

Synthesizing Methanol from Nitrogen-Ballasted Syngas

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Received February 24, 2010

Abstract—The possibility of the effective catalytic synthesis of methanol from nitrogen-ballasted syngas was studied. Syngas was obtained during the operation of power machines such as diesel engines or gas turbines. The dependences of CO and CO₂ conversion per cycle, the quality of methanol, et cetera on the composition of syngas are characterized. The kinetic dependences of methanol synthesis on G-79-7GL catalyst (Zud Chemie) are described. For nitrogen-ballasted syngas, the dependences of the CO and CO₂ conversion and the output and quality of methanol on the reaction conditions (pressure, temperature, and gas mixture feed rate) are the same as for nitrogen-free syngas, though the CO conversion declined considerably when the concentration of ballast nitrogen was increased. These studies served as the basis for the creation of energy-independent units for processing hydrocarbon gases into methanol and motor fuels.

Key words: methanol synthesis, nitrogen-ballasted syngas, kinetics.

DOI: 10.1134/S2070050410040112

INTRODUCTION

According to modern economic requirements for producing liquid fuel from natural or casing-head gas, these gases must be transformed into syngas (a mixture of hydrogen and carbon oxide) and then into liquid synthetic products directly at the deposit sites [1].

The conventional processes for the production of liquid products from natural gas involve considerable capital outlays and are justified only for large volumes of the gas being processed. For fields where less than 100 million m³ of gas is produced per year, new technologies must be created, particularly those of syngas production. Our new method for producing a mixture of CO and H₂ is based on the partial oxidation of the gas with atmospheric oxygen in a gas turbine or diesel engine. The quality of the obtained syngas, as determined by the CO/H₂ ratio and the presence of CO₂, H₂O, and hydrocarbon impurities, depends on the composition of the initial natural and casing-head gas and the partial oxidation reaction.

The aim of this work was to study the possibility of an effective catalytic synthesis leading to high yields of methanol from nitrogen-containing syngas obtained by the partial oxidation of natural gas in a power machine. The parameters of the reaction (CO and CO₂ conversions per cycle, the quality of the starting methanol, et cetera) in relation to the composition of the syngas were determined. The kinetic dependences of the reaction on the C-79-7GL catalyst (Zud Che-

mie) were obtained. Studies of this kind have never been performed elsewhere.

EXPERIMENTAL

Methanol was synthesized on a laboratory catalytic unit in a flow isothermal reactor using a 100 cm³ batch of the catalyst. The height of the catalyst bed was 25 cm.

We used the following gas compositions as raw material (vol %):

Rawmaterial	No. 1	No. 2	No. 3	No. 4
CO	6.7	19.35	32.79	37.31
CO ₂	9.7	5.98	4.98	4.65
H ₂	70.1	58.14	48.45	45.19
CH ₄	13.5	16.52	13.78	12.85
H ₂ /CO	10.4	3	1.5	1.21

The raw material of each type was diluted (ballasted) with 20, 40, and 60 vol % nitrogen (an example of the designation for syngas is 1–20%N₂). The space velocity of the gas was varied from 1000 to 7000 h⁻¹; the methanol temperature, from 200 to 250°C; and the pressure, from 3 to 5 MPa. The gaseous raw material (syngas) was fed under pressure to the reactor using a Bronkhorst High Tech high-precision flowmeter (accuracy of measurement, ±1%).

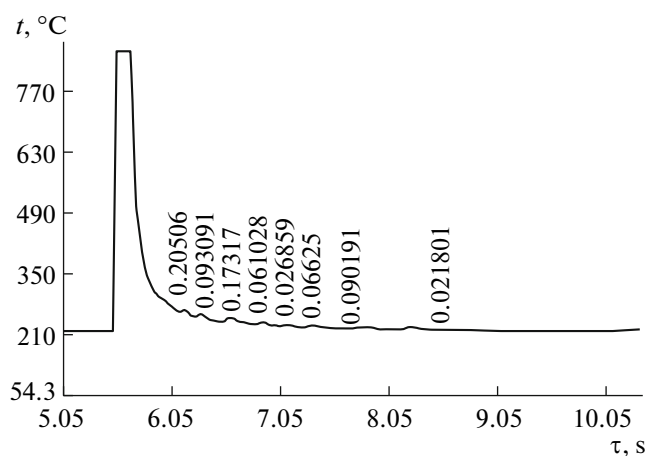


Fig. 1. Chromatogram of crude methanol obtained from raw gas material no. 3 with $H_2/CO = 1.5$ (0.69% organic impurities).

The temperature was measured along the catalyst bed using a moving thermocouple placed in a metal cup in the middle of the bed's diametrical cut.

The gas was analyzed at the outlet on a 3700 chromatograph; a catharometer with two Hayesep-Q packed columns ($CO + H_2$, CH_4 , CO_2 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8) and 5A molecular sieves (H_2 , CH_4 , and CO) was used as a detector in the isothermal mode at $55^\circ C$.

The liquid products were analyzed on a SE-54 column in the isothermal mode at $40^\circ C$ using a flame ionization detector. The content of water in the methanol was determined on a Hayesep-Q column at $100^\circ C$. Figure 1 shows the chromatogram of the

methanol, on which various impurities can be identified.

RESULTS AND DISCUSSION

An important stage of the investigations was verifying the isothermal mode of the reactor (the constancy of temperature along the catalyst bed in reactors of different constructions). Figure 2 presents the results from temperature measurements along the catalyst bed at different compositions of syngas, temperatures of the reactor's heating unit (t_3), and pressures during the reaction. The heat effect of methanol synthesis (Q) is obviously defined as the difference between the average temperature t_{av} in the catalyst bed, calculated as the arithmetic mean over the measured temperatures along the catalyst bed and the temperature of the reactor's heating unit (t_3).

Figure 2 (curves 1 and 2) shows that the heat effect of the reaction dropped considerably on going from the initial syngas containing no ballast nitrogen to the gas with a 40% N_2 addition (the temperature changed from 27.2 to $12.7^\circ C$). The gas composition 2–40% N_2 additionally contained methane, which, like nitrogen, was a ballast gas, so that the content of ballast gases in the mixture reached 55%; i.e., the gas was an adequate model of the real syngas obtained by the oxidation of methane with air using a diesel engine [2, 3]. We can state that the reactor design copes well with heat pickup while working with the real nitrogen-ballasted syngas of a power machine, since the overheating in the catalyst bed was as high as $13^\circ C$ and the reactor was quite controllable.

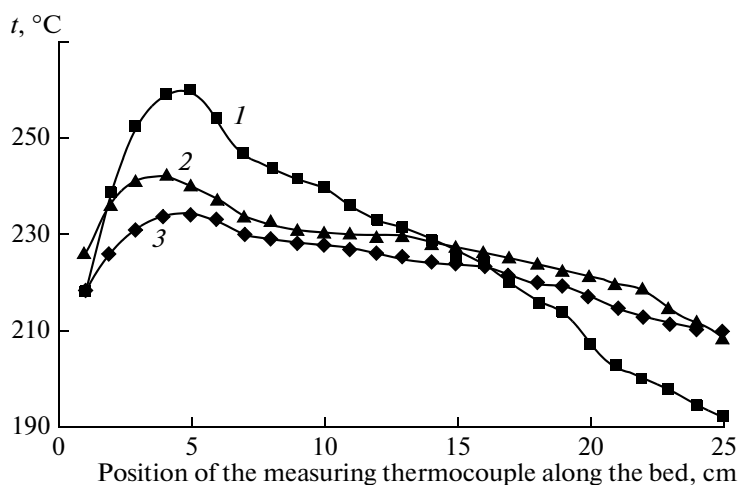


Fig. 2. Temperature profile along the catalyst bed for a space velocity of the gas raw material 3000 h^{-1} at different compositions of syngas, heater temperatures (t_3), and pressures: (1) $t_3 = 200^\circ C$, raw material 2, 5 MPa ($t_{av} = 227.2^\circ C$); (2) $t_3 = 215^\circ C$, raw material 2 (40% N_2), 5 MPa ($t_{av} = 227.7^\circ C$); and (3) $t_3 = 215^\circ C$, raw material 2 (40% N_2), 4 MPa ($t_{av} = 223.2^\circ C$).

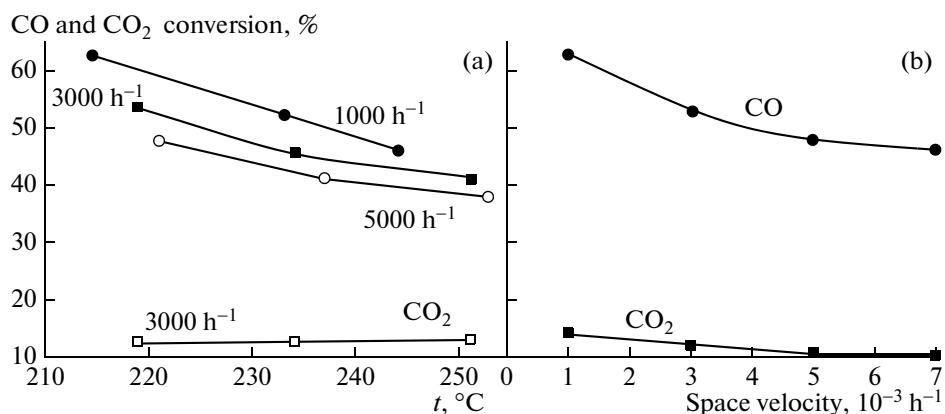


Fig. 3. Dependences of CO and CO₂ conversion at 5 MPa on (a) the temperature at different space velocities of gas mixture 1; (b) the space velocity of raw material 1 at an average temperature of 215°C in the bed.

Figure 3 shows the CO and CO₂ conversions at different average temperatures in the catalyst bed and space velocities of the gas raw material for gas composition 1 ($H_2/CO = 10.5$; $CO_2 = 9.7$ vol %). The data presented for nonballasted syngas suggest that CO conversion can be as high as 60% or more per cycle and falls when the temperature rises to 260°C, and that CO₂ conversion does not exceed 12% even at a pressure of 5 MPa and rises slightly with the temperature (e.g., by 3% for a space velocity of 3000 h⁻¹; Fig. 3a).

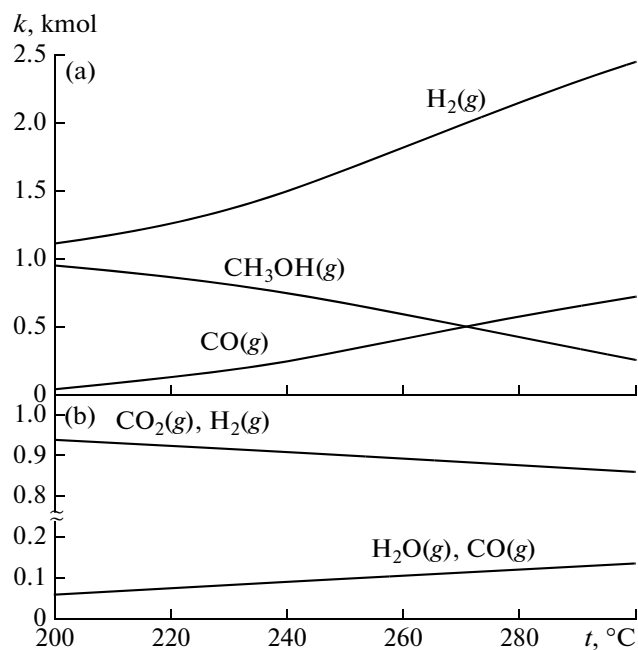
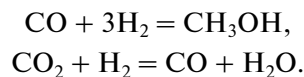


Fig. 4. Equilibrium curves of the component concentrations at 5 MPa in the reactions (a) $CO + 3H_2 = CH_3OH$ and (b) $CO_2 + H_2 = CO + H_2O$.

The experimental data on methanol synthesis on the specified catalyst (Zud Chemie) agree well with the results of thermodynamic calculations (using the HSC4 program designed at Haldor Topsoe) of the equilibrium concentrations of the components in the reactions



The calculated curves are shown in Fig. 4. According to Fig. 4a ($CH_3OH_{(g)}$ curve), the equilibrium concentration of methanol at low temperatures (200–220°C) can exceed 0.8 kmol/l. This means that CO conversion per cycle can also be as high as 80% or more and declines at elevated temperatures. CO₂ conversion by the reaction $CO_2 + H_2 = CO + H_2O$, however, does not exceed 12–14% over the temperature range (200–300°C; Fig. 4b, $CO_{2(g)}$ curve).

The laws presented in Fig. 3a for the initial syngas containing no nitrogen hold for nitrogen-ballasted syngas, though CO conversion drops considerably at increased concentrations of ballast nitrogen.

Figure 5 presents the dependence of CO and CO₂ conversion on the nitrogen content in a gas mixture with $H_2/CO = 10.4$. CO conversion dropped from 53 to 18% (at 60% dilution with nitrogen) and was obviously very sensitive to dilution with nitrogen, though the conversions are given for slightly different temperatures. The drop in conversion by only 8–10% for a temperature rise of 20°C (Fig. 3a) is further evidence for this.

Studies of methanol synthesis in hydrogen-stripped mixtures are of great interest because H_2/CO is always 2 or smaller (usually 1.6–1.8) in the syngas obtained by the partial oxidation of methane using diesel engines and fine control gates. For gas mixture 3 with

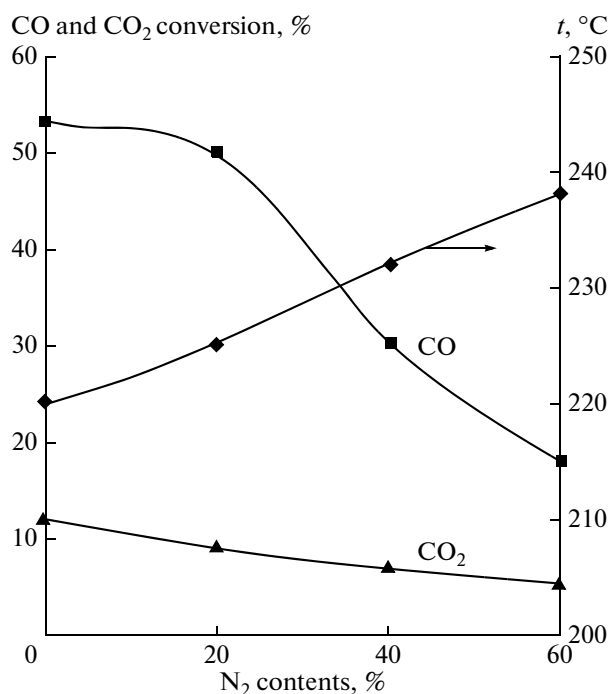


Fig. 5. Dependences of CO and CO₂ conversion at $W = 3000 \text{ h}^{-1}$ on the nitrogen content in gas mixtures ($H_2/CO = 10.4$) 1, 1–20% N₂, 1–40% N₂, and 1–60% N₂.

$H_2/CO = 1.5$, the CO conversion cannot be higher than 75%. For this syngas, therefore, the notation “CO conversion in percent of theoretical” was introduced.

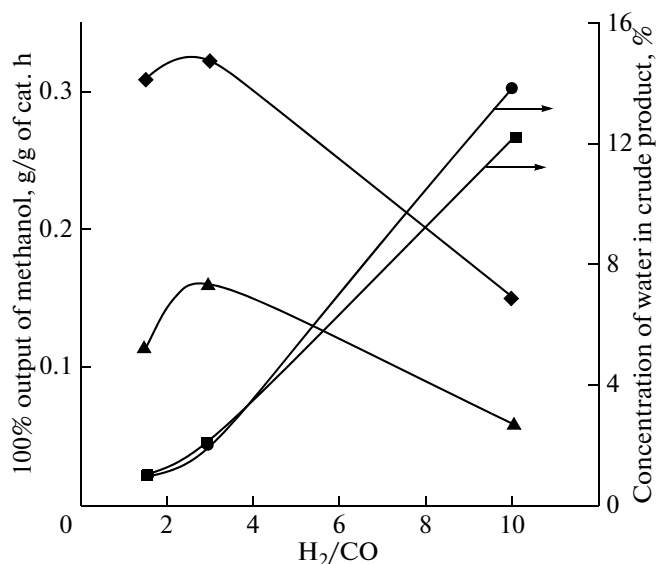


Fig. 6. Dependences of methanol output and water concentration on the H_2/CO ratio at a space velocity of syngas of 3000 h^{-1} for the (a) initial and (b) 40% nitrogen-ballasted syngas.

We compared the CO conversions obtained earlier (Fig. 5) for nitrogen-ballasted mixtures (1–40%) with $H_2/CO = 10.4$ and hydrogen-stripped mixtures (3–40%) with $H_2/CO = 1.5$. The Table 1 lists the results for the starting mixture and the mixture with 40% ballast nitrogen with $H_2/CO = 1.5$. For C-79-7GL catalyst at pressures above 4 MPa, the CO conversion was

Table 1. Synthesis of methanol from the starting ($H_2/CO = 1.5$) and ballasted syngas on the Zud Chemie catalyst at a space velocity of 3000 h^{-1} and pressures of 5.0, 4.3, and 3.0 MPa

Raw material	No. 3		No. 3 (40% N ₂)	
	5.0	4.3	5.0	3.0
Pressure, MPa	5.0	4.3	5.0	3.0
Temperature, °C	in the bed	200	205	210
	of the controller	230.0	220.0	222.0
Thermal effect, °C	30	14	12	7
Gas composition at the outlet, vol %				
CO	32.82	17.87	18.30	18.74
CO ₂	6.57	3.38	3.25	3.14
H ₂	41.97	23.95	25.03	26.18
CH ₄	18.64	9.30	9.15	8.90
N ₂	—	45.50	44.27	43.04
Outlet gas, l/h	221.8	263.2	271.0	278.8
CO ₂ conversion, %	2.5	1.5	1.8	2.4
CO conversion, % of theoretical	34.6	28.3	21.4	15.4
Crude methanol in a trap, g/h	37.4	15.8	13.9	10.2
Water concentration in the crude product, wt %	0.8	0.8	0.9	1.7
H ₂ /CO at the output	1.3	1.4	1.4	1.4

Table 2. Dependence of the parameters of methanol synthesis at 5 MPa and $W = 3000 \text{ h}^{-1}$ on the content of CO, CO₂, and H₂/CO

Raw material	No. 1	No. 2	No. 3	No. 4
Starting gas, vol %				
CO	6.7	19.35	32.79	37.31
CO ₂	9.7	5.98	4.98	4.65
H ₂	70.1	58.14	48.45	45.19
CH ₄	13.5	16.52	13.78	12.85
H ₂ /CO	10.4	3.0	1.5	1.2
(H ₂ -CO)/(CO + CO ₂)	3.9	1.5	0.4	0.2
H ₂ /CO ₂	7.2	9.7	9.7	9.7
CO/CO ₂	0.7	3.2	6.6	8.0
Temperature, °C	234	227	230	238
CO conversion, %	45.8	45.0	34.6*	29.1*
CO ₂ conversion, %	12.7	5.2	2.5	4.0
Thermal effect, °C	4.1	17.2	30.0	38
Water concentration in the crude product, vol %	13.9	1.9	0.8	1.5
Amount of organic impurities, vol %	0.01	0.15	0.69	1.08

higher than 20% even for syngas with 40% ballast nitrogen with a nonoptimal ratio of H₂/CO = 1.5. In addition, the concentration of H₂O in the raw material and the conversion of CO₂ increased slightly when the pressure of the reaction was lowered, while

the CO conversion dropped substantially, making methanol synthesis unviable.

Figure 6 and Table 2 present the dependences of the parameters of methanol synthesis on the composition of the initial syngas. According to Table 2, CO conversion drops 1.5-fold, from 45.8 to 29.1% when the H₂/CO ratio falls from 10.4 to 1.2, and the amount of organic impurities increases 100-fold. The change is parabolic for CO₂ conversion and the concentration of water in the methanol, with a minimum for H₂/CO = 1.5. Methanol can thus be obtained upon high CO conversion in an isothermal reactor even in highly ballasted mixtures (H₂/CO = 1.2).

According to the quantitative dependence of methanol output per unit of catalyst on the composition of syngas (Fig. 6), syngas with H₂/CO ≈ 2.5 is optimum for the maximum output of methanol; 40% dilution with nitrogen led to a smaller amount of methanol (half of the maximum output).

Table 3 gives the reaction order (n) estimated by the kinetic equation and two arguable hypotheses ($n = 1$ and $n = 2$) with respect to hydrogen for three selected experiments. It was assumed that the reaction occurring at a rate of

$$V = K[\text{CO}][\text{H}_2]^n / (1 + K_1[\text{CH}_3\text{OH}])$$

was not retarded by the methanol product ($1 + K_1[\text{CH}_3\text{OH}]$).

According to Table 3, $n = 1$ is preferable because there is a good convergence of results, indicating that the reaction order with respect to hydrogen is 1.

Table 3

Raw material	No. 1 (40% N ₂)	No. 2	No. 3	Convergence
Temperature, °C	232	227	230	
[CO], %	4.02	19.35	32.8	
[H ₂], %	42.06	58.14	48.5	
CO conversion, %	30.0	45.0	34.6	
Reaction rate (V), rel. units = CO [CO] conversion*	0.012	0.085	0.11	
[CO][H ₂]	0.017	0.11	0.15	
[CO][H ₂] ²	0.007	0.064	0.073	
K , rel. units, assuming that				
$n = 1$	0.71	0.77	0.73	++
$n = 2$	1.71	1.33	1.51	--

* In percents of the theoretical value.

CONCLUSIONS

Our experiments showed that methanol can be effectively synthesized from syngas of highly (up to 40–60%) nitrogen-ballasted methane oxidation products obtained during the operation of power machines (diesel or gas turbine). For nitrogen-ballasted syngas, the tendencies are the same as for syngas containing no nitrogen, but this depends on the reaction conditions (pressure, temperature, and the space velocity of the gas mixture); the CO conversion declines substantially at higher concentrations of ballast nitrogen. For highly ballasted syngas, the optimum ratio is $H_2/CO \approx$

2.5 for the maximum output of methanol, but the process must be conducted at moderate temperatures (220–240°C) and a pressure of no lower than 5 MPa. Our study has created conditions for the design of energy-independent units for the processing of hydrocarbon gases into methanol and motor fuels.

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