
ARTICLES

Chromatographic Procedure for the Determination of Products of the Direct Synthesis of Dimethyl Ether

P. V. Samokhin^a, I. A. Belostotskii^a, I. I. Marshev^a, and M. A. Kipnis^{a, *}

^a*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*

**e-mail: kipnis@ips.ac.ru*

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Abstract—We developed an original gas chromatographic procedure for determining the products and reagents for the catalytic synthesis of dimethyl ether (DME) from synthesis gas, which enables the simultaneous detection of CH₃OH, DME, CO, CO₂, H₂, H₂O, N₂, and hydrocarbons to C₆. The gas circuit includes four detectors, three packed columns, two precolumns (to prevent water and organic compounds from entering molecular sieve columns) in combination with two relief valves and two pressure regulators for the implementation of the back purging of precolumns. The system is assembled based on a Khromatek-Kristall 5000 chromatograph. The determination is carried out at a constant temperature of 140°C. The duration of analysis is not more than 12 min. Because of the presence of a flame ionization detector, it is possible to detect trace amounts of hydrocarbons, as well as ethane in the presence of large amounts of CO₂.

Keywords: gas chromatography, dimethyl ether, determination of methanol and water, Porapak T, 13X molecular sieves (NaX), absolute calibration

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Despite the existing assumptions about the inexhaustibility of oil and gas reserves, technologies for processing various non-oil feedstock (natural gas, associated petroleum refinery gas, household waste, biomass, coal, etc.) are in steady demand. For example, using oxidative conversion (the oxidant is water vapor, air, or oxygen), the non-oil feedstock is converted into synthesis gas using the known industrial technologies, from which methanol and/or dimethyl ether is then synthesized [1–5]. Interest in DME is associated with the known possibilities for its use. DME can be used as a propellant in devices for spraying liquid substances, refrigerant [6], and motor fuel as an alternative to diesel fuel [7]. DME is also considered as a raw material for the production of some hydrocarbons (olefins, gasoline, aromatics, and trip-tans) [8–11].

An experimental study of the direct synthesis of DME from synthesis gas involves the calculation of the composition and consumption of the converted gas containing easily condensable components (water, methanol) and components that can dissolve under pressure in the condensate in appreciable amounts (DME, CO₂). Therefore, a method of the direct gas chromatographic analysis of hot gas from the reactor is needed up to the moment of the condensation of its components. Such an analysis was used in recent works [12–17]; however, the conditions for its implementation and the necessary hardware design, as a

rule, were not described in detail. The complexity of chromatographic analysis in catalytic studies is associated with the need in identifying different groups of substances, conventionally separated on adsorbents operating at different temperatures, simultaneously. The analysis is limited in time, and the range of detectable concentrations is rather broad. Additional complexity is introduced by the adverse effect of some components of the reaction gas on the adsorption capacity of a number of the used adsorbents.

In catalytic studies related to the synthesis of dimethyl ether or methanol, the problem is the calculation of the consumption of hot converted gas at the outlet of the reactor. Often the calculation is performed based on maintaining the material balance for the inert component of the synthesis gas, for example, nitrogen. When a direct chromatographic determination of all components of the gas flow at the outlet of the reactor is performed, an additional opportunity appears to control the flow of hot gas after the reactor, based on the balance of carbon.

The aim of this work was to develop a gas chromatographic procedure for the determination of the products and reagents of the catalytic synthesis of DME in the isothermal mode, using columns packed with Porapak T and 13X molecular sieves.

EXPERIMENTAL

A Khromatek-Kristall 5000 chromatograph (Khromatek, Yoshkar-Ola, Russia) was assembled by the manufacturer for the analysis of hot gas in the process of DME synthesis in accordance with the preliminary order.

The original chromatograph included a heated input line for the gas to be analyzed, one thermostat, three thermal conductivity detectors (TCDs), a flame ionization detector (FID), heated automatic dosing valves for 6 and 10 inlets, two identical packed columns with 13X molecular sieves (NaX zeolite) 3 m in length and 2 mm in internal diameter (one for working with a carrier gas helium for determining simple gases, except hydrogen; another for working with a carrier gas argon for determining hydrogen), two precolumns installed before separation columns with a HayeSep R adsorbent (for the sorption of water and organic compounds from the sample, which are harmful to molecular sieves), a column with HayeSep Q 3 m in length and 2 mm in internal diameter, three injection loops, two relief valves for back purging of precolumns (to remove water and organic compounds from them before each analysis), and flow and pressure regulators (mass electronic). The determination was performed in a programmable heating mode.

The diagram of the modified chromatograph with an injection unit of the hot gas sample from the reactor for analysis is shown in Fig. 1. The analyzed gas enters the hot zone of the chromatograph through the heated line 27 (80°C), where it is split into two equal flows, passing through two metering valves 1 and 2 and washing three injection loops 3–5. At the outlet of the chromatograph, the analyzed gas flows from valves 1 and 2 are combined, pass trap 21 maintained at a temperature of 0°C, where water and methanol are condensed, and are sent to rheometer 22 to control the flow rate of the analyzed gas. The strength of the adsorption of water and organic compounds on the HayeSep R adsorbent is higher than that of simple gases; therefore, precolumns 9 and 10 absorb water and organic compounds and pass only simple gases into the main columns 11 and 12 with molecular sieves. In each analysis, after the release of the last target component from precolumns 9 and 10, they are back purged for desorption and removal of water and organic compounds. For the back purge, valves 17 and 18 open, and the carrier gas flow (argon, helium) is directed through precolumns in the opposite direction through pressure regulators 19 and 20. The gas flow rate is determined by pneumatic resistances, which are located in the lines after valves 17 and 18. The flows through the main columns 11 and 12 do not change due to the constant pressure in front of them set by the downstream pressure regulators 19 and 20 (semi-back purging method). The use of a semi-back purge circuit enabled the use of molecular sieves as an adsorbent for the determination of simple gases in complex, multi-

component samples, excluded regular conditioning of molecular sieve columns (heating up to 350°C), and offered the placement of columns with maximum allowable temperatures below 350°C in the same thermostat.

Helium (grade A, TU (Technical Conditions) 0271-135-31323949-2005, 99.995 vol %) and argon (highest grade, GOST (State Standard) 10157-79, 99.993 vol %) were used as the carrier gas. Hydrogen (grade A, GOST 3022-80, 99.99 vol %) was used for FID.

Calibration gas mixtures. To carry out an absolute calibration of the chromatograph, we used calibration gas mixtures manufactured by certified manufacturers, as well as mixtures that we prepared using a specially designed installation by mixing individual gases by pressure. We used nitrogen 99.999 vol % (TU 6-21-39-96), hydrogen 99.99 vol % (GOST 3022-80), carbon oxide 99.98 vol %, carbon dioxide 99.5 vol % (GOST 8050-85), DME 99.4 vol % (Azot, Russia) or 99.99 vol % (Akzo Nobel). Gases were successively added to a pre-evacuated cylinder in a predetermined proportion at controlled cylinder pressure and cylinder temperature. To prevent the ingress of oil vapors from the vacuum pump into the cylinder during the evacuation, we used a trap maintained above the surface of liquid nitrogen.

Absolute coefficients for water and methanol. Molar coefficients for water and methanol were determined using an independent laboratory setup, which was equipped with a plunger pump for supplying liquids and a Kristall Lyuks 4000M chromatograph. Liquid mixtures of water and methanol of known composition were pumped to an evaporator (145°C) with a mass flow meter (Bronkhorst, the Netherlands). The mixture was diluted with a flow of pure nitrogen, DME, or a mixture of nitrogen and DME of known composition. The flow rate was varied by a mass regulator of gas flow (Bronkhorst, the Netherlands). Data on the concentration and flow rate of the feed mixtures enabled the calculation of the composition of the final mixture. The mixture was supplied to the metering valve of the chromatograph through the heated line (145°C). Comparison of the data for DME for two chromatographs made it possible to calculate the corresponding coefficients for water and methanol as applied to the Khromatek-Kristall 5000 chromatograph.

All flow rates are given below, normalized to the conditions of 25°C and 101.3 kPa.

RESULTS AND DISCUSSION

In studying the kinetics of DME synthesis, it is required to perform a series of analyzes with minimal time intervals between them. However, analysis in the programmed heating mode, proposed by the manufacturer, takes considerable time. In this regard, we

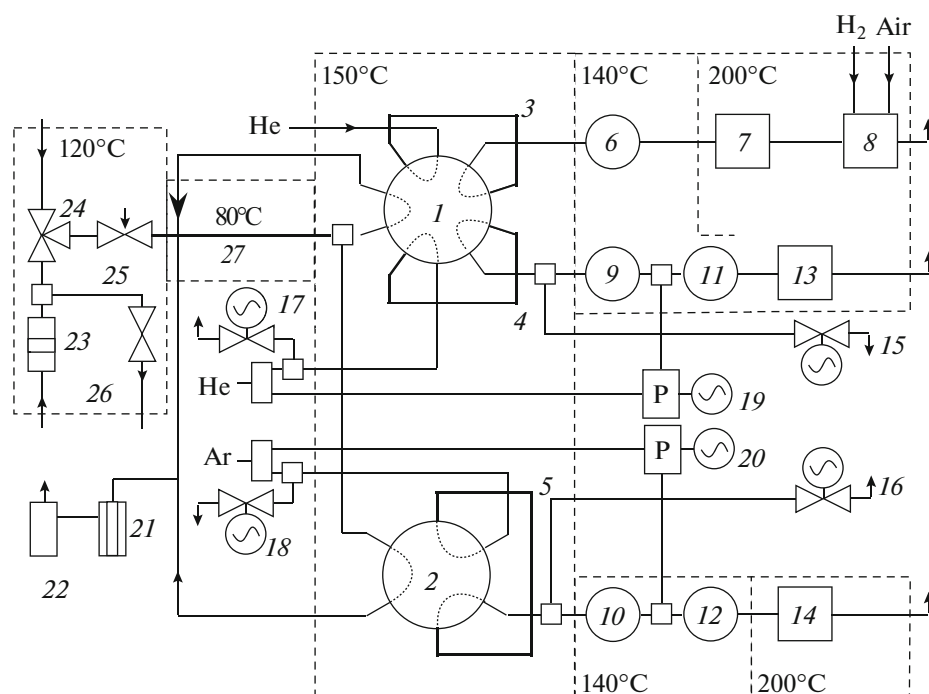


Fig. 1. Schematic gas diagram of a chromatograph with a hot gas sample-injection unit for analysis (the position of the metering valves 1 and 2 corresponds to the injection of the sample into the columns): (1) 10-channel metering valve, (2) 6-channel metering valve, (3–5) injection loops, (6) column with Porapak T (column with HayeSep Q in the factory supply), (7) TCD-1, (8) FID, (9, 10) precolumns with HayeSep R, (11) 13X molecular sieve column (helium carrier gas), (12) 13X molecular sieve column (argon carrier gas), (13) TCD-2, (14) TCD-3, (15–18) relief valves for the back purging of precolumns (position 15 and 16 in the factory supply), (19 and 20) downstream pressure regulators, (21) trap (0°C), (22) rheometer, (23) filter, (24) three-way valve, (25) microinjection valve, (26) stop valve, and (27) heated input line.

optimized the conditions for chromatographic analysis under the constant temperature of the thermostat. For the proper selection of a constant temperature, we solved inherent methodological problems.

Gas sampling circuit. A gas circuit was installed to collect a sample of the gas (Fig. 1, 23–26). To avoid the condensation of water and methanol at the reactor exit, all circuit elements up to the heated input line for the gas sample to the chromatograph were placed in a heated electric furnace (120°C). Gas valves with a maximum allowable operating temperature of 145°C (Swagelok, HOKE) were used.

The laboratory synthesis of dimethyl ether is usually carried out at pressures up to 3 MPa. Laboratory experience has shown that the smooth adjustment of the flow rate of the gas sent to the chromatograph with a pressure drop of 3 MPa on the control element can be ensured only in using control valves with a throughput coefficient (C_v) of not higher than 0.001. We used a Micromite 1600 (HOKE) micrometering valve with a C_v of 0.0008. For the reliable operation of the valve after the reactor, from which the removal of catalyst dust may occur, an anti-dust filter 23 with a cermet filter element (pore size, 0.5 μm) is installed before the valve. The flow rate of the analyzed gas was maintained constant (controlled by rheometer 22) and so

small (less than 2 L/h) that no excessive pressure was created in the injection loops.

The main part of flow from the reactor, through filter 23 and valve 26, enters the separator of the catalytic installation, cooled by running water, and then, after depressurization to atmospheric pressure, reaches the mass flow meter through the downstream pressure regulator. Three-way valve 24 enables either gas after the reactor or the original synthesis gas to be sent for analysis.

Correction of gas chromatograph circuit. According to the results of test analyzes performed using the initial configuration of the chromatograph, it was noted that the peaks had a delayed back front, and the baseline went to the horizontal level for a long time after sample injection.

We found that this was because, in the factory version of the gas circuit of the device, the relief valves for semi-back purge (lines of TCD-2 and TCD-3) were set before the precolumns after the metering valves (Fig. 1, 15 and 16); stagnant zones that affected the quality of the chromatogram recording were created in gas lines supplying them. The splitting of the gas line in the course of the sample led to a decrease in the gas sample because of its partial stagnation, the subsequent exit of the sample from the zone of stagnation,

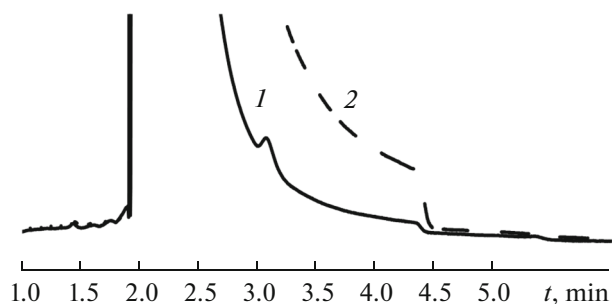


Fig. 2. Effect of the location of the relief valve for semi-back purging on the shape of the peaks and baseline: (1) before and (2) after the metering valve. Conditions: peak of argon, 80°C, carrier gas He, flow rate 14.6 mL/min, column with 13X molecular sieves (5 m × 2 mm).

and the dilution of the carrier gas after passing through the main front of the sample by this stagnated portion. To avoid these problems, the relief valves were rebuilt in before metering valves 17 and 18. This yielded stability of the horizontal baseline and narrowed the peaks (Fig. 2).

Selection of the time interval from the start of analysis to the opening of the relief valve for the semi-back purge. It was noted above that the quality of samples for molecular sieve columns was provided by two precolumns and a semi-back purge system. The efficiency of the operation of precolumns depends on the proper selection of the opening time of the relief valves. The opening time of the valve was selected based on the values of the peak areas of the last target component separated in the main column, obtained in sequential analyzes with different valve opening times from the beginning of the analysis. When the valve is opened early, only part of this component has time to leave the precolumn, and the peak area is underestimated. If the opening is delayed, the components that elute immediately after the last target component and negatively affect the ability of the column to separate substances enter the main column.

The stability of the flow rate of the carrier gas through the main columns at the time of opening of the relief valves depends on the response of pressure regulators 19 and 20 to the pressure change that occurs. To shorten the response time of the regulators, a constant minimum pressure drop was set on them and, as a result, the minimum flow rate, so that the pressure can be stabilized without noticeable changes in the baseline in the main column.

Selection of conditions for chromatographic analysis at a steady-state thermostat temperature. We solved the problem of selecting a satisfactory stationary temperature for columns with 13X molecular sieves and columns with Porapak T, which conventionally work in different temperature ranges.

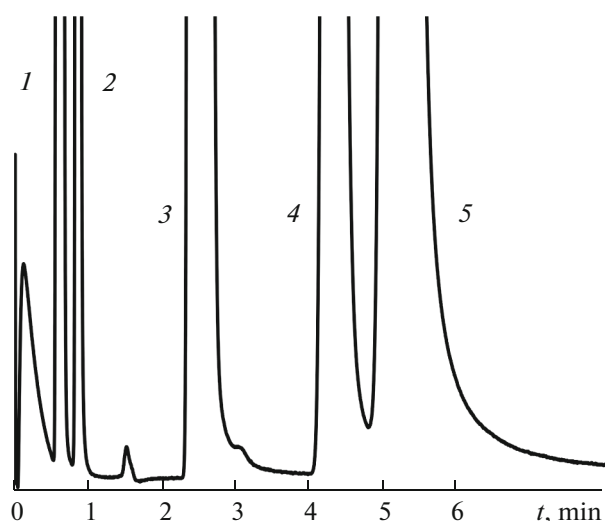


Fig. 3. Separation of CO₂, DME, water, and methanol in a column with Porapak T (4 m × 2 mm) at 140°C (helium carrier gas flow rate, 30 mL/min): (1) H₂ + O₂ + N₂ + CH₄ + CO, (2) CO₂ (1.19 vol %), (3) DME (9.61 vol %), (4) H₂O (2.26 vol %), and (5) CH₃OH (3.55 vol %).

Adsorbents HayeSep and Porapak are widely used for separating carbon dioxide, DME, methanol, and water at a constant temperature of approximately 100°C. The difficulty of selecting the optimal adsorbent for the separation of these substances is associated with a possible presence of components with close retention times in the sample. The column with HayeSep Q (3 m × 2 mm), proposed by the manufacturer for operation in the programmed heating mode, did not meet the requirements for the separation of the peaks of components and for their retention times at a constant temperature. Finally, we selected a column with Porapak T (4 m × 2 mm) instead of a column with HayeSep Q. An example of the chromatogram is shown in Fig. 3. The instability of the baseline after sample injection during the first 0.5 min is related to the pressure difference in the analysis line and in the carrier gas line. In using Porapak T, the retention times of DME (Fig. 3) and *n*-butane (Fig. 4) coincide, and the peak of methanol partially overlaps the peaks of pentane and *i*-pentane (Fig. 4).

The quality of peak separation in the selection of the separation parameters was checked by analyzing a multicomponent gas mixture saturated with water and methanol while bubbling through a water–methanol solution. Commercial columns 11 and 12 with molecular sieves (Fig. 1) showed a poor quality of the separation of the peaks; we increased their length as follows: by 2 m for column 11 and by 1 m for column 12.

Thus, by replacing the HayeSep Q column, proposed by the manufacturer for operating in the programmed heating mode, with the Porapak T column, increasing column length with 13X molecular sieves, and varying the constant temperature of the thermo-

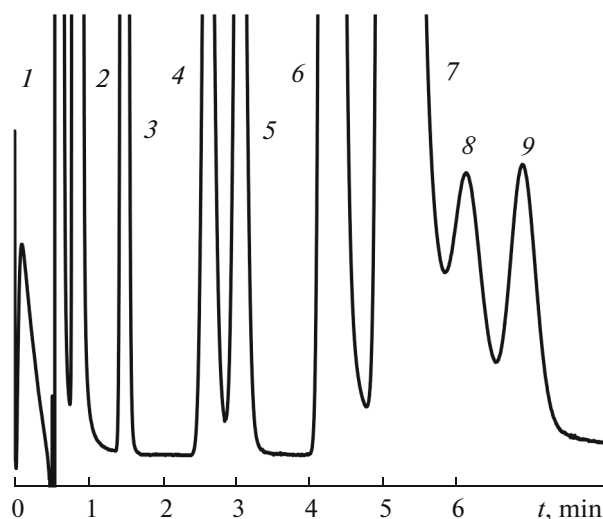


Fig. 4. Separation of a mixture of hydrocarbons with water and methanol in a column with Porapak T (4 m × 2 mm) at 140°C (helium carrier gas flow rate, 30 mL/min): (1) H₂ + O₂ + N₂ + CH₄ + CO, (2) CO₂ + ethane, (3) propane, (4) *n*-butane (0.10 vol %), and (5) *i*-butane (0.107 vol %), (6) water, (7) methanol, (8) *n*-pentane (0.058 vol %), and (9) *i*-pentane (0.052 vol %). The concentration of hydrocarbons is based on dry gas.

stat and the flow rates of carrier gases, we managed to find a satisfactory separation temperature (140°C) and other conditions for the detection of all reagents and products of direct synthesis of DME. The separation quality was satisfactory for all components in a wide range of concentrations, with the detection limits of 0.0005–0.01 vol %. The analysis time does not exceed 12 min.

Conditions of determination. The analysis was carried out at a constant temperature of the column thermostat of 140°C. The temperature of the detectors was 200°C, and the temperature of the metering valves was 150°C.

Carbon dioxide, DME, water, methanol, and C₁–C₆ hydrocarbons were separated in a Porapak T column (4 m × 2 mm); the detection with a TCD-1 was performed. Helium was used as a carrier gas with a flow rate of 30 mL/min; the injection loop volume was 1 mL. An FID, built-in sequentially, detects the trace amounts of hydrocarbons, as well as ethane in the presence of CO₂. Nitrogen, CO, CH₄, and, if necessary, O₂ were separated in a column with 13X molecular sieves (5 m × 2 mm) using helium as a carrier gas at a flow rate of 15 mL/min with the injection loop volume of 1 mL and determined by the TCD-2 with a limit of detection of 0.0005 vol %. The precolumn was packed with HayeSep R (1 m × 2 mm). The overpressure at the inlet of the main column was 330 kPa. The flow rate of the carrier gas through the line of pressure maintenance for the implementation of a semi-back purge was 0.8 mL/min. The carrier gas flow rate was

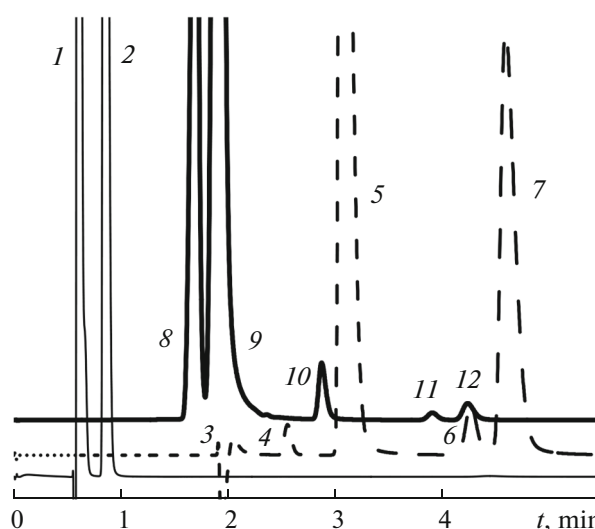


Fig. 5. Chromatograms recorded by (solid thin line) TCD-1, (dotted line) TCD-2, and (solid thick line) TCD-3: (1) N₂ + CO, (2) CO₂, (3) H₂ (49.9 vol %), (4) O₂, (5) N₂, (6) CH₄ (0.51 vol %), (7) CO (4.9 vol %), (8) He, (9) H₂, (10) N₂, (11) CH₄, and (12) CO. Conditions: column thermostat temperature 140°C, temperature of detectors 200°C; carrier gas flow rate: helium 30 mL/min (TCD-1) and 15.8 mL/min (TCD-2), argon 16.4 mL/min (TCD-3).

kept constant at 15.8 mL/min. The semi-back purge valve opened 65 s after turning on the metering valve. The flow rate through the precolumn in the opposite direction was 52 mL/min.

Hydrogen was determined using a 13X molecular sieve column with a TCD-3 with a limit of detection of 0.0005 vol %; argon was used as a carrier gas at a flow rate of 15 mL/min with the injection loop volume of 0.25 mL. The precolumn was packed with HayeSep R (1 m × 2 mm). The overpressure at the inlet of the column was 335 kPa; the flow rate of the carrier gas in the line of pressure maintenance was 1.4 mL/min. The total carrier gas flow rate was kept constant at 16.4 mL/min. The semi-back purge valve opens 60 s after turning on the metering valve. The flow rate through the precolumn in the opposite direction was 41 mL/min.

The magnitude of the responses of TCD-3 to N₂, CH₄, and CO with argon as a carrier gas is much smaller (Fig. 5, peaks 10–12) than the responses of TCD-2 to the same components (in the same analysis) with helium as a carrier gas (Fig. 5, peaks 5–7), even with a sample volume decreased four times for TCD-3. A similar conclusion can be made by comparing peaks 10 and 11 with peaks 7 and 8 in Fig. 6.

Quantitative determination was performed using the correction factors obtained by absolute calibration. For this purpose, 32 multicomponent calibration gas mixtures and individual gases were used, which ensured the necessary level of accuracy in determining

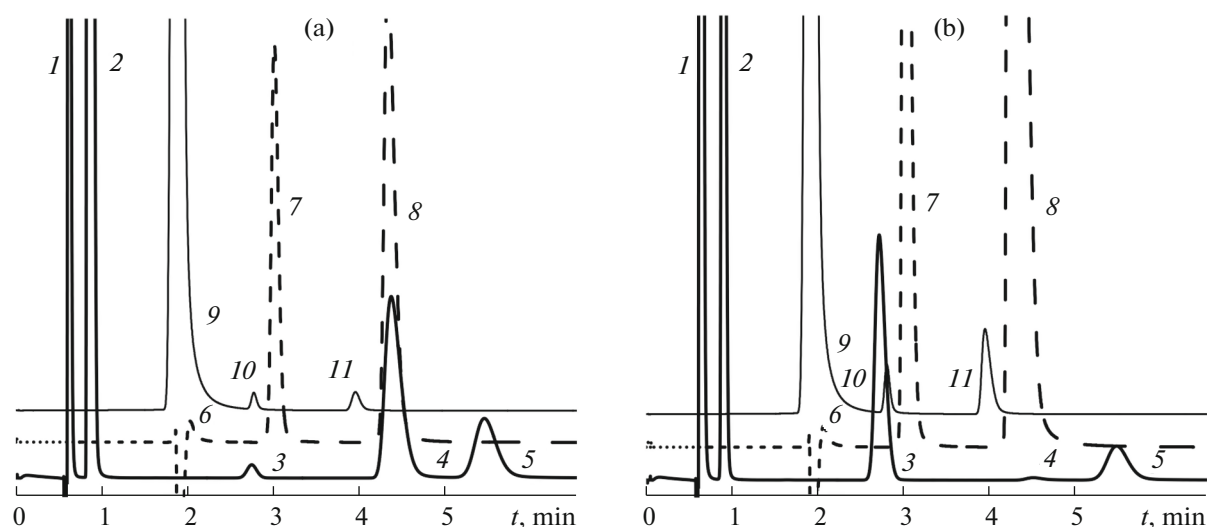


Fig. 6. Chromatograms of the products of DME synthesis from synthesis gas based on (a) CO_2 or (b) CO , obtained from (solid thick line) TCD-1, (dotted line) TCD-2, and (solid thin line) TCD-3: (1) $\text{N}_2 + \text{CO}$, (2) CO_2 , (3) DME, (4) H_2O , (5) CH_3OH , (6) H_2 , (7) N_2 , (8) CO , (9) H_2 , (10) N_2 , and (11) CO . Conditions of chromatographic determination: column thermostat temperature 140°C , temperature of detectors 200°C ; carrier gas flow rate: helium 30 mL/min (TCD-1) and 15.8 mL/min (TCD-2), argon 16.4 mL/min (TCD-3). Synthesis gas composition (vol %): (a) N_2 2.1, CO_2 26.9, and H_2 71; (b) N_2 5.3, CO 21.8, CO_2 5.2, and H_2 67.7.

the absolute coefficients in the required range of concentrations of a number of substances, which can be used to solve problems other than DME synthesis but associated with the use of synthesis gas.

Results of typical experiments of the direct synthesis of dimethyl ether. Figure 6 shows chromatograms of the reaction gas in experiments with synthesis gas rich in (a) CO_2 and (b) CO in one scale. Usually, the sum of the experimentally determined concentrations of components is approximately 100 vol % (deviation of no more than 3–4%), which requires a normalization procedure. Table 1 gives examples of experimental data obtained in the synthesis of DME from synthesis gas containing (vol %) CO , 21.4; CO_2 , 6.5; H_2 , 66.5; and N_2 , 5.6. A bifunctional catalyst $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ [18] was used; the catalyst weight was 1.6 g. The data were obtained at a pressure of 3 MPa and a temperature of 260°C . Based on the consumption of synthesis gas at the reactor inlet (V_{in}) and the ratio of nitrogen concentrations at the reactor inlet and outlet (K_{N}), we could calculate the gas consumption at the reactor

outlet. It is characteristic that the ratio of nitrogen concentrations at the reactor inlet and outlet practically coincides with the ratio of total concentrations of carbon-containing components at the reactor inlet and outlet (K_{C}), which indicates the correctness of the results of chromatographic analysis.

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Table 1. Composition of the converted gas (vol %) in the synthesis of dimethyl ether from synthesis gas

V_{in} , L/h	CO_2	DME	H_2O	CH_3OH	N_2	CO	H_2	K_{C}	K_{N}
9.8	8.7	1.97	0.70	2.5	6.2	16.5	63.5	0.88	0.90
14.8	7.8	1.22	0.61	2.1	6.0	18.3	64.0	0.91	0.92
19.7	7.3	0.85	0.58	1.8	5.9	19.2	64.4	0.93	0.94
24.6	7.0	0.59	0.56	1.6	5.8	19.9	64.6	0.94	0.95

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