

Evaluation of the Possibility to Use Coalbed Methane to Produce Methanol Both by Direct Partial Oxidation and From Synthesis Gas

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Abstract

The possibility of using coalbed methane to produce methanol is assessed. Methanol can be obtained from methane both by direct partial oxidation and from synthesis gas formed through the oxidative conversion of methane. Thermodynamic analysis of coalbed methane conversion was carried out to determine the conditions for obtaining synthesis gas with the ratio $[H_2]/[CO] = 2$, which is optimal for methanol production. The system consisting of methane, nitrogen, and oxygen, with different contents of oxygen and water vapor, was considered. The fuel-air equivalence ratio varied in the range from 2 to 4. The optimal conditions for obtaining synthesis gas for the production of methanol is the use of a mixture with an equivalence ratio of at least 4. It has also been shown that the addition of water vapor leads to an increase in the $[H_2]/[CO]$ ratio. Direct gas-phase oxidation of methane to methanol opens up the possibility of complex use of coal mining waste, including not only coalbed methane but also a large amount of coal waste accumulated during coal mining and beneficiation.

1. Introduction

The Program Methane of Kuzbass has been adopted in Russia [1]. Kuzbass may produce about 20 billion m³ of methane per year. Methane resources in Kuzbass are estimated as 13 trillion m³. The Program Methane of Kuzbass is to be implemented in three stages: prospecting-appraisal and geological-prospecting works, experimental-industrial production with the buildup of the output, and attainment of projected output. The first field for methane production from coal beds of the Kuznetsk Basin was launched in 2010 at the Talda zone.

Methane is formed in coal beds during coal metamorphism, which is accompanied by the low-temperature decomposition of the organic matter. Decomposition of the functional groups leads to the transition of a part of organic matter into the gas phase in the form of such molecules as CO₂, CO,

CH₄, etc. The homogeneous solid-phase process of the isomeric rearrangement of atoms proceeds spontaneously and is characterized by low activation energy 29–53 kJ/mol [2]. Due to adsorption, methane is accumulated in coal: in the vertical fractures and cracks of coal beds, cleavages and cracks between them. The amount of gas released per one ton of coal is usually 4–8 m³ [3]. The world resources of coal are approximately 1070 billion tons, so gas content in coal fields is comparable with the content in gas deposits. According to different sources, the coal-bearing fields of the world coal basins contain up to 262 trillion m³ of natural gas. According to estimations of the number of natural resources of the Russian Federation, predicted resources of coalbed methane in the major coal basins of Russia in 2014 accounted for approximately 80 trillion m³, which is approximately one-third of the total world resources [4].

For this reason, even moderate production of gas from coal beds might make a substantial contribution to the provision of natural gas to the world.

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In addition, methane entering the atmosphere as a result of coal mining accounts for about 8% of the total anthropogenic emission of methane, which makes about 17% of the anthropogenic contribution to the greenhouse effect [5].

Most of the black coal basins in Russia are gas-coal basins. The methane bearing capacity of these highly metamorphized coal beds increases with an increase in the depth of their occurrence and reaches 40–50 m³/t. Preliminary degassing of coal beds is the necessary condition for the safe work of miners and the source of associated methane. Though the amount of methane released into the atmosphere from Russian coal mines every year is more than 7.5 billion m³, it remains almost completely non-utilized yet. A rare exclusion is the use of coalbed methane for local power engineering. The use of coalbed methane is complicated by the low well rates and their substantial variations, which may range from 2 to 200 thousand m³/day, but usually is equal to 5–15 thousand m³/day [6, 7].

The industrial production of methane from coal beds is based on gas desorption from the coal surface through degassing. For this purpose, it is necessary to reduce the pressure in the coal bed, which will promote the evolution of free gas, entering the well through a system of cracks. For the maximal increase in the draining area, the influx from the wells is intensified using several methods: hydraulic fracturing treatment, pneumo-hydrodynamic action of coal beds with the formation of caverns in them. Depending on the composition and/or final destination of capped gas, it is either transported to a site for its further processing or burnt at a location to generate energy for the mine [8, 9].

Methane-air mixtures may be divided into three groups depending on the concentration: the 1st group includes the mixtures extracted using ventilation, as a rule, their concentration is 0.2–0.7%; the 2nd group brings together the mixtures extracted using degassing, with the concentration 5 to 25% (substandard for explosion hazard); the 3rd group includes the mixtures extracted using degassing, with the concentration above 25%. In world practice, the most efficiently utilized mixtures are those of the 3rd group [10].

Depending on methane content in the captured coalbed gas, the directions of its use may include fuel for steam generating to heat industrial and residential buildings, as well as generating the energy at thermal power stations [11, 12]; engine fuel for internal-combustion engines for energy generation, a replacement for petrol and diesel fuel in au-

tomobiles and compressors [13, 14]; household gas by adding it into gas pipeline networks; feedstock for chemical industry – catalytic reforming to obtain synthesis gas [15], and direct conversion into target products (methanol, methyl chloride, methylene chloride, nitromethane, etc.) [16–18].

The goal of the work is an evaluation of the possibility to use coalbed methane for producing methanol. It is possible to obtain methanol from methane both through direct partial oxidation and from synthesis gas produced from methane.

2. Theory

2.1. Non-catalytic conversion of hydrocarbon gases into synthesis gas

Methane-containing gas may be converted into synthesis gas through the implementation of superadiabatic combustion based on surface matrix combustion, which is arranged in the gas phase in the vicinity of the inner surface of the matrix made of gas-permeable heat-resistant material [19]. As a result of intense convective and radiation heat exchange of the flame front with the surface of the matrix, which serves as a heat exchange element, reagents are heated due to the heat of reaction products. Recovery of the heat of products and the absence of radiation losses in the closed cavity of the matrix lead to a substantial broadening of combustion limits in comparison with well-known flat matrix infrared burner facilities and open-flame burners. This allows maintaining steady oxidation of the rich natural gas mixtures with the ratio $[O_2]/[CH_4] = 0.66–0.7$, which is impossible in other types of reformers and provides a high yield of the hydrogen-containing gas. The effect of energy recovery is also well implemented for solid fuel processing [20–23].

The major advantages of matrix reforming in comparison with the known industrial technologies of producing hydrogen-containing gas are:

- matrix reforming of coalbed methane is an autothermal process requiring no additional heat or energy input;
- the process is characterized by high volume production, which is an order of magnitude higher than that of steam reforming, which makes it more compact, less metal-consuming and thus less capital-intensive in comparison with conventional reforming types;
- the high volume productivity, absence of catalysts, and manufacturing and operation simplicity allow a substantial reduction of industrial expenses;

- the absence of a catalyst lowers requirements for gas preparation allowing single-stage conversion of hydrocarbon gases of almost any composition and origin into hydrogen-containing gas, excluding the stages of their preliminary fractionation or deep purification [19];

- low capital and operational expenses make the operation of small-scale installations economically rational.

The indicated advantages of matrix reforming make it potentially attractive, first of all, for low-tonnage processing of hydrocarbon gases from nonconventional sources, for example, associated petroleum gas, biogas [24], or coalbed methane. To enhance hydrogen yield, the matrix conversion of hydrocarbon gas may be supplemented with the subsequent catalytic process of steam reforming of the formed CO (Fig. 1) [25, 26].

To improve the technological parameters of the process, gas-phase processes in the post-flame zone of the reformer are under investigation and optimization. In this zone, hydrogen concentration increases substantially as a result of steam and carbon dioxide conversion of the products by water vapor and CO₂ formed during partial oxidation [27]. Synthesis gas obtained in the described process may be used directly to obtain methanol using the traditional catalytic processes.

The composition of synthesis gas plays an important part in the synthesis of methanol. In synthesis gas obtained by the partial oxidation of hydrocarbons, in particular, through the matrix conversion of methane, the molar ratio of hydro-

gen to carbon monoxide is lower than in the synthesis gas obtained through autothermal reforming and steam conversion, usually used in methanol production, and is H₂/CO = 1.8. At the same time, in the industrial processes of methanol production, this parameter should be equal to or slightly larger than 2.0 [28].

In the small-scale production of methanol, the specific contribution from energy consumption for recirculation of unreacted synthesis gas sharply increases. For this reason, the flow schemes of methanol synthesis are considered [29], in which CO conversion per single pass does not exceed 50%, and the ratio H₂/CO in the initial synthesis gas can be lower. During small-scale production of methanol in the cascade reactors flowchart without recycling hydrogen conversion turns out to be lower than CO conversion, because of the water vapor reaction, which results in difficulties with the utilization of unreacted synthesis gas. Hydrogen possesses a lower heat value than natural gas and cannot be used efficiently as fuel at the stage of methane conversion. Reduction of hydrogen content in synthesis gas in the case when it is obtained through partial oxidation of methane by air can reduce expenses for obtaining and compressing synthesis gas.

Calculations involving the models of thermodynamic equilibrium are often used in industrial and research literature to study the behavior of complicated chemical systems [30, 31]. The establishment of phase and chemical equilibrium in any system is an irreversible process, characterized by an increase in entropy, by the second law of thermodynamics. As a consequence, the calculation of equilibrium parameters of isolated multicomponent thermodynamic systems is reduced to the problem of establishing the state characterized by the maximal entropy. Another possible way to search for a minimum of Gibbs free energy of the system is the application of an approach that involves the calculation of thermodynamic equilibrium [32–36]. These approaches are equally significant.

3. Results and discussion

To determine the conditions for obtaining synthesis gas with the ratio [H₂]/[CO] = 2, a thermodynamic analysis of coalbed methane conversion was carried out with the help of TERRA software for the calculation of high-temperature thermochemical equilibria [30], with variations of initial composition and process temperature.

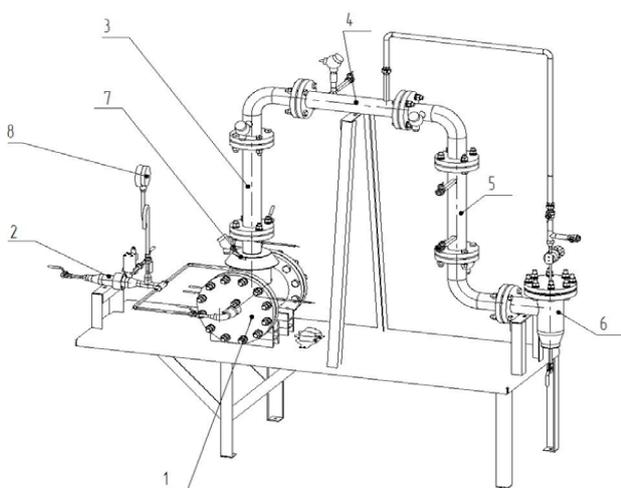


Fig. 1. Schematic of the demonstration installation for combined matrix and catalytic reforming for producing hydrogen: 1 – matrix reformer; 2 – mixer; 3 – catalytic reactor for steam conversion; 4 – recuperative heat exchanger; 5 – water cooler; 6 – separator; 7 – steam generator unit; 8 – manometer.

The system composed of methane, nitrogen and oxygen, with different concentrations of oxygen (21 and 100% vol. in mixture with nitrogen) and water vapor (0 and 5% vol. as a total in the mixture) was considered. The fuel – air equivalence ratio ϕ , which is equal to the ratio of the amount of oxygen necessary for complete oxidation of methane to the supplied amount of oxygen, was varied within the range from 2 to 4. Rich fuel mixtures have an equivalence ratio of more than 1, while at $\phi = 1$ complete oxidation of methane into carbon dioxide and water takes place. Calculations were carried out at the atmospheric pressure (0.1 MPa), varying the initial temperature of reagents. For any initial temperature, water was conventionally considered to be in the gaseous state. As a result of calculations, the equilibrium composition of products was obtained, from which the ratio $[H_2]/[CO]$ was calculated. Results of calculations at conversion temperatures below 1300 K are not presented in the work because unreacted methane appears in conversion products. The rate of the chemical reaction is strongly dependent on temperature, and at a low temperature, it takes a rather long time for thermodynamic equilibrium to get established [37, 38].

Results obtained in the calculations of $[H_2]/[CO]$ ratios depending on the temperature at different ϕ values for air and steam – air (marked with *) methane conversion are presented in Fig. 2. Numerical values of ϕ are marked on curves. In the case of air conversion of methane, with $\phi = 2$ (curve 2), $[H_2]/[CO]$ ratio decreases from 1.67 to 1.32 with temperature rise. This may be explained in terms of hydrogen oxidation by carbon dioxide

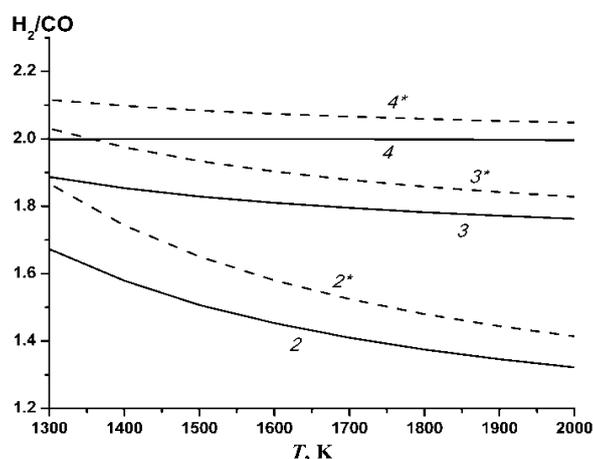


Fig. 2. Dependences of $[H_2]/[CO]$ ratios on conversion temperature (T) at different values of ϕ coefficient for air and steam-air (marked with *) methane conversion. The numerical values of ϕ are shown on the curves.

(the reverse process of the water – gas shift reaction) with the formation of CO. During the steam-air conversion of methane, the ratio $[H_2]/[CO]$ is higher in comparison with air conversion, and this difference is higher for lower temperature. The value reached at 1300 K is $[H_2]/[CO] = 1.87$, which is higher than the minimal threshold required for the synthesis of methanol. In other cases, at a temperature ≥ 1400 K, for $\phi = 2$ the ratio is $[H_2]/[CO] \leq 1.8$.

With an increase in the fuel – air equivalence ratio, the ratio $[H_2]/[CO]$ also increases: at $\phi = 3$ the ratio $[H_2]/[CO]$ is within the range 1.76–2.03 for the case without steam and with its addition. Dependences of $[H_2]/[CO]$ ratios on process temperature and the presence of water vapor are similar to the dependences at $\phi = 2$. For $\phi = 4$, an ideal value is obtained without vapor addition $[H_2]/[CO] = 2$, because the reaction proceeding in this case is $CH_4 + 0.5O_2 = CO + 2H_2$. The addition of water vapor causes an increase in $[H_2]/[CO]$ because carbon monoxide is oxidized with the formation of hydrogen and carbon dioxide (the direct water-gas shift reaction). So, it may be concluded that the optimal condition for obtaining synthesis gas for the production of methanol is the use of a mixture with an equivalence ratio not less than 4.

Results of the calculations of the $[H_2]/[CO]$ ratio values depending on process temperature at different values of coefficient ϕ for oxygen and vapor-oxygen (marked with *) conversion of methane are presented in Fig. 3. The numerical values of ϕ are shown on the curves. In the case of oxygen conversion of methane, similar dependences of $[H_2]/[CO]$ ratios on temperature have been

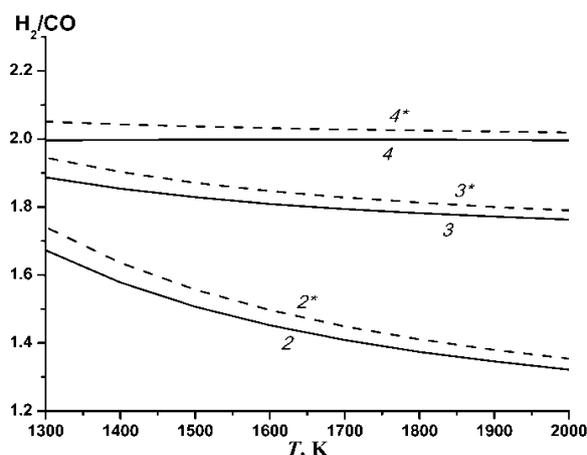


Fig. 3. Dependences of $[H_2]/[CO]$ ratios on conversion temperature (T) at different values of ϕ coefficient for oxygen and steam-oxygen (marked with *) methane conversion. The numerical values of ϕ are shown on the curves.

obtained, but the difference between the cases without water vapor and with it is smaller in this case. Similarly to the previous case, it may be concluded that the optimal condition for obtaining synthesis gas for the production of methanol is the use of a mixture with a fuel – air equivalence ratio not less than 4. An essential advantage of the oxygen conversion of methane into synthesis gas is the absence of an inert component, which is nitrogen.

The principal possibility to produce methanol from synthesis gas with a relatively low ratio $[H_2]/[CO] \approx 1.8$ and functional $SN \leq 1.5$ over the catalysts of low-temperature conversion of CO was demonstrated [39]. The achieved degree of CO conversion is within the range of 12–28%, depending on pressure. Methanol concentration in the obtained liquid product varied from 80 to 99% in all experiments. The activity of the catalysts of low-temperature CO conversion decreased only slightly in the course of experiments, which is evidence of the possibility to use them for the synthesis of methanol. For this reason, in this case, if catalysts are used, it is possible to obtain synthesis gas from less concentrated mixtures with the equivalence ratio equal to 3.

3.1. Direct partial oxidation of coalbed methane into methanol

Another promising direction of the low-tonnage processing of hydrocarbon gases including coalbed

methane is their direct oxidative conversion to obtain various products, first of all methanol [40]. In particular, direct gas-phase oxidation of methane into methanol opens the possibilities of integrated use of coal mining wastes, including not only coalbed methane but also a large amount of coal wastes accumulated during mining and concentrating: fine coal sludge (riddlings), which is accumulated in enormous amounts and forms a substantial ecological problem in coal mining regions.

The process is shown schematically in Fig. 4. Coalbed methane containing a definite admixture of air enters the oxidation facility, where it is compressed to a pressure of 6–7 MPa, heated in recuperative heat exchanging unit, and supplied into the reactor. The liquid condensate (methanol product) containing up to 40% methanol and up to 5–8% other organic compounds is released after cooling of the partially oxidized vapor-air mixture, and then it is transferred together with crushed and concentrated coal waste, without any treatment or rectification, to the preparation of methanol-coal fuel. The outlet gas containing methane with a concentration of not less than 25% is supplied to the energy installation that supplies energy to the entire works and meets the needs of coal mining facilities. One of the major advantages of this technology is the possibility to use the produced liquid methanol product directly without any processing and rectification to prepare methanol-coal fuel.

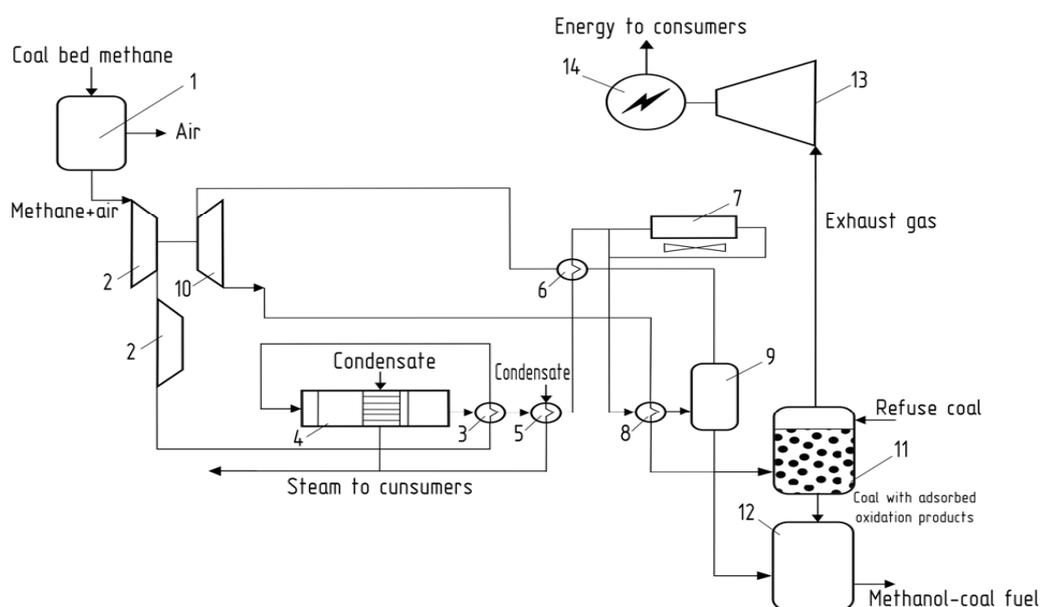


Fig. 4. Schematic diagram of the conversion of coalbed methane and coal wastes into methanol-coal fuel: 1 – separator for enriching methane-air mixture; 2 – stages of compressor for enriched methane-air mixture; 3 – recuperative heat exchanger for heating methane-air mixture; 4 – two-step reactor for methane-air mixture oxidation with an inter-sectional heat exchanger; 5 – steam generator; 6 and 8 – heat exchangers; 7 – air cooler; 9 – separator; 10 – turbo expander; 11 – adsorber for residual oxidation products from the exhaust gas; 12 – cavitation mixer of liquid and solid products; 13 – gas turbine; 14 – electric generating unit.

The process of obtaining methanol product through methane oxidation by atmospheric oxygen is almost identical to the traditional flowchart of methanol production by the direct oxidation of methane [40], except for the absence of the system supplying compressed air, because, as a rule, coalbed methane already contains its sufficient amount as admixture. The flow process, which is the simplest concerning technology, allows obtaining methanol in the specific yield of up to 16 kg/1000·m³ of methane. In this case, the relief gas meets all the requirements to fuel gas for gas reciprocating engines, as well as combustible gases for industrial and household purposes.

The process with the fractional supply of the oxidizer to several points of the reactor, with intermediate cooling of the reaction mixture between reactor sections, allows for increasing the specific yield of methanol. In this case, however, the relief gas meets only the requirements to fuel gas reciprocating engines. The process with more than two points of oxidizer supply is unreasonable because of further oxidation of already formed methanol.

4. Conclusion

The possibility to use coalbed methane to produce methanol is evaluated in the work. It is possible to obtain methanol from methane both through direct partial oxidation and from synthesis gas formed in the oxidative conversion of methane. To determine the conditions for obtaining synthesis gas with the ratio $[H_2]/[CO] = 2$, a thermodynamic analysis of coalbed methane conversion was carried out with the help of TERRA software for the calculations of high-temperature thermochemical equilibrium. Synthesis gas with the ratio $[H_2]/[CO] = 2$ is optimal for producing methanol. The system composed of methane, nitrogen and oxygen was considered, with different concentrations of oxygen (21 and 100% vol. in mixture with nitrogen) and water vapor (0 and 5% vol. in the overall mixture). The fuel-air equivalence ratio ϕ , which is equal to the ratio of the amount of oxygen necessary for complete oxidation of methane to the amount of supplied oxygen, was varied within the range from 2 to 4. The optimal conditions for obtaining synthesis gas for non-catalytic methanol production is the use of a mixture with an equivalence ratio not less than 4. In the case catalysts are used, it is possible to obtain synthesis gas from leaner mixtures with the equivalence ratio equal to 3. In this case, it is possible to obtain synthesis gas with

the ratio $[H_2]/[CO] = 1.8$. It is also demonstrated that the addition of water vapor leads to an increase in $[H_2]/[CO]$ ratio. Direct gas-phase oxidation of methane into methanol opens the possibility of the integrated use of coal mining wastes, including not only coalbed methane but also a large number of coal wastes that are accumulated during coal mining and concentrating.

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