis gas. Existing catalysts are variations of Cu-Zn-Al-oxide systems with modifying additives MgO, Cr<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, etc. Almost all of the listed catalysts have high activity and selectivity at temperatures in the range of 200-350°C. However, these systems have one major drawback: at temperatures above 350°C, copper-containing catalysts are gradually deactivated during the reaction due to sintering of the active component. In this regard, it became necessary to search for thermostable catalysts capable of operating at high temperatures (400-700°C), i.e. in the area optimal for the application of the synthesis gas obtained in a power plant based on solid oxide fuel cells.

### Theoretical analysis

Mathematical simulation of the reactor for steam reforming of methanol was carried out with the aim of calculating the distribution of concentrations and temperatures for various options for the realization of the process of steam reforming of methanol (direct flow or counter-flow). Equations of heat and material balances for endothermic channels,  $0 \leq z \leq H$ ,  $0 \leq l \leq L$  where  $l$  is longitudinal coordinate;  $z$  is transverse coordinate [3-5]:

$$G_{en} \frac{\partial y_i}{\partial l} = (v_i^{con} \omega_{con} + v_i^{dec} \omega_{dec} + v_i^{sh} \omega_{sh}) m_i \quad [3]$$

$$c_p^{en} G_{en} \frac{\partial T_g^{en}}{\partial l} = \alpha_{en} S (T_c - T_g^{en}) \quad [4]$$

$$\lambda_z \frac{\partial^2 T_c}{\partial z^2} + \Delta H_{con} \omega_{con} + \Delta H_{dec} \omega_{dec} + \Delta H_{sh} \omega_{sh} = \alpha_{en} S (T_c - T_g^{en}) \quad [5]$$

where  $G_{en}$  is mass flow rate of gas in endothermic channels, kg/h;  $v_i^j$  are stoichiometric coefficients of the corresponding stages;  $y_i$  are mole fractions of gas components;  $m_i$  are molar masses of gas components, kg/mol;  $i = \{H_2O, CH_3OH, H_2, CO, CO_2\}$ ;  $c_p^{en}$  is heat capacity of the gas mixture in endothermic channels, J/m<sup>3</sup> K;  $T_g^{en}$  is gas temperature in endothermic channel, °C;  $\alpha_{en}$  is heat transfer coefficient between gas and catalyst in endothermic channels, W/(m K);  $S$  is specific area of catalysts, m<sup>-1</sup>;  $T_c$  is catalyst temperature, °C;  $\lambda_z$  is coefficient of thermal conductivity, W/(m K);  $\Delta H_i$  is reaction thermal effect, J;  $\omega_i$  is reaction rate, mol/(m<sup>3</sup> s). Equations of heat and material balances for exothermic channels,  $0 \leq l \leq L$  [6-7]:

$$c_p^{ex} g \frac{dT_g^{ex}}{dl} = \alpha_{ex} (T_w - T_g^{ex}) \quad [6]$$

$$g \frac{dx_j}{dl} = v_j^{met} \omega_{CH_4O}^{ox} m_j \quad [7]$$

where  $c_p^{ex}$  is heat capacity of gas mixture in exothermic channels, J/m<sup>3</sup> K;  $g$  is half of mass gas velocity in exothermic channels, kg/h;  $\alpha_{ex}$  is heat transfer coefficient between the channel wall and gas in exothermic channels, W/(m K);  $T_w$  is temperature of channel wall, °C;  $T_g^{ex}$  is gas temperature in exothermic channels, °C;  $x_j$  is mass fraction of mixture component,  $j = \{CH_3OH, N_2, O_2, CO_2, H_2O\}$ . Heat balance equation for a wall separating exothermic and endothermic channels,  $z=1$ ,  $0 \leq l \leq L$ ,  $T_c = T_w$  [8]:

$$\lambda_z \frac{\partial T_c}{\partial z} + \alpha_{ex} (T_w - T_g^{ex}) = w_{CH_4O}^{ox} \Delta H_{CH_4O} + \lambda_w \delta_w \frac{d^2 T_w}{dl^2} \quad [8]$$

Boundary conditions are following [9-11]:

$$\text{For } \ell = 0, 0 < z < H: \frac{dT_w}{d\ell} = 0, y_i = y_{i0}, x_j = x_{j0}, T_g^{en} = T_{g0}^{en}, T_g^{ex} = T_{g0}^{ex}. \quad [9]$$

$$\text{For } \ell = L: \frac{dT_w}{d\ell} = 0. \quad [10]$$

$$\text{For } z = 0, 0 < \ell < L: \frac{\partial T_c}{\partial z} = 0. \quad [11]$$

The kinetic models and their parameters were estimated on the basis of the data from work (47) for methanol and were refined according to the results of the experiments performed. The oxidation rate of CH<sub>3</sub>OH in accordance with (47) [12]:

$$\omega_{CH_4O}^{ox} = \left( \frac{P \times 10^5}{R_g T_g^{ex}} \right) x_{CH_4O}^m \left( \frac{k_{CH_4O} \beta_{CH_4O}^{ex}}{\beta_{CH_4O}^{ex} + k_{CH_4O}} \right), k_{CH_4O} = k_{CH_4O}^0 \exp\left( \frac{-E_{CH_4O}}{R_g T_w} \right), \quad [12]$$

where  $\omega_{CH_4O}^{ox}$  is rate of methanol oxidation reaction, mol/(m<sup>3</sup> s);  $R_g$  is gas constant, J/mol K;  $P$  is pressure, atm;  $\beta_{CH_4O}^{ex}$  is mass transfer coefficient of CH<sub>3</sub>OH between gas and wall of exothermic channel, m/s;  $k_{CH_4O}$  is constant of methanol oxidation reaction rate;  $E_i$  is activation energy, J/mol.

Rate of CH<sub>3</sub>OH steam reforming (47) [13-14]:

$$r_{con} = \frac{k_{con} P_{CH_4O} \left[ 1 - \frac{P_{CO_2} (P_{H_2})^3}{K_e^{con} P_{CH_4O} P_{H_2O}} \right] C_{cat}}{(\sqrt{P_{H_2}} + K_1 P_{CH_4O} + K_2 P_{CO_2} P_{H_2} + K_3 P_{H_2O}) (1 + \sqrt{K_4 P_{H_2}})} \quad [13]$$

$$k_{con} = k_{con}^0 \exp\left( \frac{-E_{con}}{R_g T_c} \right), P_i = P y_i^m, i = \{CH_4O, H_2O, CO, CO_2, H_2\}, \quad [14]$$

where  $r_{con}$  is rate of CH<sub>3</sub>OH steam reforming, mol/(m<sup>3</sup> s);  $C_{cat}$  is volumetric concentration of catalyst of reforming block, kg/m<sup>3</sup>;  $P_i$  are partial pressures, atm;  $k_{con}$  is rate constant of methanol steam reforming reaction;  $K_i$  are stoichiometric coefficients. Rate of shift reaction (47) [15]:

$$r_{sh} = \frac{k_{sh} \sqrt{P_{H_2}} P_{CO} P_{H_2O} \left( 1 - \frac{P_{CO_2} P_{H_2}}{K_e^{sh} P_{CO} P_{H_2O}} \right) C_{cat}}{(\sqrt{P_{H_2}} + K_1 P_{CH_4O} + K_2 P_{CO_2} P_{H_2} + K_3 P_{H_2O})^2} k_{sh} = k_{sh}^0 \exp\left( \frac{-E_{sh}}{R_g T_c} \right) \quad [15]$$

where  $r_{sh}$  is rate of shift reaction, mol/(m<sup>3</sup> s);  $k_{sh}$  is constant of shift reaction rate. Rate of methanol decomposition (47) [16-17]:

$$r_{dec} = \frac{k_{dec} P_{CH_4O} \left[ 1 - \frac{P_{CO} (P_{H_2})^2}{K_e^{dec} P_{CH_4O}} \right] C_{cat}}{(\sqrt{P_{H_2}} + K_5 P_{CH_4O} + K_6 P_{H_2O}) (1 + \sqrt{K_7 P_{H_2}})} \quad [16]$$

$$k_{dec} = k_{dec}^0 \exp\left(\frac{-E_{dec}}{R_g T_c}\right), K_n = K_n^0 \exp\left(\frac{-Q_n}{R_g T_c}\right), n = 1, 2, 3 \dots 7. \quad [17]$$

where  $r_{dec}$  is rate of CH<sub>3</sub>OH decomposition reaction, mol/(m<sup>3</sup> s);  $k_{dec}$  is constant of CH<sub>3</sub>OH decomposition reaction. Kinetic parameters of these equations are  $E_{con} = 82,8$  kJ/mol,  $E_{sh} = 67,6$  kJ/mol,  $E_{dec} = 150$  kJ/mol,  $E_{CH_4O} = 26$  kJ/mol,  $k_{con}^0 = 5.6 \times 10^7$ ,  $k_{sh}^0 = 1.6 \times 10^6$ ,  $k_{dec}^0 = 1,6 \times 10^{17}$ ,  $k_{CH_4O}^0 = 10^4$ ,  $C_{cat} = 200$  kg/m<sup>3</sup>.

## Experimental Technique

In order to verify the performance and optimization of the design, as well as to verify the adequacy of the model, tests of a laboratory sample of a fuel processor for the conversion of alcohols were carried out on an experimental test bench. It consisted of a burner, an alcohol conversion reactor and a capillary system for supplying liquids. The reactor was a "tube-in-tube" type apparatus consisting of an inner tube with a diameter of 20 mm with a catalyst placed in an outer tube with a diameter of 40 mm and a length of 45 cm. We used a gas analyzer "Siemens" for samples analysis of output gases from the hydrocarbon feed conversion unit for H<sub>2</sub>, NO, NO<sub>2</sub> and O<sub>2</sub>.

## Results and Discussion

### Numerical Analysis of alcohol conversion reactor

The results of numerical analysis of temperature distributions, the degree of CH<sub>3</sub>OH conversion and H<sub>2</sub> concentration along the reactor for both direct (figures 1a and 2a) and counter (figures 1b and 2b) flows of reagents and hot gas in endothermic and exothermic channels are presented. All calculations were made for a catalytic layer length of 40 cm. It can be seen that a more uniform temperature profile over the catalyst and the wall, as well as a larger margin in the degree of CH<sub>3</sub>OH conversion, is observed during direct flow. So, with a counter-flow, the wall and the catalyst on the inlet side of the vapor-methanol mixture have  $T < 250^\circ\text{C}$ , on the outlet side of the vapor-methanol mixture  $T \sim 400^\circ\text{C}$ , thus overheating of the catalyst layer is possible. At direct flow, both temperatures are always  $< 350^\circ\text{C}$ . Therefore, the preferred implementation of the process in the reactor is direct flow.

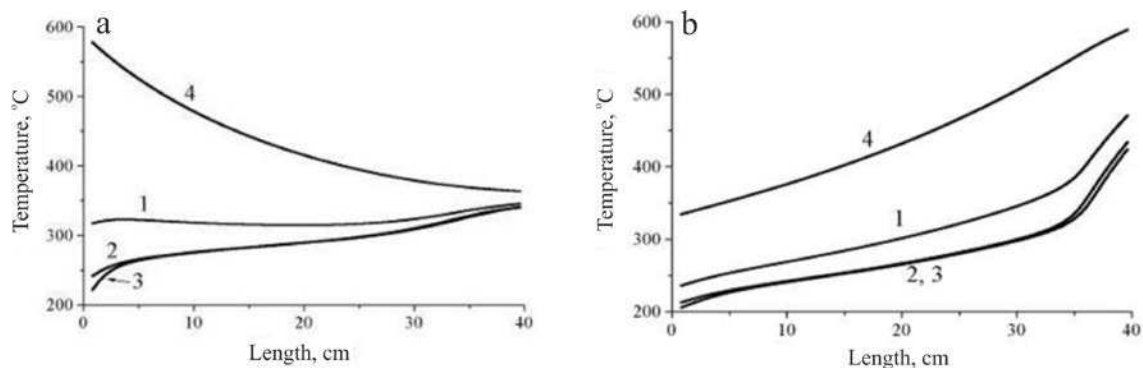


Figure 1. Temperature distribution along the length of the catalyst bed: a – direct flow, b – counter flow. 1 – wall, 2 – catalyst, 3 – vapor-methanol mixture, 4 – outlet gases.

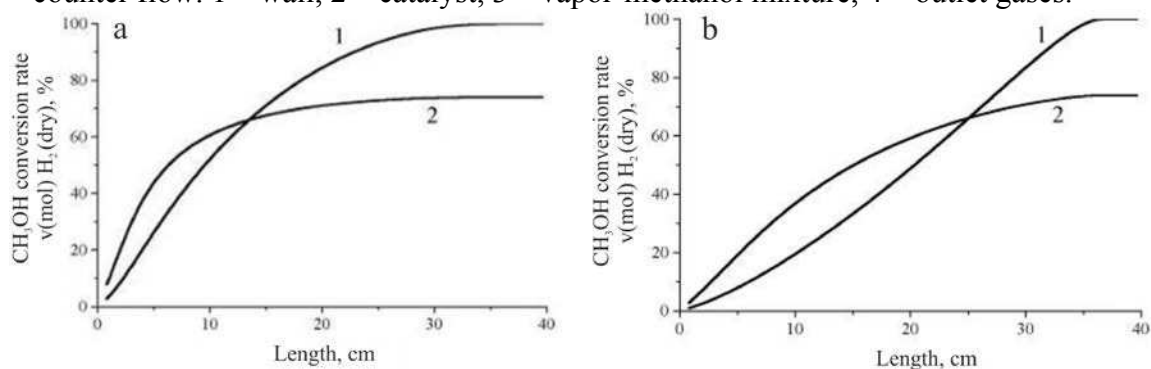


Figure 2. The distribution of conversion rate along the length of the catalyst bed: a – direct flow, b – counter flow. 1 – CH<sub>3</sub>OH conversion rate, 2 – H<sub>2</sub> (dry) mol fraction.

### Experimental Verification of Alcohol Conversion Reactor

From the presented experimental data, it follows that under the conditions studied, almost complete conversion of CH<sub>3</sub>OH is achieved (table 1).

TABLE I. Test results of a model CH<sub>3</sub>OH steam reforming reactor.

Flows to the burner, l/min			Flows to reactor, g/h		Temperature, °C		Composition of conversion products, %			
CH <sub>4</sub>	Air <sub>1</sub>	Air <sub>2</sub>	CH <sub>3</sub> OH	H <sub>2</sub> O	Inlet	Outlet	CO	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>
9	90	260	640	360	520	383	7,8	22	0,068	69,44
9	90	300	800	450	450	375	6,7	22,6	0,086	69,97
9	90	360	800	450	425	338	5,5	24	0	70,16
9	90	400	800	450	407	325	4,7	24,5	0	70,3
9	90	420	800	450	391	318	4,8	24,6	0	70,22
9	90	420	1200	675	373	271	3,1	26,2	0	70,48

### Comparison of Experimental and Model Data

Figures 3 and 4 show comparison of the calculations results using a mathematical model with experimental data obtained at a model reactor. Kinetic data is taken from work (47).

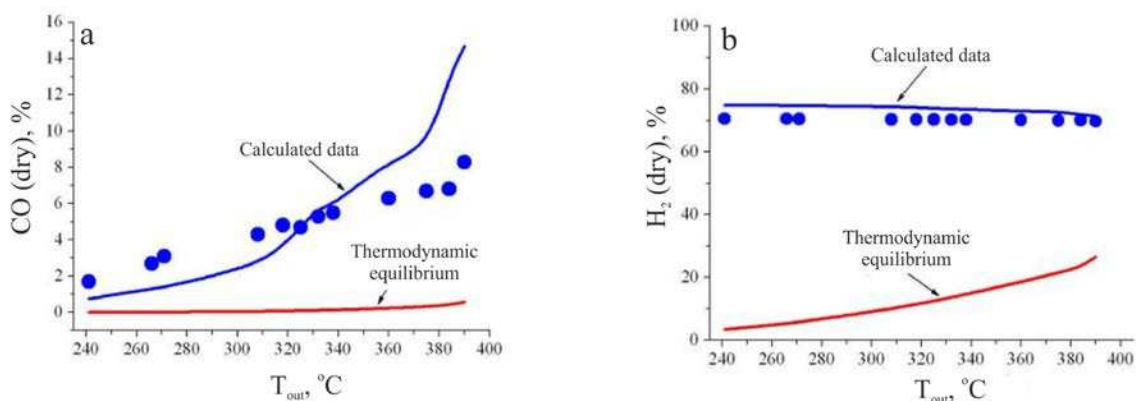


Figure 3. Comparison of experimental data (dots) on the concentration of CO (a) and H<sub>2</sub> (b) depending on the temperature at the outlet of a model reactor with thermodynamic equilibrium and model (lines).

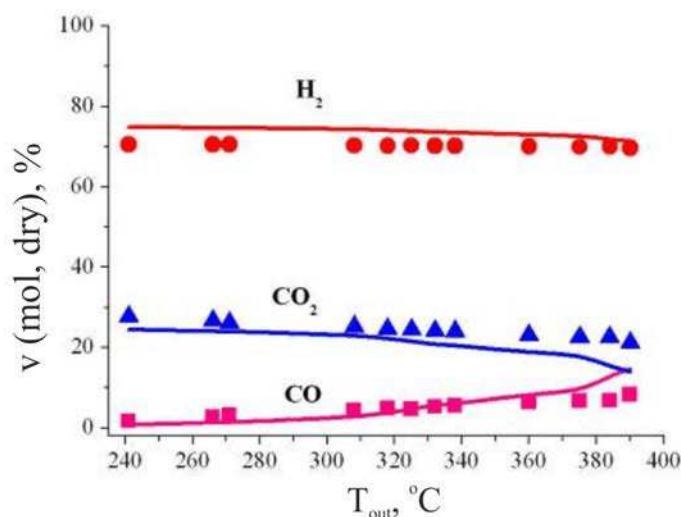


Figure 4. Comparison of experimental data on H<sub>2</sub>, CO, CO<sub>2</sub> (symbols) as a function of temperature at the outlet of a model reactor with calculation using a mathematical model (lines)

From the above data follows:

- the mathematical model describes quite well the experimental data obtained in experiments on a model reactor over the whole range of experimental conditions. Therefore, it can be used to calculate the fuel processor integrated with SOFC stack;
- the resulting compositions of the conversion products significantly differ from the equilibrium values.

## Conclusions

The paper proposes a mathematical model of the processes occurring in the methanol conversion reactor for solid oxide fuel cells. The concentration and temperature profiles were calculated, the geometrical parameters of the reactor were optimized. There is a good agreement between the results of calculations and experimental data.



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