Analysis and Modeling of Synthesis Gas Conversion to Methanol: New Trends toward Increasing Methanol Production Profitability

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Abstract—Technologies for methanol production from synthesis gas are analyzed. Their main advantages and disadvantages are determined, and a new methanol synthesis technology without feed circulation is proposed, which, in particular, is also applicable at a significant nitrogen content of the synthesis gas feed. On the basis of the results of laboratory and bench tests of the new process, mathematical models of a catalyst grain and a catalytic reactor and a kinetic model of methanol synthesis are constructed and their parameters are estimated. It is shown that the models fit experimental data. A three-reactor methanol synthesis unit providing 75–80% conversion of the synthesis gas feed is calculated. The crude methanol obtained has a high content of the desired product of 94–99 wt %. It is demonstrated that this process is characterized by much lower feed and energy consumption.

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In view of the reduction of the world's oil reserves, it is more and more important to involve such sources of hydrocarbon and carbon raw materials as, e.g., natural gas and coal in industrial processing [1–3]. To efficiently replace oil, it is necessary to develop highly profitable technologies for producing the key products of chemical and petrochemical synthesis and environmentally clean motor fuels based on them [4, 5]. Coal and natural gas can replace oil only if the cost of the desired products is no higher than that of petroleum products. Note that, in particular, motor fuels obtained from natural gas are virtually free of sulfur- and nitrogen-containing organic compounds and, hence, produce much less harmful emissions into the environment [6–13].

In industry, conversion of coal and natural gas to motor fuels and the key products of chemical synthesis is usually performed by two processes, namely, the Fischer–Tropsch synthesis and the Mobil process. In both processes, hydrocarbon products are obtained from synthesis gas. However, the selectivity of the Mobil process with respect to hydrocarbon components of gasolines is higher. These components are synthesized in the Mobil process by the reaction synthesis gas ⟶ methanol and/or dimethyl ether ⟶ motor fuel hydrocarbons.

The main drawbacks of conventional industrial technologies are the following:

the necessity of using the circulation of synthesis gas because of its low conversion to methanol (the volumetric flow rate of the circulating gas is 8–15 times higher than that of the feed flow);

insufficiently high selectivity of the catalytic process, which leads to the formation of a large amount of organic products hindering the subsequent separation of pure methanol from crude methanol.

A new variant of synthesis gas conversion to methanol without these drawbacks is considered. To predict the operation of equipment with high energy and resource savings, it is necessary to construct new models that would allow one to calculate the concentrations of the desired products and the byproducts in individual stages of methanol production with high accuracy.

The purpose of this work is to analyze and model synthesis gas conversion to methanol in order to enhance this process for reducing the product cost.
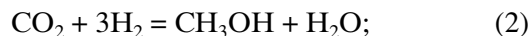
KINETICS OF METHANOL SYNTHESIS AND STEAM REFORMING OF CARBON MONOXIDE

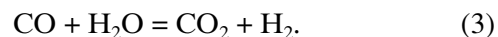In methanol production, the following reactions occur:

methanol synthesis from carbon monoxide,

$$CO + 2H_2 = CH_3OH; \tag{1}$$

methanol synthesis from carbon dioxide,

$$CO_2 + 3H_2 = CH_3OH + H_2O; \tag{2}$$

and steam reforming of carbon monoxide,

$$CO + H_2O = CO_2 + H_2. \tag{3}$$

Each of the reactions is reversible; therefore, in the reactor, 100% feed conversion cannot be reached. With a decrease in temperature and an increase in pressure,

Table 1. Results of kinetic experiments on steam reforming of carbon monoxide

Experiment no.	Catalyst weight, g	$v \times 10^3$, m³/h	T, K	Molar flow rates of feed reactants, $\times 10^3$ kmol/h					CO concentration at reactor outlet, vol %
				CO	H₂	CO₂	N₂	H₂O	
1	1.657	19.9	523	3.26×10^{-2}	5.18×10^{-3}	–	0.123	0.727	8.3
2	1.657	20.2	493	3.20×10^{-2}	5.12×10^{-3}	–	0.125	0.725	8.6
3	1.657	19.8	453	3.36×10^{-2}	5.14×10^{-3}	–	0.123	0.726	11.8
4	1.420	12.55	523	9.1×10^{-3}	1.4×10^{-3}	–	3.4×10^{-2}	0.337	12.7
5	1.420	12.6	493	9.0×10^{-3}	1.39×10^{-3}	–	3.4×10^{-2}	0.337	14.7
6	1.420	12.58	453	9.0×10^{-3}	1.41×10^{-3}	–	3.3×10^{-2}	0.337	17.6
7	1.404	11.07	523	1.72×10^{-2}	2.68×10^{-3}	–	6.94×10^{-2}	0.405	8.0
8	1.404	11.06	493	1.72×10^{-2}	2.66×10^{-3}	–	6.93×10^{-2}	0.405	8.8
9	1.404	11.05	453	1.73×10^{-2}	2.69×10^{-3}	–	6.94×10^{-2}	0.407	16.7
10	1.642	11.08	523	8.75×10^{-3}	3.12×10^{-3}	Traces	3.89×10^{-2}	0.406	11.4

the equilibrium amount of forming methane increases. The equilibrium feed conversion usually does not exceed 75% within the temperature range 453–553 K and the pressure range 4.0–8.0 MPa.

Various kinetic models of methanol synthesis and steam reforming of carbon monoxide at high hydrogen-to-carbon monoxide ratios have been proposed [14–21]. However, these kinetic models are unsuitable for calculations at significant concentrations of inert components (nitrogen, methane) in the synthesis gas feed. Moreover, published works usually do not mention the accuracy of estimates of constants of kinetic models, which also complicates their further use.

The mechanism and kinetics of methanol synthesis over promoted copper oxide catalysts of the KS-1 type were studied in a Carberry-type flow circulation reactor at atmospheric pressure, a flow circulation reactor under pressure with internal control of gas circulation, and a single-pass flow reactor under pressure. In the last two laboratory reactors, the pressure and temperature were varied within the ranges 0.1–6.0 MPa and 373–653 K, respectively. The reactors were equipped with heat exchangers that preheated the reaction mixture. The temperature in the reaction zone was measured with several thermocouples. From the circulation circuit and the reaction zone, the vapor–gas mixture came to a cooler for condensation of water vapor and methanol. After each experiment, the laboratory setup was purged with nitrogen from which oxygen was preliminarily removed. Steam reforming of carbon monoxide was performed over 2 ml of catalyst, and methanol synthesis was carried out over 2 ml of catalyst in the single-pass flow

reactor and over 10 ml of catalyst in the flow circulation reactors.

The catalyst was regenerated by a hydrogen–nitrogen mixture containing 2 vol % hydrogen for 10 h. The temperature was increased at a rate of 10–15 K/h. At 428 K, the catalyst was regenerated for 2 h. The regeneration was terminated at 503 K at a hydrogen concentration in the gas of 30 vol %.

The conditions and results of studying the kinetics of steam reforming of carbon monoxide and methanol synthesis are presented in Tables 1 and 2.

On the basis of the literature data [16–19] and the results of preliminary experiments, we chose a seven-step mechanism of methanol synthesis (Fig. 1) with two reaction routes N_1 and N_2 and two overall stoichiometric equations of the routes. The first and second stoichiometric routes correspond to steam reforming of carbon monoxide and methanol synthesis, respectively.

For this two-route multistep mechanism using the Horiuchi method, a kinetic model of methanol synthesis and steam reforming of carbon monoxide with 22 constants was constructed. The key components were chosen to be carbon monoxide and water. Three equations of invariants for non-Bodenstein substances (carbon dioxide, water, and methanol) were obtained, which allow one to reduce the dimension of the problem being solved. To simplify the estimation of all the constants of the full model, a kinetic model of steam reforming of carbon monoxide (the first route) was initially constructed and its 12 constants were estimated. The found values of the constants were used as initial approximations in determining the values of the con-

Table 2. Results of kinetic experiments on methanol synthesis

Experi-ment no.	$v \times 10^3$, m^3/h	T, K	P, MPa	Feed composition, kmol/m^3			Methanol concentration at reactor outlet, kmol/m^3
				H$_2$	CO$_2$	CO	
1	24.12	513	4.5	0.714	0.065	0.258	0.068
2	65.85	513	4.5	1.940	0.175	0.701	0.090
3	18.95	513	4.5	0.688	0.051	0.088	0.050
4	25.71	513	4.0	0.831	0.069	0.180	0.058
5	25.71	513	5.0	0.848	0.069	0.174	0.069
6	25.71	513	5.5	0.834	0.069	0.179	0.079
7	30.00	513	4.5	0.890	0.080	0.320	0.073
8	24.83	513	4.5	0.900	0.070	0.120	0.055
9	31.30	513	4.5	1.130	0.084	0.145	0.056
10	32.79	513	5.5	1.060	0.090	0.230	0.073

stants in the full kinetic model of methanol synthesis and steam reforming of carbon monoxide.

KINETIC MODEL OF METHANOL SYNTHESIS AND STEAM REFORMING OF CARBON MONOXIDE

The kinetic model of methanol synthesis involves the concentrations of five stable substances (hydrogen, carbon dioxide, carbon monoxide, water, and methanol) and six intermediate complexes. The invariant relations obtained enable one to calculate the rates of change in the concentrations of the nonkey substances (carbon dioxide, water, and methanol) through the rates of change in the concentrations of the key substances (hydrogen and carbon monoxide):

$$R_1 = -W_{(1)} - W_{(5)} - W_{(6)} = -W_{(3)} - 3W_{(7)}$$
$$= -k_{(+3)}x_8 + k_{(-3)}x_9 x_3 - 3[k_{(+7)}x_{11}x_4 - k_{(-7)}x_5 x_9], \quad (4)$$

$$R_3 = W_{(3)} = k_{(+3)}x_8 - k_{(-3)}x_9 x_3. \quad (5)$$

Equations of chemical invariants:

$$R_2 = \frac{1}{3}R_1 - \frac{2}{3}R_3, \quad (6)$$

$$R_4 = -\frac{1}{3}R_1 + \frac{2}{3}R_3, \quad (7)$$

$$R_5 = \frac{1}{3}R_1 - \frac{1}{3}R_3, \quad (8)$$

$$n_1 = \frac{k_{(+7)}k_6 x_1 x_4}{k_{(+3)} + k_{(-2)}}, \quad (9)$$

$$n_2 = \frac{k_{(-7)}}{K_{(4)}k_{(+5)}} \frac{x_4 x_5}{x_1}, \quad (10)$$

$$n_3 = \frac{(k_{(-3)}x_3 + k_{(-7)}x_5)(K_{(4)})^{-1}x_4 + k_{(+2)}x_2 K_{(1)}x_1}{k_{(+3)} + k_{(-2)}}, \quad (11)$$

$$n_4 = \frac{k_{(-5)}x_4}{k_{(+5)}x_1} + \frac{K_{(6)}k_{(+7)}x_4}{k_{(+5)}}, \quad (12)$$
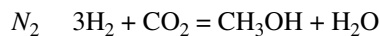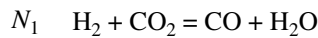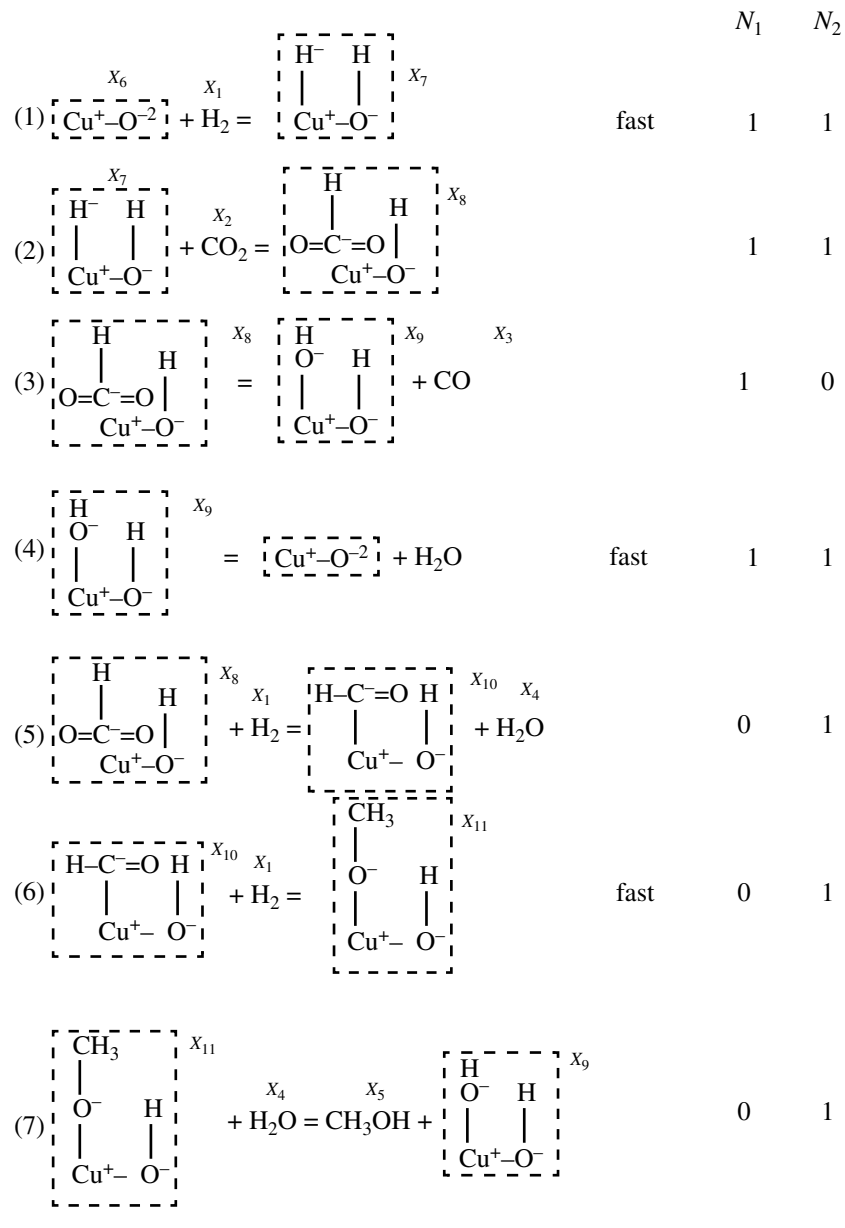
$$x_6 = \frac{1.0}{\left(1.0 + K_{(6)}x_1 + \frac{n_4(n_2 + n_3)}{n_1 + n_4} - n_2 + \frac{x_4}{K_{(4)}} + \frac{(n_2 + n_3)(K_{(6)} + 1.0)}{n_1 + n_4}\right)}, \quad (13)$$

$$x_7 = K_{(6)}x_1 x_6, \quad (14)$$

$$x_8 = \left(\frac{n_4(n_2 + n_3)}{n_1 + n_4} - n_2\right)x_6, \quad (15)$$

$$x_9 = \frac{x_4 x_6}{K_{(4)}}, \quad (16)$$

$$x_{10} = \left(\frac{n_2 + n_3}{n_1 + n_4}\right)x_6, \quad (17)$$

Fig. 1. Mechanism of methanol synthesis and steam reforming of carbon monoxide.

$$x_{11} = K_{(6)}x_1 x_{10}. \qquad (18)$$

The constants of the kinetic model obtained were estimated by least squares using methods for minimizing functions of many variables, such as the simplex method and random search using the best sample.

Numerical values of the kinetic constants K_p and $k_{(i)}$ were obtained. In particular, for the process at $P = 6$ MPa and $T = 503$ K, they are the following:

for methanol synthesis, $K_{p,\text{met}} = 1.4 \times 10^{-2}$;

for steam reforming of carbon monoxide, $K_{p,\text{ref}} = 1.28 \times 10^2$;

for elementary steps, $k_{(+2)} = 7.73 \times 10^2$, $k_{(-2)} = 1.18 \times 10^2$, $k_{(+3)} = 1.16 \times 10$, $k_{(+5)} = 3.54 \times 10^2$, and $k_{(+7)} = 3.64 \times 10^3$.

The other constants were determined as complexes of these constants.

The goodness of fit of the kinetic model of methanol synthesis to the experimental data was tested by Bartlett's test. This test is used for testing the hypothesis of equality of two variance–covariance matrices, one of which is calculated from the results of a replicate experiment and the other of which is computed from the residual vector calculated from the model constructed. The key substances in testing the model for goodness of fit were carbon monoxide and methanol:

$$V_1 = \frac{\prod_{g=1}^{q} |A_g|^{l_g/2}}{|B_1|^{l_0/2}}, \tag{19}$$

$$B_1 = \sum_{g=1}^{q} A_g, \tag{20}$$

$$A_1 = \sum_{\alpha=1}^{l_1} (\mathbf{c}_\alpha - \bar{\mathbf{c}})(\mathbf{c}_\alpha - \bar{\mathbf{c}})^T, \tag{21}$$

$$A_2 = \sum_{\alpha=1}^{l_2} (\mathbf{c}_\alpha - \eta)(\bar{\mathbf{c}}_\alpha - \eta)^T, \tag{22}$$

$$W_1 = V_1 n^{\frac{1}{2}p_1 l_0} \prod_{g=1}^{q} l_g^{-\frac{1}{2}p_1 l_g}, \tag{23}$$

$$\rho_1 = 1 - \left[\left(\sum_{g=1}^{2}\frac{1}{l_g} - \frac{1}{l_0}\right)\left(\frac{2p_1^2 + 3p_1 - 1}{6(q-1)(p_1+3)}\right) + \frac{1}{l_0}\frac{p_1 - q + 2}{p_1 + 3}\right], \tag{24}$$

$$\omega_2 = \frac{p_1}{288\rho_1^2}\left[\begin{array}{l} 6\left(\sum_{g=1}^{2}\frac{1}{l_g^2} - \frac{1}{l_0^2}\right)(p_1+1)(p_1-1)(p_1+2) - \left(\sum_{g=1}^{2}\frac{1}{l_g} - \frac{1}{l_0}\right)^2 \\ \times \frac{(2p_1^2+3p_1-1)^2}{(q-1)(p_1+3)} - 12\left(\sum_{g=1}^{2}\frac{1}{l_g} - \frac{1}{l_0}\right)\frac{(2p_1^2+3p_1-1)(p_1-q+2)}{l_0(p_1+3)} \\ - 36\frac{(q-1)(p_1-q+2)^2}{l_0^2(p_1+3)} - 12\frac{(q-1)}{l_0^8}(-2q^2+7q+3p_1q-2p_1^2-6p_1-4) \end{array}\right], \tag{25}$$

$$P\{-2\rho_1 \ln W_1 \le z\} = P\{\chi_f^2 \le z\}$$
$$+ \omega^2[P\{\chi_{f+4}^2 \le z\} - P\{\chi_f^2 \le z\}] + 0(n^{-3}),$$

$$A_1 = \begin{bmatrix} 8.96 \times 10^{-4} & 2.52 \times 10^{-4} \\ 2.52 \times 10^{-4} & 86.8 \times 10^{-6} \end{bmatrix},$$

$$l_1 = 14,$$

$$A_2 = \begin{bmatrix} 16.0 \times 10^{-4} & 4.0 \times 10^{-4} \\ 4.0 \times 10^{-4} & 144.0 \times 10^{-6} \end{bmatrix},$$

$$l_2 = 20,$$

$$B_1 = \begin{bmatrix} 24.94 \times 10^{-4} & 6.52 \times 10^{-4} \\ 6.52 \times 10^{-4} & 230.8 \times 10^{-6} \end{bmatrix},$$

$$l_0 = 34,$$

$$\det A_1 = 1.42 \times 10^{-8}, \quad \det A_2 = 7.05 \times 10^{-8},$$

$$\det B_1 = 15.10 \times 10^{-8}, \quad -\ln W_1 = 1.13,$$

$$\rho_1 = 0.948, \quad \omega_2 = 0.0005, \quad \alpha = 0.05, \quad z = 7.81.$$

Since $-2\rho_1 \ln W_1 < z$, the model fits well the experimental results.

MODELING OF METHANOL SYNTHESIS IN A CATALYST GRAIN

The processes in a catalyst grain were mathematically described using a quasi-homogeneous model under the additional assumption that the grain is spherically symmetric. Under these conditions, the model has the form

$$\frac{d}{dr}\left([D_1(r)]r^2\frac{d\mathbf{c}_1}{dr}\right) + r^2\mathbf{R}_k(\mathbf{c}, T) = 0, \tag{26}$$

$$\frac{d}{dr}\left([D_2(r)]r^2\frac{d\mathbf{c}_2}{dr}\right) + r^2\mathbf{R}_{nk}(\mathbf{c}, T) = 0, \tag{27}$$

$$\frac{d}{dr}\left(\tilde{\lambda}(r)r^2\frac{dT}{dr}\right) + r^2\Delta\mathbf{H}^T\mathbf{r}(\mathbf{c}, T) = 0. \qquad (28)$$

The Dirichlet boundary conditions are imposed:

$$r = 0, \quad \frac{d\mathbf{c}_1}{dr} = 0, \quad \frac{d\mathbf{c}_2}{dr} = 0, \quad \frac{dT}{dr} = 0, \qquad (29)$$

$$r = R, \quad \mathbf{c}_1(R) = \mathbf{c}_{1s},$$
$$\mathbf{c}_2(R) = \mathbf{c}_{2s}, \quad T(R) = T_s. \qquad (30)$$

Let us represent the matrix B_0 of the overall equations of the routes as

$$B_0 = [B_{01} \mid B_{02}],$$

where the rank of the matrix B_{01} is equal to the number p of reaction routes. Then, the first vector equation of diffusion stoichiometry in differential form is written as

$$\frac{d\mathbf{c}_2}{dr} = [D_2(r)]^{-1}B_{02}^T B_{01}^{T^{-1}}[D_1(r)]\frac{d\mathbf{c}_1}{dr}. \qquad (31)$$

Equation (31) in integral form appears as

$$\mathbf{c}_2(R) - \mathbf{c}_2(r) = \int_r^R [D_2(r)]^{-1}B_{02}^T B_{01}^{T^{-1}}[D_1(r)]d\mathbf{c}_1. \qquad (32)$$

Obviously, if $[D_2(r)]$ and $[D_1(r)]$ are constant matrices, then Eq. (32) takes the form

$$B_{02}^T B_{01}^{T^{-1}}[D_1]\mathbf{c}_1 - [D_2]\mathbf{c}_2 = B_{02}^T B_{01}^{T^{-1}}[D_1]\mathbf{c}_{1s} \qquad (33)$$
$$- [D_2]\mathbf{c}_{2s}.$$

Similarly, the diffusion stoichiometry equations in differential and integral forms for the Dirichlet problem with the vector of the key substances and the temperature in the grain are written

$$\frac{dT}{dr} = \tilde{\lambda}(r)^{-1}\Delta\mathbf{H}^T B_{01}^{T^{-1}}[D_1(r)]\frac{d\mathbf{c}_1}{dr}, \qquad (34)$$

$$T(R) - T(r) = \int_r^R \tilde{\lambda}(r)^{-1}\Delta\mathbf{H}^T B_{01}^{T^{-1}}[D_1(r)]d\mathbf{c}_1. \qquad (35)$$

At constant $[D_1(r)]$ and $\tilde{\lambda}$, Eq. (35) takes the form

$$\Delta\mathbf{H}^T B_{01}^{T^{-1}}[D_1(r)]\mathbf{c}_1 - \tilde{\lambda}T = \Delta\mathbf{H}^T B_{01}^{T^{-1}}[D_1(r)]\mathbf{c}_{1s} \qquad (36)$$
$$- \tilde{\lambda}T_s.$$

Using Eqs. (28)–(36), we calculated the catalyst grain efficiency factors η_1 and η_2 for steam reforming of carbon monoxide and methanol synthesis, respectively. At $P = 4.0$–6.0 MPa and $T = 453$–513 K, we have $0.9 < \eta_1 < 0.96$ and $0.99 < \eta_2 < 1.09$.

MODELING OF A CATALYTIC REACTOR FOR METHANOL SYNTHESIS

The final step of modeling of a catalytic process is to calculate the designs of the reactor unit and its constituent individual reactors and to determine the operating conditions of the reactor unit under which a given output, feed conversion, and energy consumption are ensured [22–42]. It was necessary to design a reactor unit fed by synthesis gas with a significant (up to 40–60 vol %) nitrogen concentration. The residual synthesis gas should have a calorific value no less than 2400 kJ/m³ so that it can be used to generate power sufficient for the process to be closed in energy. Low-output methanol synthesis plants can be placed directly at gas production sites for providing immediate transport of the liquid products of gas processing from the north of the Russian Federation to its central regions and abroad.

The base reactor was chosen to be a shell-and-tube reactor with 5-m-long tubes each 32 mm i.d. The heat-transfer media are water and water vapor. In reactors of such design, the formation of local hot spots within the catalyst bed can be avoided and low temperature gradients in the reaction zone along the axis and radius of reactor tubes can be maintained. High heat removal, which is characteristic of boiling heat-transfer media, also allows one to ensure that the operating conditions of individual tubes in the tube bundle are close [22].

The base model was chosen to be a one-parameter diffusion model of a polytropic reactor of the form

$$\frac{d}{dl}\left(D(l)\frac{d\mathbf{c}_1}{dl}\right) - \frac{d(u\mathbf{c}_1)}{dl} = [\eta_1]\mathbf{R}_k, \qquad (37)$$

$$\frac{d}{dl}\left(D(l)\frac{d\mathbf{c}_2}{dl}\right) - \frac{d(u\mathbf{c}_2)}{dl} = [\eta_2]\mathbf{R}_{nk}, \qquad (38)$$

$$\frac{d}{dl}\left(\lambda(l)\frac{dT}{dl}\right) - \frac{d(uc_d\rho T)}{dl} - \frac{4\alpha}{d_d}(T - T_c) \qquad (39)$$
$$= \Delta\mathbf{H}^T[\eta]\mathbf{r}.$$

The following boundary conditions are imposed:

$$l = 0, \quad -D\frac{d\mathbf{c}_1}{dl} = u(\mathbf{c}_{1f} - \mathbf{c}_1), \quad -D\frac{d\mathbf{c}_2}{dl}$$

$$= u(\mathbf{c}_{2f} - \mathbf{c}_2), \quad -\lambda\frac{dT}{dl} = uc_p\rho(T_f - T),$$

$$l = L, \quad \frac{d\mathbf{c}_1}{dl} = 0, \quad \frac{d\mathbf{c}_2}{dl} = 0, \quad \frac{dT}{dl} = 0. \qquad (40)$$

All the macrokinetic parameters of model (37)–(41) were assumed to depend on spatial coordinates. Equations (37)–(41) were transformed to a system of Cauchy-normal first-order differential equations, which were then integrated by explicit, semiexplicit, and implicit Runge–Kutta methods. The operation of the bench catalytic reactors was analyzed using model (37)–(41).
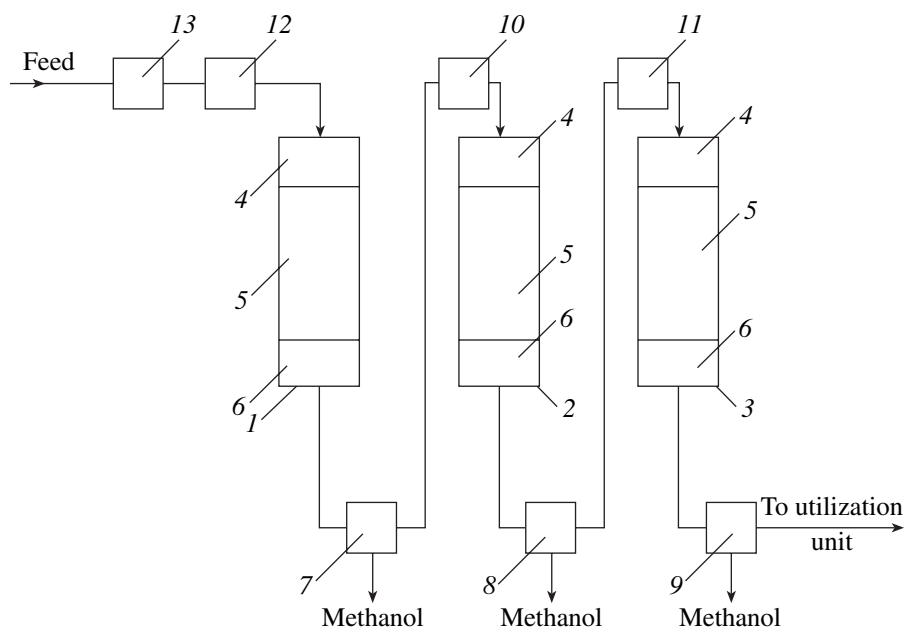
Fig. 2. Flowsheet of the reactor unit for methanol synthesis: (*1–3*) catalytic reactors for methanol synthesis, (*4*) inlet zone of reactors *1–3*, (*5*) main zone of reactors *1–3*, (*6*) outlet zone of reactors *1–3*, *(7–9)* separators, (*10–12*) heat exchanger, and (*13*) compressor.

CHEMICAL ENGINEERING SYSTEM OF METHANOL PRODUCTION WITHOUT SYNTHESIS GAS CIRCULATION

A general chemical engineering system for natural gas conversion to methanol was constructed (Fig. 2). The operating conditions of this chemical engineering system were optimized. It was shown that a 15–20% reduction in the cost of the desired product requires the introduction of a new reactor unit for methanol synthesis. This unit should consist of three single-pass shell-and-tube reactors without feed recirculation. The crude methanol obtained over the KS-1 promoted copper–zinc catalyst contains almost no organic impurities. This enables one to significantly simplify the distillation unit, which should contain only two columns, rather than three as usual. Consequently, the specific metal content of the distillation unit and the energy consumption for its operation decrease.

The energy–chemical method for methanol production is implemented in the setup as follows. The feed is synthesis gas obtained by the partial oxidation of natural gas in internal combustion engines, gas turbines, or catalytic reactors. The feed is fed at a volumetric flow rate of 500–10000 h^{-1} to compressor *13* and is compressed there to a pressure of, e.g., 6.0 MPa. Then, the gas flow enters heat exchanger *12*, where it is heated by the product flows from the first reactor to a temperature close to the methanol synthesis temperature. After heat exchanger *12*, the synthesis gas comes to zone *4* of reactor *1* and is heated there to the temperature of the heat-transfer medium with a temperature gradient of no more than 10 K/dm. The heat-transfer medium can be, e.g., water. Further, the gas flow passes through zone *5*

of reactor *1*, in which much of the synthesis gas is converted to methanol, and zone *6* of reactor *1*. In zone *5* of reactor *1*, the gas flow is heated by the heat of chemical reaction at a temperature gradient along the reactor axis of no more than 3 K/dm. In zone *6* of reactor *1*, the gas flow is cooled and the temperature gradient along the reactor axis is negative.

From reactor *1*, the gas flow arrives at heat exchanger *10*, which heats the feed to a temperature close to the temperature in reactor *1*. Next, the flow enters separator *7*, where methanol is condensed, and incondensable gases pass through heat exchanger *10* into zone *4* of reactor *2*.

The operating conditions of reactors *2* and *3* are similar to those of reactor *1*. From reactor *3*, the gas flow is fed to separator *9*, where the liquid products of methanol synthesis are condensed, and incondensable gases are sent to a residual gas utilization unit.

The total conversion of synthesis gas (with a significant nitrogen concentration) in this reaction system in the three-reactor unit is 75–80 vol %. A higher synthesis gas conversion should not be obtained because, otherwise, the residual gas cannot be used as a gas fuel for power machines.

According to the flowsheet in Fig. 2, a bench setup was designed and put into operation. To each of the reactors, 4.5l of the KS-1 catalyst was loaded. Several experiments on this setup were carried out. The results of the operation of individual reactors were precalculated using the corresponding models. The calculated and experimental data in all the sets of experiments agreed well. For example, in the second set of experiments, at a pressure in the reactors of 6 MPa, methanol

was synthesized from a reaction mixture comprising 17.4 wt % carbon monoxide, 30.5 wt % hydrogen, and 2.06 wt % carbon dioxide at a total feed flow rate of 0.765 kmol/h. The results obtained are presented below.

Reactor	Temperature, K	Methanol yield, l/h	
		experiment	calculation
1	487	2.62	2.45
2	477	0.79	0.68
3	473	0.41	0.38

The experiments on the bench setups showed the possibility of efficient operation of the three-reactor unit in synthesis gas conversion to methane at various hydrogen contents of 26–70 vol %. In all the cases, the methanol obtained had a high quality.

RESULTS AND DISCUSSION

In Russia, there is currently a significant demand for high-octane environmentally clean motor fuels. In the country, oil production in the decades to come will gradually decrease but natural gas reserves are so large that they can satisfy the country's demand until at least 2150. Consequently, it is of prime importance to improve technologies for methanol production from natural gas. Methanol is a raw material for producing hydrocarbon and oxygenated motor fuels and the key products of chemical and petrochemical synthesis (ethylene, propylene, lubricating oils, and α-olefins). Methanol production will occupy a key place in industry if the cost of produced methanol can be reduced by 15–20%. The results of the experimental investigation of the kinetics of methanol synthesis and the modeling of this process in batch reactors revealed a region in which methanol synthesis is highly selective. In the crude methanol obtained by the new technology, there were no azeotropes and the concentration of byproduct water was several times lower than that in currently produced industrial crude methanol. A set of experiments performed with bench packed distillation columns showed that, even in a single column 1.5–2.0 m in height, the methanol concentration in the product flow reaches 99.9 wt % and water is present in trace amounts. It was experimentally shown that regions of highly selective synthesis gas conversion can be formed in catalytic reactors by regularizing the catalyst beds, adding inert heat-transfer media to the feed, and externally heating the catalyst beds.

Note that the crude methanol obtained by the new technology has high purity; therefore, for a number of industries, this can be either a marketable product, e.g., for the gas industry, or a raw material for producing dimethyl ether, ethylene, propylene, and motor fuels. For the highly purified methanol obtained, the number and volume of industrial distillation columns are much smaller, which reduces the specific metal content of the process equipment and the energy consumption. Moreover, the absence of feed circulation in the methanol production by the new technology results in additional energy savings. This also increases the methanol production profitability. Last, since methanol is synthesized under mild operating conditions, the service life of industrial catalysts is also prolonged.

NOTATION

A_1—auxiliary matrix used to estimate the sample variance–covariance matrix of the measurement error vector;

A_2—auxiliary matrix used to estimate the sample variance–covariance matrix of observations using the mathematical model;

B_0—matrix of the stoichiometric coefficients of the overall equations of the routes;

B_{01}—matrix of the stoichiometric coefficients of the key substances;

B_{02}—matrix of the stoichiometric coefficients of the nonkey substances;

B_1—auxiliary matrix that is the sum of the matrices A_1 and A_2;

$\mathbf{c}_p$—specific heat of the reaction mixture, J/(kg K);

$\mathbf{c}_\alpha$—vector of the concentrations of the reactants, kmol/m^3;

$\mathbf{c}_1$—vector of the concentrations of the key substances (carbon monoxide and hydrogen), kmol/m^3;

$\mathbf{c}_{1f}$—vector of the concentrations of the key substances (carbon monoxide and hydrogen) in the flow core, kmol/m^3;

$\mathbf{c}_{1s}$—vector of the concentrations of the key substances (carbon monoxide and hydrogen) at the catalyst grain surface, kmol/m^3;

$\mathbf{c}_2$—vector of the concentrations of the nonkey substances (methanol, carbon dioxide, and water), kmol/m^3;

$\mathbf{c}_{2f}$—vector of the concentrations of the nonkey substances (methanol, carbon dioxide, and water) in the flow core, kmol/m^3;

c_{2s}—vector of the concentrations of the nonkey substances (methanol, carbon dioxide, and water) at the catalyst grain surface, $kmol/m^3$;

$D(l)$—longitudinal dispersion coefficient, m^2/s;

$[D_1(r)]$—diagonal matrix of the effective diffusion coefficients of the key substances, m^2/s;

$[D_2(r)]$—diagonal matrix of the effective diffusion coefficients of the nonkey substances, m^2/s;

d—reactor tube diameter, m;

$K_{(i)}$—equilibrium constant for the ith step;

$k_{(+i)}$—rate constant for the forward reaction of the ith step;

$k_{(-i)}$—rate constant for the reverse reaction of the ith step;

L—catalyst bed length, m;

l—current reactor length, m;

l_g—integer number characterizing the size of a sample from the gth population;

l_o—integer number characterizing the size of samples from all the populations being tested;

l_1—number of degrees of freedom for estimating elements of the sample variance–covariance matrix of replicate observations;

l_2—number of degrees of freedom for estimating elements of the sample variance–covariance matrix calculated from the residual vector of the model;

N_1—overall equation of the route of methanol synthesis;

N_2—overall equation of the route of steam reforming of carbon monoxide;

n_1, n_2, n_3, n_4—auxiliary variables in the kinetic model;

P—probability of a given event;

p—number of the overall equations of the routes;

p_1—dimension of the vector of observations;

q—number of samples being tested;

$\mathbf{R}$—catalyst grain radius, m;

$\mathbf{R}_k$—vector of the rates of change in the concentrations of the key substances, $kmol/(m^3\ s)$;

$\mathbf{R}_{nk}$—vector of the rates of change in the concentrations of the nonkey substances, $kmol/(m^3\ s)$;

R_1—rate of change in the hydrogen concentration, $kmol/(m^3\ s)$;

R_2—rate of change in the carbon dioxide concentration, $kmol/(m^3\ s)$;

R_3—rate of change in the carbon monoxide concentration, $kmol/(m^3\ s)$;

R_4—rate of change in the water concentration, $kmol/(m^3\ s)$;

R_5—rate of change in the methanol concentration, $kmol/(m^3\ s)$;

r—current catalyst grain radius, m;

$\mathbf{r}$—vector of the rates of the overall reactions along the routes, $kmol/(m^3\ s)$;

T—temperature in the reactor, K;

T_c—temperature of the cooling agent, K;

T_f—temperature of the reaction flow, K;

T_s—temperature on the catalyst grain surface, K;

u—linear velocity of the flow, m/s;

v—volumetric flow rate, m^3/h;

V, W_1—statistics used in testing hypotheses of equality of two variance–covariance matrices;

$\mathbf{W}$—vector of the rates of elementary chemical reactions, $kmol/(m^3\ s)$;

x_1, x_2, x_3, x_4, x_5—stable species (hydrogen, carbon dioxide, carbon monoxide, water, and methanol) in the kinetic model of methanol synthesis;

x_6, x_7, x_8, x_9, x_{10}, x_{11}—unstable species (intermediates) in the kinetic model of methanol synthesis;

α—heat-transfer coefficient from the gas flow to the reactor wall, $W/(m^2\ K)$;

$\Delta\mathbf{H}$—vector of the heats of the overall reactions along the routes, J/kmol;

η—vector of responses of the system;

$[\eta]$—diagonal matrix of the efficiency factors of the reactions corresponding to the overall equations along the routes;

$[\eta_1]$—diagonal matrix of the efficiency factors of the key substances;

$[\eta_2]$—diagonal matrix of the efficiency factors of the nonkey substances;

$\lambda(l)$—thermal conductivity along the axis of the catalytic zone, $W/(m\ K)$;

$\tilde{\lambda}(r)$—thermal conductivity of a catalyst grain, $W/(m\ K)$;

ρ—density of the reaction mixture, kg/m^3;

ρ_1—auxiliary variable;

χ_f^2—χ^2 distribution with f degrees of freedom.

SUBSCRIPTS AND SUPERSCRIPTS

$g = 1, 2$;

1—hydrogen;

2—carbon dioxide;

3—carbon monoxide;

4—water;

5—methanol;

(1), (2), (3), (4), (5), (6), (7)—elementary chemical reactions (steps of the mechanism).

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