**Technology for the Production of Methanol and Dimethyl Ether based on Local Raw Materials**

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**Abstract.** In the course of the study, a complex of physicochemical research methods was applied, including gas chromatography, scanning electron microscopy, IR spectroscopy, X-ray phase analysis, and standard analytical techniques. The technology for preparing catalysts based on local raw materials for dimethyl ether synthesis, as well as the reaction for obtaining methanol and dimethyl ether from a mixture of hydrogen and carbon monoxide, was developed. The qualitative and quantitative compositions of the initial and reaction mixtures were analyzed using a “Kristall 5000.2” gas chromatograph. The results were obtained using a Rigaku NEX-DE X-ray fluorescence spectrometer and a Shimadzu IRAffinity-1S IR-Fourier spectrometer. The results of the elemental analysis of the natural bentonite were examined. A “sol-gel” method was developed to obtain novel bifunctional catalysts with the compositions ZnO·CuO·Al2O3/bentonite and CuO·ZnO·Al2O3·ZrO2·CaO/bentonite, characterized by high catalytic activity, thermal stability, productivity, and selectivity in the synthesis of methanol and dimethyl ether from a mixture of synthesis gas and hydrogen based on local raw materials.

**Keywords:** Dimethyl ether, hydrogen, synthesis gas, bentonite, chromatography, scanning electron microscopy, IR spectroscopy, catalyst.

**INTRODUCTION**

At present, dimethyl ether and methanol are among the most widely used organic products in the world and are extensively applied as primary intermediates in the chemical and petrochemical industries. Currently, the annual demand for methanol is increasing at a rate of 5.5%, and by 2028, this figure is expected to reach 135 million tons. The current consumption of dimethyl ether amounts to 4.52 million tons, with a projected demand of 6.88 million tons by 2028 [1-3]. Therefore, expanding the raw material base for dimethyl ether and methanol production is an urgent issue. The use of synthesis gas as a feedstock for their production offers the advantage of reducing the cost of the final product. In this regard, the localization of imported raw material sources, introduction of new types of catalysts into practice, and improvement of dimethyl ether synthesis technology are of great significance [4-5]. A mixture of synthesis gas and hydrogen, especially synthesis gas with a CO:H₂ ratio of 1:2, serves as the primary raw material for the synthesis of valuable chemical products, including methanol — the first representative of alcohols — and dimethyl ether. The technology for producing methanol, the first representative of alcohols, has been well developed, and its production is widespread in industry due to the extensive use of methanol. In recent years, the production and utilization of dimethyl ether has become increasingly relevant; its production is based either on the intramolecular dehydration of methanol or on the direct synthesis from a mixture of synthesis gas and hydrogen [6]. Syntheses based on synthesis gas and hydrogen mixtures represent one of the cost-effective and widely applied methods of processing hydrocarbon raw materials, such as natural gas and valuable products of the petrochemical industry [7–9]. The compositions of catalysts intended for obtaining low- and high-molecular hydrocarbons, methanol, and dimethyl ether from a synthesis gas and hydrogen mixture are diverse. In the first industrial plants, zinc–chromium oxide catalysts were used at temperatures of 340–400℃ and pressures of 30 MPa. Currently, about 80% of the world’s methanol production is carried out under processes operating at 230–270℃ and medium pressures of 3–6 MPa on CuO–ZnO–Al₂O₃ (Cr₂O₃) catalysts.

The use of dimethyl ether in diesel engines was first introduced by Haldor Topsøe. Dimethyl ether burns very cleanly, producing neither soot nor SO₂ or NOₓ gases, and although only a small amount of exhaust gases is formed during combustion, purification is not required. According to the ecological classification of European researchers, dimethyl ether emissions meet the EURO-4 standards, and vehicles equipped with NOₓ purification systems satisfy the strict requirements of EURO-5. From both economic and environmental perspectives, the physicochemical study of the process of producing dimethyl ether from a mixture of synthesis gas and hydrogen using industrial catalysts is promising.

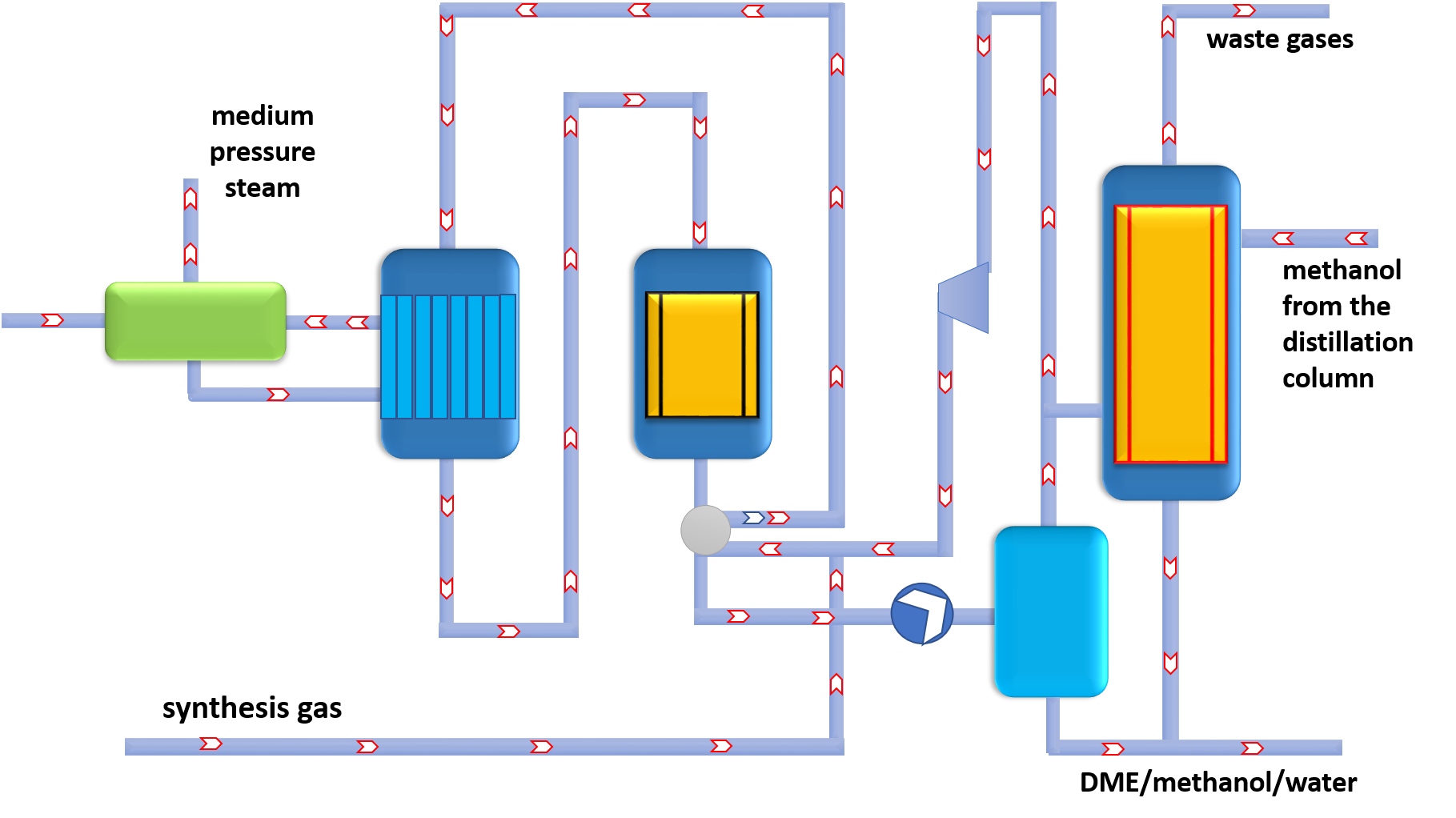
Natural bentonite is an important local raw material in Uzbekistan, widely used in various sectors of the chemical industry and the national economy. Bentonite is not an expensive raw material, yet it is an effective material broadly applied in many technological processes, for example, in the purification of wastewater, oil, and petroleum products, and most importantly, in catalyst synthesis.

Cu-Zn-Al–containing catalysts are considered the main type for the synthesis of dimethyl ether and methanol. The dehydration of methanol (obtained from synthesis gas and hydrogen mixtures) to dimethyl ether in the gas phase is most effectively catalyzed by γ-Al₂O₃, as it prevents the sequential transformation of the formed dimethyl ether into olefins. However, an efficient energy-saving technological scheme for dimethyl ether synthesis from a mixture of synthesis gas and hydrogen has not yet been developed, and an effective catalyst has not been obtained.

Each of the described technological processes has its own advantages and disadvantages. The scheme for producing dimethyl ether from synthesis gas is characterized by high capital costs but low operating expenses. Nevertheless, both processes are sufficiently energy-intensive, since such reactions are exothermic. The main consumer of energy is the distillation columns designed to separate the target dimethyl ether and the unreacted methanol from the reaction mixture.

**MATERIALS AND METHODS**

Production of dimethyl ether from synthesis gas: The scheme for obtaining dimethyl ether from synthesis gas is characterized by low operating costs with high capital expenditures. Nevertheless, both processes are sufficiently energy-intensive, since such reactions are exothermic. The main consumers of energy are distillation columns intended for separating the target dimethyl ether and unreacted methanol from the reaction mixture. In this case, the use of an integrated technology is considered an optimal solution. The efficiency of applying the integrated process is determined by the following parameters: 1) Due to the efficient removal of dimethyl ether from the reaction zone, the chemical equilibrium strongly shifts to the right. 2) The conversion of unreacted methanol exiting the first reactor can be increased up to 100%. 3) Reduction of equipment from three units to one result in a decrease in material costs. 4) Reduction of operating costs due to the utilization of reaction heat during separation processes, as well as the elimination of recycle from the technological scheme. It is known that from an economic point of view, the use of the integrated process is more efficient compared to the simple scheme of obtaining dimethyl ether from methanol. It consists of a chemical reactor and a set of distillation columns. When using the integrated process, the scheme is significantly simplified, Fig. 1.



**FIGURE 1.** Technological scheme for the production of dimethyl ether and methanol from synthesis   
gas in the integrated process

Reactor conditions of the process of obtaining dimethyl ether from synthesis gas: reaction temperature 200–300 ℃, pressure 0.1–1.0 MPa, hydrogen to carbon monoxide ratio 0.5–2.5, and space velocity in the range of 500–3500 h⁻¹. As a result of the research, the influence of various factors on the reaction rate was studied. The obtained experimental data are presented. Catalysts: in a layered loading with a 2:1:2 mass ratio of ZnO·CuO·Al₂O₃/bentonite: CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite: γ-Al₂O₃, the mixture of carbon monoxide and hydrogen first passes through the ZnO·CuO·Al₂O₃/bentonite catalyst layer, then the unreacted gases and formed products pass through the intermediate CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite layer, and finally through γ-Al₂O₃, where the formed methanol is converted into dimethyl ether.

In the distillation column, the temperature is 60–65 ℃ and the pressure is 0.1–0.2 MPa; under these conditions, the main product methanol boils and separates from the upper layer, and methanol boils at 64.7 ℃, while the remaining alcohols and water remain in liquid state. The substances separated at the bottom of the distillation column boil at the following temperatures: ethanol 78.3 ℃, propanol 97.2 ℃, water 100 ℃, and butanol 117.8 ℃, therefore at this temperature they remain in liquid state.

The temperature of the condenser is –25 ℃, the pressure is 0.5 MPa, since under these conditions dimethyl ether condenses in liquid form and separates from the bottom of the condenser, while the remaining substances are in gaseous state under these conditions and separate from the upper layer; CO boils at –191.5 ℃, CH₄ at –161.5 ℃, CO₂ at –78.5 ℃ and passes into liquid.

**RESULTS AND DISCUSSION**

The volumetric feed rate of the raw material is 0.8 ml/s; the contact time of the carbon monoxide and hydrogen mixture with the catalyst intended for carrying out the process is 3 s; the amount of CO per unit volume at the inlet of the reactor designed for obtaining dimethyl ether from the carbon monoxide and hydrogen mixture is 0.27 vol.%; P = 0.5 MPa; R = 8.314 kJ/mol; Tdes = 290 ℃.

*Gaseous substances*

1. The volume of CO (Vco\_transmitted) passed through the reactor designed for obtaining dimethyl ether from the carbon monoxide and hydrogen mixture:

*VCO(passed)=v⋅τ⋅CCO(in)=48ml/min⋅180min⋅0.27⋅10−6=0.00233m3or 2,33l l*

where *v* is the volumetric flow rate (ml/min); τ – contact time (min); *CCO(in)–* the volumetric fraction of CO at the reactor inlet (vol.%).

The amount of CO (*nCO(in)*) in the reaction mixture entering the reactor designed for dimethyl ether production from synthesis gas and hydrogen mixture:

=0,2389 mol,

the volume of CO passed through the reactor designed for the production of dimethyl ether from the synthesis gas and hydrogen mixture, l.

2. The volume of CO in the reaction mixture at the outlet of the reactor designed for the production of dimethyl ether from the synthesis gas and hydrogen mixture ()

0,31∙2,330,7223 *l*

Here, *CCO* is the volumetric concentration of CO.

The amount of CO in the reaction mixture at the inlet of the reactor designed for the production of dimethyl ether from the synthesis gas and hydrogen mixture. ():

=0,077156 mol

3. The volume of CO₂ in the reaction mixture at the outlet of the reactor designed for the production of dimethyl ether from the synthesis gas and hydrogen mixture ()

0,12∙2,330,2796 *l*

Here, CCO₂ is the volumetric concentration of CO₂.

The amount of CO₂ in the reaction mixture at the inlet of the reactor designed for the production of dimethyl ether from the synthesis gas and hydrogen mixture ():

=0,02986 mol

4. The volume of CH₄ in the reaction mixture at the outlet of the reactor designed for obtaining dimethyl ether from a mixture of synthesis gas and hydrogen ()

0,0022∙2,330,005126 *l*

Here, CCH₄ is the amount of CH₄ per unit volume.

The amount of CH₄ at the outlet of the reactor designed for obtaining dimethyl ether from a mixture of synthesis gas and hydrogen ():

= 0,0005475 mol

5. The volume of dimethyl ether in the reaction mixture at the outlet of the reactor designed for obtaining dimethyl ether from a mixture of synthesis gas and hydrogen ()

0,44∙2,331,0252 *l*

Here, CCH₄ is the amount of CH₄ per unit volume.

The amount of dimethyl ether at the outlet of the reactor designed for obtaining dimethyl ether from a mixture of synthesis gas and hydrogen ():

=0,1095 mol

*Substances in the liquid phase*

The amount of methanol at the outlet of the reactor designed for obtaining dimethyl ether from a mixture of synthesis gas and hydrogen, and other substances: here, is the amount in the liquid phase.

the accumulated mass of CH₃OH;

Molecular mass of CH₃OH (g/mol).

=0,00264

0,000171

0,00000139

0,000000278

0,011

Table 1 shows the results of the material balance calculations for the process of obtaining dimethyl ether from a mixture of synthesis gas and hydrogen.

**TABLE 1.** Results of material balance calculations

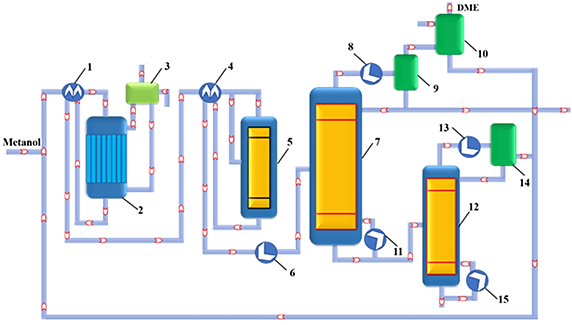
|  |  |  |  |
| --- | --- | --- | --- |
| **Component** | **Amount, mol** | | **Balance, %** |
| **COin** | 0,2389 | |  |
| **COout** | 0,077 | Total: 0,23136 |
| **CO2 out** | 0,03 |
| **CH4 out** | 0,00055 |
| **CH3OCH3 out** | 0,11 |
| **CH3OH out** | 0,00264 |
| **C2H5OH** | 0,000171 |
| **C3H7OH** | 0,00000139 |
| **C4H9OH** | 0,000000278 |
| **H2O** | 0,011 |

The material balance was calculated based on the decrease in the amount of synthesis gas: taking into account the number of moles of synthesis gas at the inlet and outlet, a value of 96.85% was obtained. Methanol was analyzed only in the liquid phase, and not in the gas phase. In the gas phase, the following components were analyzed: CO, CO₂, CH₄, and CH₃OCH₃.

The performance characteristics of the reactor unit designed to carry out the catalytic conversion process of methanol to dimethyl ether were calculated for a methanol consumption of 9 t/h·m³. To improve the regulation of temperature fields in the catalytic zones of the reactor intended for dimethyl ether production from methanol, both tubular and sectional reactors can be used.

Technical characteristics of the catalytic reactor for methanol-to-dimethyl ether conversion: welded vertical apparatus made of nickel–chromium steel. The sectional reactor is divided into three compartments with catalyst volumes of 3 m³, 4 m³, and 5 m³. External diameter – 2000 mm, height – 10,000 mm, operating pressure – 0.1–1.0 MPa, operating temperature – 100–180 °C. The process scheme is shown in Figure 2.

The unit operates as follows: the initial methanol stream is mixed with the recycle methanol stream coming from separators 10 and 14. The combined stream is heated in the reactor heat exchanger by the product stream (2), where methanol is converted into water and dimethyl ether.

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**FIGURE 2.** Process flow diagram of dimethyl ether synthesis from methanol (1, 4 – heat exchangers; 2, 5 – reactors for carrying out the chemical process of dimethyl ether production; 3 – steam drum; 6, 8, 13 – condenser–coolers; 9, 10, 14 – separators; 11, 15 – reboilers; 7, 12 – distillation columns).

Subsequently, the product stream from reactor 2 is directed to heat exchanger 4, where it is heated together with the product stream from reactor 5 up to the temperature at which the methanol dehydration reaction begins in reactor 5. The product stream from reactor 5 is cooled and fed into distillation column 7, where dimethyl ether is separated from water and unreacted methanol. These are then sent to column 12.

**TABLE 2.** Material balance of the reactor for dimethyl ether production via methanol dehydration

|  |  |  |
| --- | --- | --- |
| Section I of the reactor for dimethyl ether production from methanol (catalytic zone): Feed stream | | |
| CH3OH-Methanol | (CH3)2O-dimethyl ether | H2O-water |
| 280 kmol/h | 0.0 kmol/h | 0.0 kmol/h |
| Product stream: | | |
| 84.5 kmol/h | 98 kmol/h | 98 mol/h |
| Section II of the reactor for dimethyl ether production from methanol (catalytic zone):  Feed stream | | |
| 42 kmol/h | 31 kmol/h | 119.2 kmol/h |
| Section III of the reactor for dimethyl ether production from methanol (catalytic zone):  Feed stream | | |
| 25 kmol/h | 11.34 kmol/h | 126.5 kmol/h |
| Section I of the reactor | | |
| 0.84 kmol/h | 88.6 kmol/h | 0.12 kmol/h |
| Section II of the reactor | | |
| 0,41 kmol/h | 27.65 kmol/h | 1.1 kmol/h |
| Section III of the reactor | | |
| 0,65 kmol/h | 10.21 kmol/h | 1,25 kmol/h |
| Total: | | |
| 1,9 kmol/h | 126,46 kmol/h | 2.47 kmol/h |
| Product stream composition (mol %): | | |
| 2.20% | 93.95% | 1.87% |

Methanol is withdrawn from the top of the column and fed into reactor 2. The bottom water stream of column 12 contains methanol, which allows its reuse in the technological cycle.

Long-term stability tests of the CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite catalyst, characterized by high catalytic activity and selectivity for dimethyl ether production from methanol, were conducted over 1000 hours of operation. It was found that under operating conditions of P = 0.2 MPa and T = 180 °C, this catalyst maintained its activity almost unchanged. In the catalyst, methanol can be efficiently converted to dimethyl ether at a liquid hourly space velocity (LHSV) of 0.8 h⁻¹. In the proposed reactor design, methanol conversion to dimethyl ether can reach more than 93% (see Table 2).

In conventional industrial units, the dimethyl ether conversion does not exceed 70–75 mol%, and the process is carried out at elevated temperatures of 270–320 °C. These conditions contribute to the formation of additional by-products and require a mandatory subsequent rectification step. In the present variant, fuel-grade dimethyl ether can be obtained without the use of rectification columns.

Thus, the technology of dimethyl ether production in reactors designed for methanol-to-dimethyl ether conversion has been improved.

The methanol conversion process is carried out at temperatures 100 °C lower compared to conventional technologies. This enables the production of highly pure dimethyl ether and, when necessary, simplifies the rectification stage for dimethyl ether.

**CONCLUSION**

The following optimal conditions for the one-step synthesis of dimethyl ether from synthesis gas and hydrogen were determined: P = 0.5 MPa, T = 290 °C, H₂/syngas = 2, space velocity = 1000 h⁻¹. Under these conditions, the syngas conversion did not decrease over 150 hours. As a result, the dimethyl ether yield reached 44%, while the syngas conversion was 69%.

In periodic mode, the kinetic laws of methanol synthesis from a mixture of syngas and hydrogen, as well as its subsequent conversion to dimethyl ether, were established on ZnO·CuO·Al₂O₃/bentonite and CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite catalysts. Based on kinetic studies with the developed catalysts, the mechanisms of the reactions were elucidated, showing the pathways of dimethyl ether formation.

An energy-efficient technology for the low-temperature synthesis of dimethyl ether from methanol was developed, and a mathematical model of the dimethyl ether purification process was created. Industrial tests of the catalyst for the direct synthesis of dimethyl ether from syngas were also carried out. The synthesized catalysts were applied as locally produced alternatives to imported catalysts, providing an increase in economic efficiency of up to 11.5%.

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