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Promising Directions in Chemical Processing of Methane from Coal Industry. Part 1. Thermodynamic analysis

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Abstract

For the purpose of developing technology for the chemical processing of methane from the coal industry into valuable products, thermodynamic analysis of the major chemical reactions that occur in the multicomponent system CH_4–CO_2–H_2O–air is carried out. The features of methane-containing gases differing from each other in chemical composition and corresponding to different stages of coal production are determined: ventilation air methane (VAM, methane concentration C_{CH4} less than 1 vol.%); mine/degassing methane of operating (CMM, C_{CH4} = 25–60 vol.%) or abandoned (AMM, C_{CH4} = 60–80 vol.%) coal mines; methane from unrelieved coal beds (CBM, C_{CH4} > 80 vol.%). Optimal conditions of the processes ensuring complete methane conversion and maximal yield of useful products are determined. The potential of combined reforming for efficient utilization of the methane-air mixture from coal mining into hydrogen-containing gas is demonstrated.

1. Introduction

Coal deposits contain enormous reserves of gas hydrocarbon raw material, which is composed mainly of methane (80–98 vol.%) and small amounts of other hydrocarbons: ethane, propane, and butane, as well as carbon dioxide and nitrogen. Coal bed methane (CBM) was recognized as a separate fossil resource and included in the All-Russian Classifier of Mineral Resources and Subsoil Water (code 111021111, additionally included with changes N 1/2011) [1]. The world resources of CBM are estimated as 113–201 trillion m^3, and among these, the resources promising for development are considered to be 30–42 trillion m^3 [2]. The largest resources of CBM are present in the Russian Federation, China, the USA, Canada, Australia, Indonesia, Poland, Germany and France. The resources of CBM in the Russian Federation are ~80 trillion m^3 [3]. More than half of the Russian resources are concentrated in the West Siberian (40%) and Tungus (24%) coal basins, then follow the Kuznetsk (16%), Lena (12%), Taymyr (5%) and Pechora (2%) basins [4].

The development of coal basins is accompanied by the release of gas contained in coal beds. According to the procedure elaborated for evaluation of volatile emissions from coal mining and transportation, methane emission per one ton of extracted coal depends on mining depth and is equal to 10 m^3/t on average for mining depth less than 200 m, 18 m^3/t for the depth of 200 to 400 m, and 25 m^3/t for mines deeper than 400 m [5].

Methane is known as a strong greenhouse gas, exceeding carbon dioxide in this parameter by a factor of more than 25. According to the data of the International Energy Agency for 2020, the first place in methane emission is occupied by China – 22.31 Mt, the next countries, in descending order, are the RF – 5.7 Mt, EC countries – 2.74 Mt, the USA – 2.10 Mt, India – 1.27 Mt, Indonesia – 1.18 Mt, and Australia – 1.13 Mt [6]. The total contribution of the coal industry to the emission of greenhouse gases other than CO_2 is currently 8.1% [7]. The average global concentration of methane in the surface atmospheric layer is increasing: in 1750 it was 722±25 ppb, in 2011 – 1803±2 ppb, and in 2021 it has reached 1890±2 ppb [8]. With an increase in methane concentration, the transparency of the atmosphere for infrared radiation decreases, which causes an increase in global temperature [9].

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On the other hand, methane emission from coal mining brings negative consequences from the viewpoint of mining safety because methane is explosive in a mixture with air within the concentration range 5 to 15 vol.% [10]. For this reason, methane transportation, collection, or use are to be carried out with methane concentration below the level not less than 2.5 times lower than the lower limit of the explosive range (methane concentration $C_{CH4} < 2.0$ vol.%) and at least 2 times higher than the upper limit of the explosive range ($C_{CH4} >$ 30 vol.%) [11].

According to the database of the Global Methane Initiative (GMI), in 2021 there have been ~ 260 projects operating in the world for the utilization of methane from the degassing systems of mines [12]. These are mainly projects on heat and energy generation. It should be stressed that in this case another greenhouse gas, namely CO_2, is released into the atmosphere instead of CH_4. In the Russian Federation, methane is extracted from coal beds mainly as an associated component, in the fields of operating mines through mine degassing systems. The only exclusion is the innovative Project of the Kemerovo Region Administration and Gazprom public company, aimed at the production of methane as a separate fossil resource from coal beds in Kuzbass [13]. Gas capturing from degassing systems of operating mines, its preparation and use are carried out only by some companies in the coal industry. For example, in 2020 SUEK company utilized 4.8 mln m^3 of methane which accounted for not more than 2% of the total amount of emitted methane [10]. The main direction of utilization, both for methane produced from coal beds and for methane obtained from degassing systems of operating mines in the RF, is its use for generating electricity and thermal energy [14]. In rare cases, the gas obtained from degassing systems is used for thermal treatment (drying) of riddlings at coal preparation plants [15]. The variable composition of mine gas, its high humidity and contamination with coal dust, and low pressure at the outlet of vacuum pump stations determine the features of its application in energy generating facilities. Investigation of the component composition of mine gas shows [16] that the gas, judging from its caloric value, can be used as a fuel if the oxygen content is changed from 8 to 12 vol.% and methane from 37 to 50 vol.%. However, before this gas enters gas engines mounted at gas reciprocating cogeneration plants, it is necessary to purify it from mechanical impurities and dry it. Gas emissions in the territories of abandoned mines and adjacent regions are special issues of concern because methane concentrations that are dangerous for the population are observed at these sites [17].

In general, coal bed methane is to be considered an important fossil resource. Methane processing should correspond to the principles of rational nature management, ecological safety and economic reasonableness. Similarly to natural gas, CBM is, on the one hand, the energy carrier – a fuel and energy resource for the production of thermal energy and electricity, on the other hand, it is a raw material for obtaining useful products from the chemical industry. However, due to many reasons, the potential of chemical processing of methane from the coal industry is currently taken into account only insignificantly.

One of the reasons for this situation is a specific feature of this kind of hydrocarbon raw material, namely substantial non-uniformity and variable composition. Methane content depends on the stage of coal production and varies within a very broad range, which poses definite limitations on the use of traditional technologies which are used for natural gas processing. Investigations into the chemical processing of CBM are described mainly in foreign publications, and most authors distinguish four main types of CBM differing from each other in chemical composition. The following terms are accepted:

(1) VAM – Ventilation Air Methane. Methane from the ventilation air of underground mines. Methane concentration: less than 1 vol.%.

(2) CMM – Coal Mine Methane. Methane concentration: 25–60 vol.%;

(3) AMM – Abandoned Mine Methane. Methane from abandoned coal mines. During its extraction by means of degassing, methane concentration maybe 60–80 vol.%;

(4) CBM – Coal Bed Methane. Methane from unrelieved coal beds was extracted during preliminary degassing through boreholes drilled from the surface. Methane concentration: more than 80 vol.%.

For the purpose of developing the technology of chemical processing of methane from the coal industry into valuable products, thermodynamic analysis of the major chemical reactions proceeding in the multicomponent system CH_4–CO_2–H_2O–air, which simulates methane-air mixture corresponding in its composition to different stages of coal production, is carried out.

2. Experimental

Calculation of thermodynamic parameters of the major chemical reactions proceeding in the multi-component system CH_4–CO_2–H_2O–air was carried out using IVTANTERMO software [18]. At the initial stage of work, the main reactions of reforming and side reactions going on in the system were chosen for thermodynamic analysis. The list of the reactions under investigation is shown in Table 1. Then calculations were carried out for gas mixtures modeling methane-air mixture corresponding to different stages of coal production. The effect of temperature (373–1350 K), pressure (1–50 atm) and the molar ratio of reagents on the equilibrium composition of reaction products was studied.

3. Results and discussion

The main reactions of reforming, as well as possible side reactions proceeding in the system CH_4–CO_2–H_2O–O_2 are presented in Table 1. Calculation of the temperature dependence of changes in the standard Gibbs energy (ΔG^o_T) for reactions (1–6) in the reaction mixture with the stoichiometric composition revealed the regions in which the direct reactions proceed spontaneously ($\Delta G^o_T < 0$): for steam reforming (1), dry reforming (2) and steam – carbon dioxide reforming (5) T > 900 K; tri-reforming of methane (6) – T > 630 K; autothermal reforming – T > 440 K (Fig. 1a). For partial methane oxidation, negative ΔG^o_T is observed within the entire temperature range under investigation, which points to the spontaneous reaction to the right, that is, to the formation of products. Almost all reforming reactions except partial oxidation are endothermic (Fig. 1b). In the high-temperature region, along with target reactions, carbon formation proceeds according to reaction (9) proceeds (Fig. 1c). In addition, a strongly exothermal complete oxidation reaction is possible in the oxygen-containing system (Table 1).

Table 1

Changes of the standard Gibbs energy and enthalpy for reactions at 298 and 1073 K*

No.	Reaction	Equation	Initial mixture composition, vol.%	$\Delta_rG^o_{298}$, kJ/mol	$\Delta_rH^o_{298}$, kJ/mol	$\Delta_rG^o_{1073}$, kJ/mol	$\Delta_rH^o_{1073}$, kJ/mol
			Target reactions				
1	Steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	50CH$_4$, 50H$_2$O	142.0	206.0	-45.4	225.3
2	Dry reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	50CH$_4$, 50CO$_2$	170.6	247.1	-44.7	259.4
3	Partial oxidation	$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2$	66.7CH$_4$, 33.3O$_2$	-86.6	-35.9	-234.0	-22.9
4	Autothermal reforming	$2CH_4 + H_2O + 0.5O_2 \leftrightarrow 2CO + 5H_2$	57.1CH$_4$, 28.6H$_2$O, 14.3O$_2$	27.7	85.0	-139.7	101.2
5	Steam – carbon dioxide reforming of methane	$2CH_4 + H_2O + CO_2 \leftrightarrow 3CO + 5H_2$	50.0CH$_4$, 25.0H$_2$O, 25.0CO$_2$	156.3	226.5	-45.1	242.4
6	Tri-reforming of methane	$3CH_4 + 0.5O_2 + H_2O + CO_2 \leftrightarrow 4CO + 7H_2$	54.5CH$_4$, 9.1O$_2$18.2H$_2$O, 18.2CO$_2$	75.4	139.0	-108.0	154.0
			Side reactions				
7	Complete oxidation	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$	-	-801.0	-802.6	-800.5	-801.7
8	Water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	-	-28.6	-41.2	-0.7	-34.1
9	Decomposition of methane	$CH_4 \leftrightarrow C^{**} + 2H_2$	-	50.6	74.6	-27.3	89.5
10	Disproportionation reaction	$2CO \leftrightarrow CO_2 + C$	-	-60.0	-86.2	8.7	-85.0
11	CO reduction	$CO + H_2 \leftrightarrow C + H_2O$	-	-91.4	-131.3	18.1	-135.8
12	CO$_2$ reduction	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	-	-62.8	-90.1	18.8	-101.7
13	Methanation of CO	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-	-142.0	-205.9	45.4	-225.3
14	Methanation of CO$_2$	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-	-113.4	-164.7	46.1	-191.2

* – thermodynamic potentials were calculated assuming that the extent of reaction is one mole, pressure P = 1 bar.
** – the crystal modification of carbon was considered to be graphite.

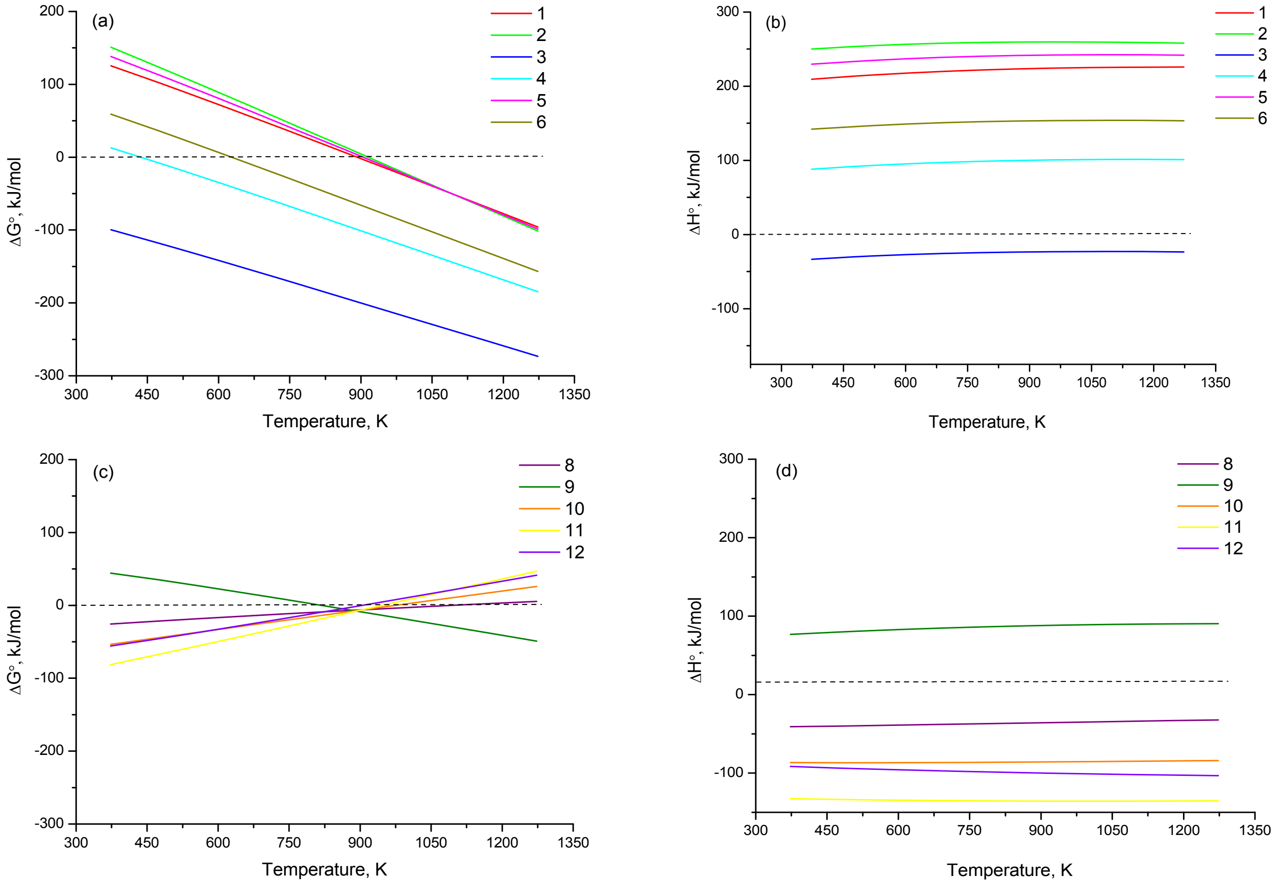

Fig. 1. Temperature dependences of Gibbs energy values (ΔG°) and standard enthalpy (ΔH°) for reactions proceeding in the multicomponent system CH_4–CO_2–H_2O–O_2. Line numbers correspond to reaction numbers in Table 1.

Calculation of temperature dependences of the equilibrium molar fractions of substances and reaction parameters demonstrated similarities in the changes of these values for reforming reactions under investigation (1–6). The data for the reactions of steam and autothermal methane reforming is presented in Fig. 2 as a typical example. One can see that the molar fraction of initial reagents, methane and water, decrease in the reaction system with an increase in temperature. The products of their conversion in the low-temperature region are hydrogen, CO_2 and carbon. Then, with an increase in temperature, CO is added. In the high-temperature region ($T > 1123$ K) the fraction of side products is insignificant, and the yields of hydrogen and CO reach the limiting values. So, in order to achieve the high reforming parameters, it is necessary to conduct the process at a temperature not lower than 1073 K. In the case oxygen is present in the reaction system, its conversion is 100% within the whole temperature range (373–1350 K).

Comparative analysis of methane conversion, hydrogen yield and carbon yield shows that the processes under consideration differ from each other in the efficiency of methane utilization, formation of target and side products (Fig. 3). One can see that in the low-temperature range methane conversion proceeds mainly into carbon. A minimal amount of carbonaceous deposits is formed in the cases of steam and autothermal reforming of methane, while the maximal one is formed in the carbon dioxide reforming of methane. So, depending on the reaction temperature, the equilibrium composition may include unreacted initial components and the products of target and side reactions: CH_4, CO_2, H_2O, CO, H_2 and C. A gas mixture with the highest hydrogen concentration is obtained as a result of steam reforming of methane, and the lowest hydrogen concentration comes from carbon dioxide reforming of methane: at a temperature of 800 °C, CH_4 is equal to 72 and 48 vol.%, respectively (Fig. 3d).

The model methane-air mixtures corresponding in their composition to different stages of coal production are presented in Table 2. Unlike for above-considered stoichiometric reforming reactions, for which the molar ratio O/C was 1, for these compositions the O/C molar ratio varies within a broad range. Calculation of the equilibrium

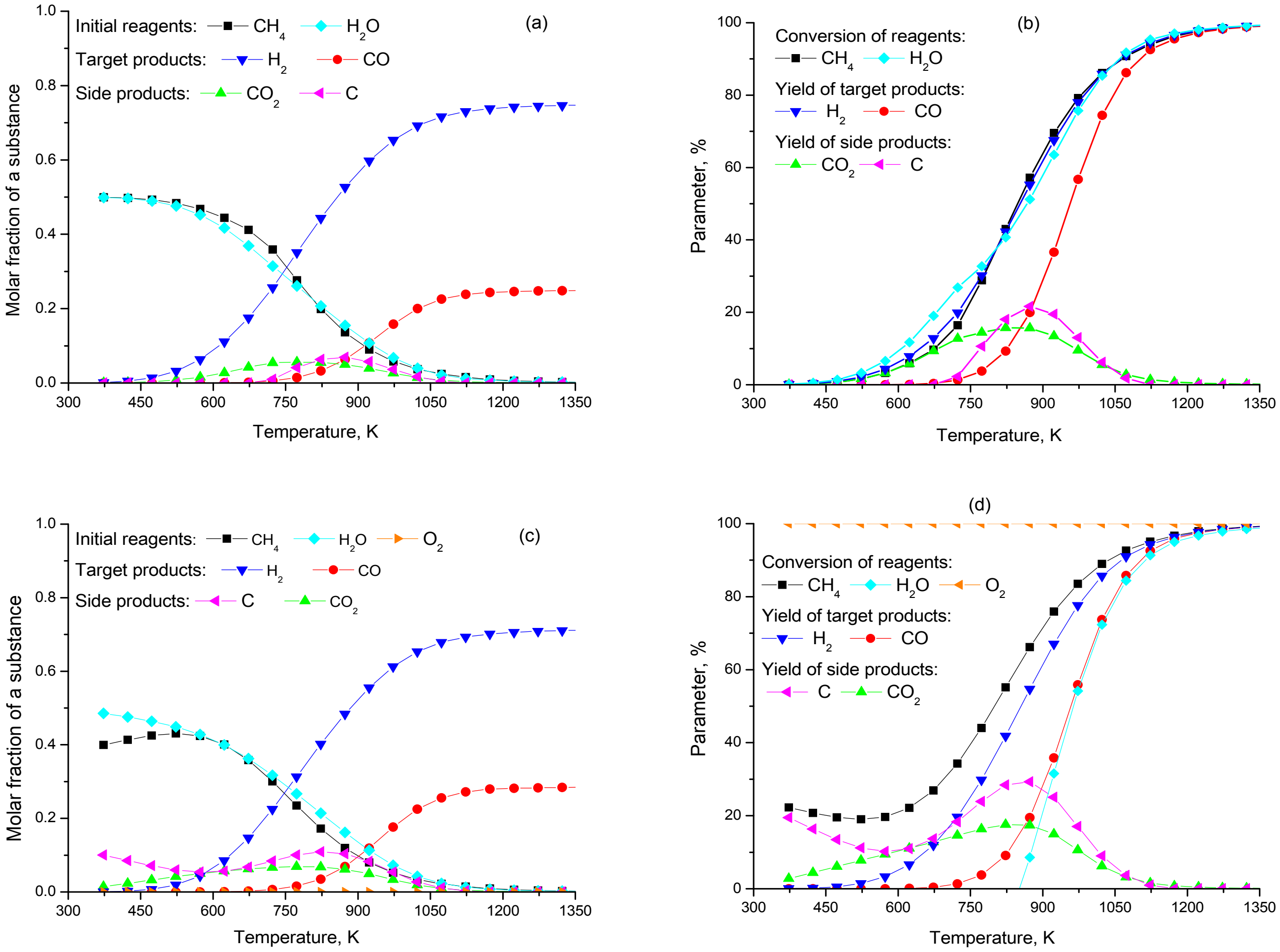

Fig. 2. Temperature dependences of the equilibrium molar fractions of substances (a, c), conversion of reagents and yield of products (b, d) for steam reforming (a, b) and autothermal reforming (c, d) of methane.

composition of the mixture at 800 °C depending on the O/C molar ratio shows (Fig. 4a) that the equilibrium product composition for the methane-air mixture of VAM type includes only the products of complete methane oxidation. In the case of methane-air mixtures of CMM type (0.3 < O/C < 1), the products that will be formed under the conditions of thermodynamic equilibrium are H$_2$, CO and carbon; the amount of the latter decreases with an increase in O/C ratio. For methane-air mixtures of AMM and CBM types, the equilibrium composition almost completely corresponds to the composition of the products of methane pyrolysis and includes hydrogen and carbon.

Table 2

List of model methane-air mixtures corresponding to different stages of coal production

Gas concentration, vol. %			O/C molar ratio	Type of methane-air mixture
CH$_4$	O$_2$	N$_2$		
1	20.9	78.1	41.8	VAM
30	14.7	55.3	0.98	CMM
40	12.6	47.4	0.63	
50	10.5	39.5	0.42	
60	8.4	31.6	0.28	
70	6.3	23.7	0.18	AMM
80	4.2	15.8	0.11	
90	2.1	7.9	0.05	CBM
100	0	0	0	

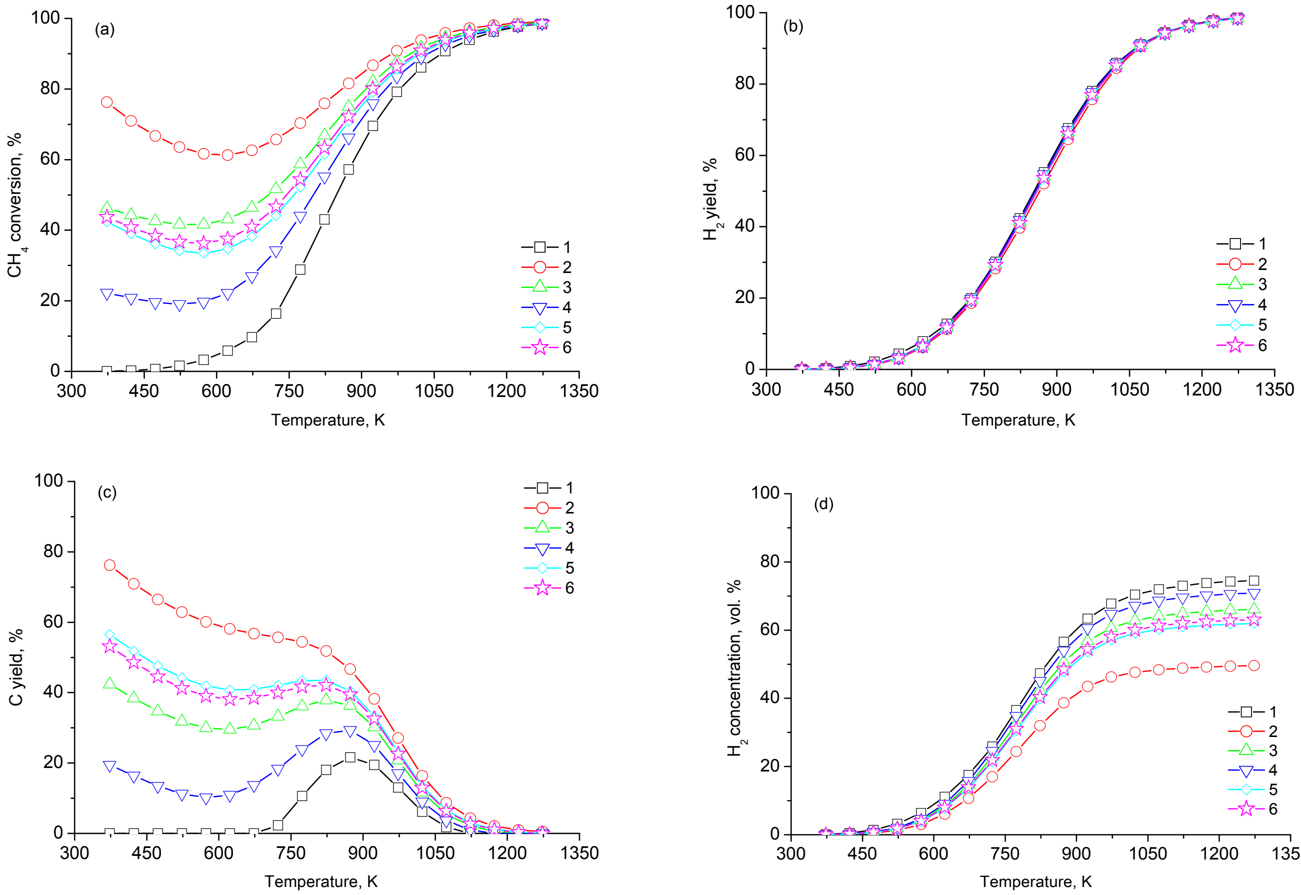

Fig. 3. Temperature dependences of the equilibrium values of methane conversion (a), hydrogen yield (b), carbon yield (c), and hydrogen concentration in the gas mixture (d) for reactions proceeding in the multicomponent system CH_4–CO_2–H_2O–O_2. Line numbers correspond to reaction numbers in Table 1.

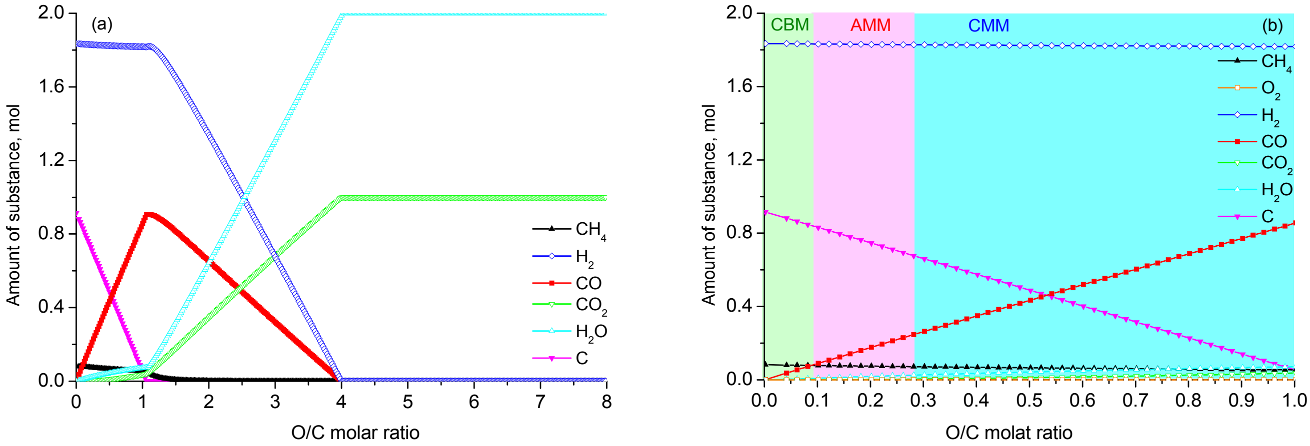

Fig. 4. Equilibrium composition of the products at 800 °C for CH_4 + O_2 mixture depending on the O/C molar ratio.

Results of the calculation of equilibrium values of the molar fractions of substances, reaction parameters, gas mixture composition and the molar fraction of C-containing mixtures corresponding in their composition to different stages of coal production are presented in Figs. 5–10.

For the VAM-type methane-air mixture, the high excess of oxygen provides the possibility of complete methane oxidation with the formation of CO_2 and H_2O within the whole temperature range under investigation 300–1350 K (Fig. 5). Oxygen conversion under the conditions of thermodynamic equilibrium is 9.5%. The equilibrium gas mixture composition at 1073 K includes 78.1% N_2, 18.9% O_2, 2% H_2O and 1% CO_2. Reaction parameters are independent of pressure (Fig. 5b).

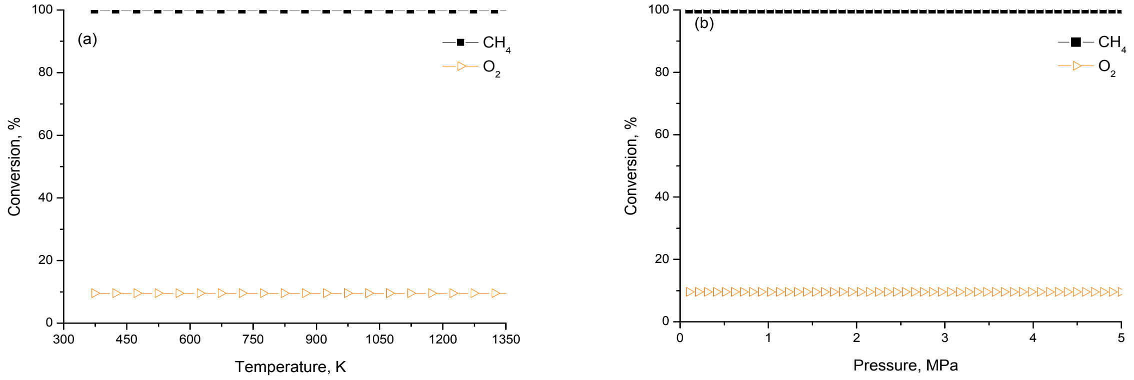

Fig. 5. Equilibrium conversion of methane and oxygen depending on temperature and pressure for the methane-air mixture of VAM type (1% CH_4, 20.9% O_2, 78.1% N_2).

For methane-air mixture of CMM type, the dependence of the equilibrium composition on temperature (Figs. 6 and 7) and pressure (Fig. 8) is more complicated and exhibits a strong dependence on the initial methane content. Thus, for CMM-type mixture containing 30 vol.% CH_4, methane conversion in the low-temperature region is not more than 50% (Fig. 6b). Methane is transformed into such products as C, CO_2 and H_2O. With an increase in temperature, methane conversion increases and reaches more than 95% at T > 1073 K. The yields of CO_2 and C pass through the maximum around 800 K and then decrease. Quite the contrary, the yields of H_2 and CO increase with temperature rise and at a temperature of 1073 K reach 94 and 88%, respectively. The equilibrium gas composition in

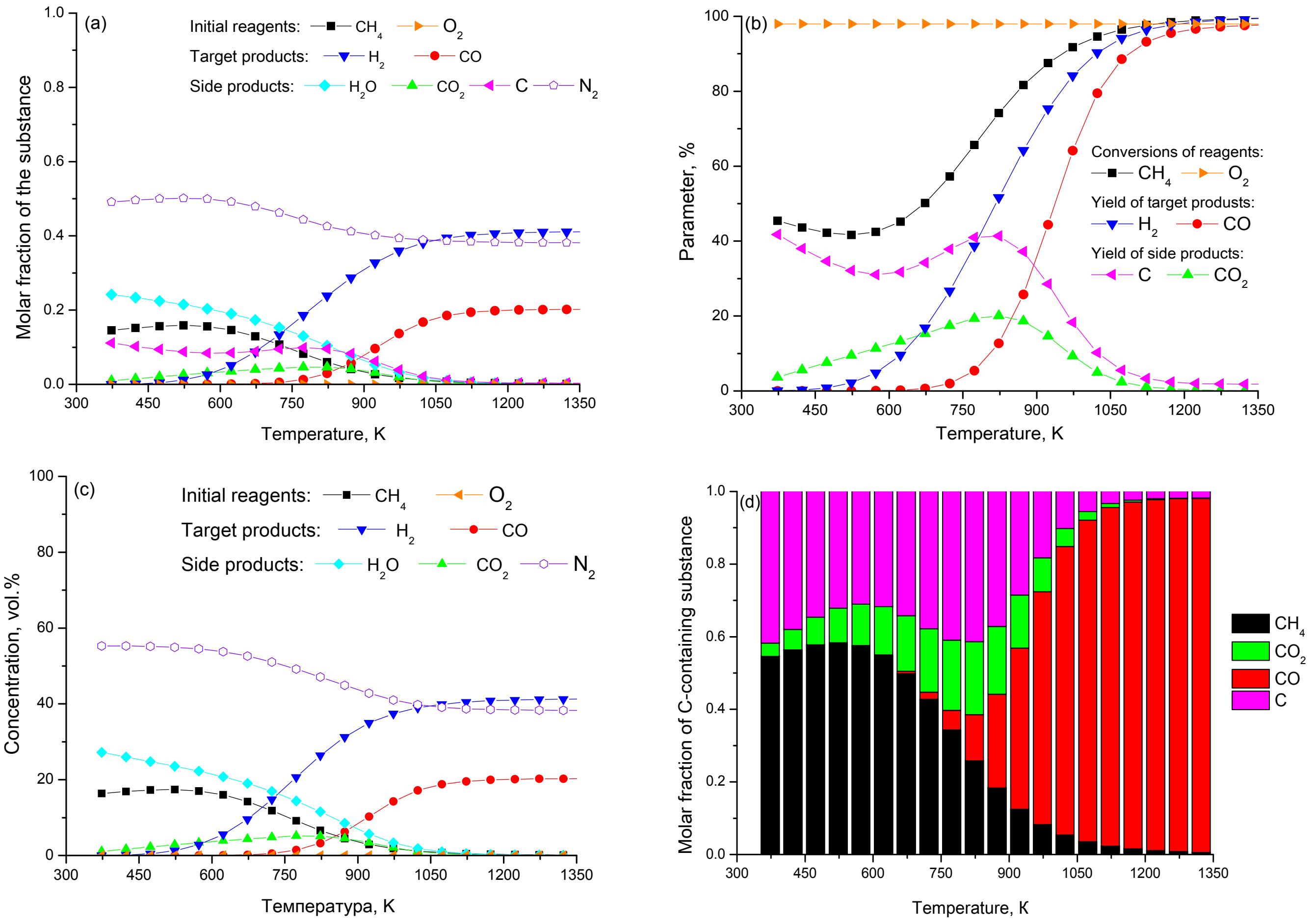

Fig. 6. Dependence of the equilibrium molar fractions of substances (a), conversion of reagents and yield of products (b), composition of the gas mixture (c) and the molar fraction of C-containing substances (d) on temperature fir methane-air mixture of CMM type (30% CH_4, 14.7% O_2, 55.3% N_2).

the high-temperature region includes the products of methane reforming (H_2, CO) and nitrogen (Fig. 6c). The hydrogen concentration in the gas mixture is ~40 vol.%, and the equilibrium molar ratio H_2/CO is equal to 2, which is similar to the value obtained for the partial oxidation of methane. Oxygen conversion within the whole temperature range under investigation is 100%.

For the methane-air mixture of CMM type, which contains higher methane concentration (50 vol.% CH_4), the dependences of the equilibrium composition on temperature, considered above for 30% mixture, remain the same (Fig. 7). A specific feature of this system is lower methane conversion in the low-temperature region and the formation of a large amount of carbon. Carbon remains the

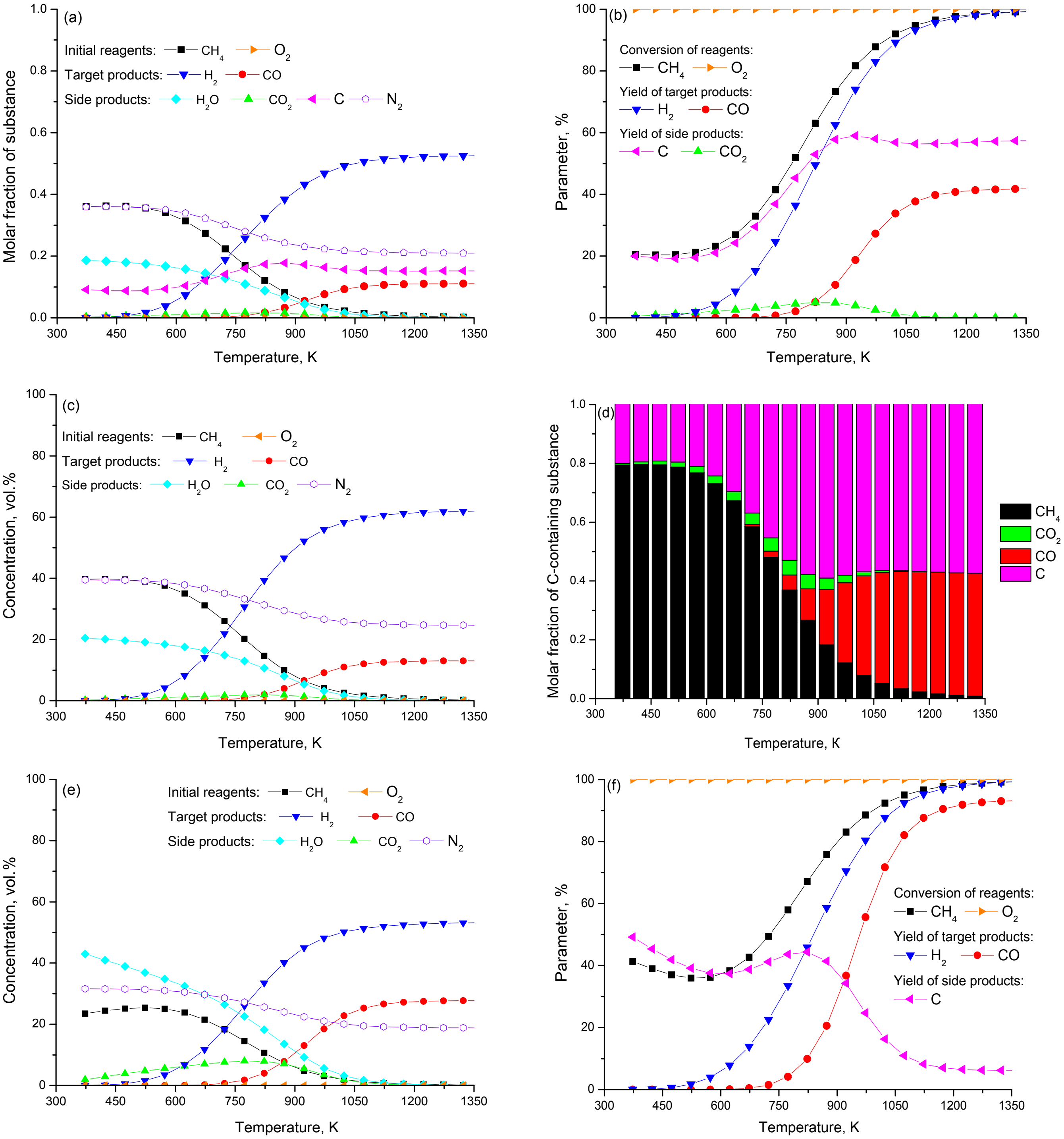

Fig. 7. Dependence of the equilibrium molar fractions of substances (a), conversion of reagents and yield of products (b, f), composition of the gas mixture (c, e) and molar fraction of C-containing substances (d) on temperature for methane-air mixture of CMM type (50% CH_4, 10.5% O_2, 39.5% N_2) (a–d) and for CMM + H_2O + CO_2 (40% CH_4, 8.4% O_2, 31.6% N_2, 10% H_2O, 10% CO_2) (e, f).

major product of methane conversion also in the high-temperature region (Fig. 7d), which is due to the low oxygen content in the initial mixture: the molar ratio O/C is equal to 0.42. Because of this, along with the high values of hydrogen and CO yields in the high-temperature region, carbon yield is more than 50% (Fig. 7b). For this CMM composition, the equilibrium concentration of hydrogen is more than 60% at T > 1073 K, the molar ratio H_2/CO is equal to 4.7. It should be noted that a real methane-air mixture is humid and may contain, in addition to methane, oxygen and nitrogen,

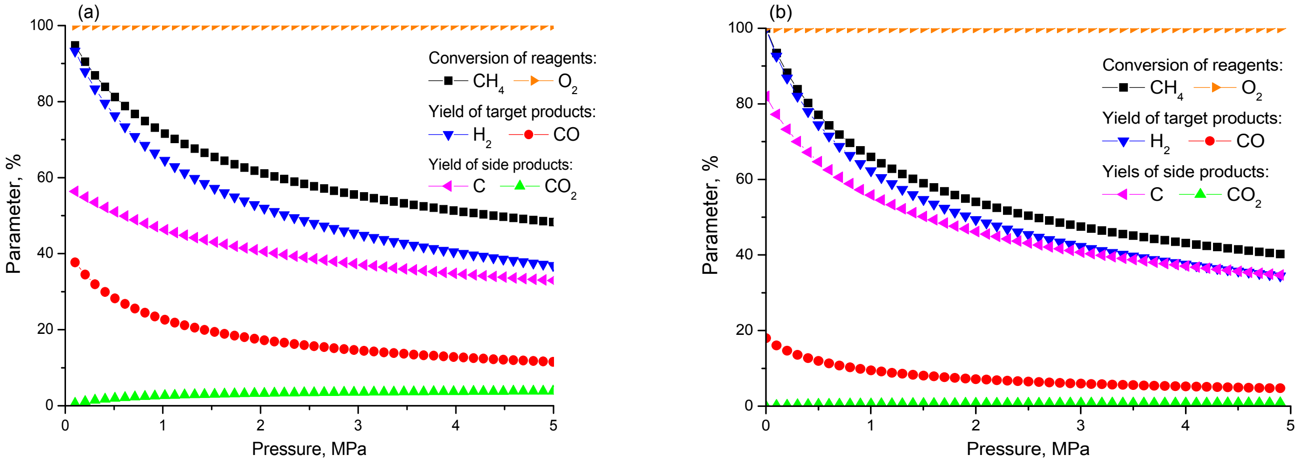

Fig. 8. Dependence of the equilibrium values of reagent conversion and product yields on pressure for methane-air mixture of CMM type (50% CH_4, 10.5% O_2, 39.5% N_2) (a) and for AMM type (70% CH_4, 6.3% O_2, 23.7% N_2) (b).

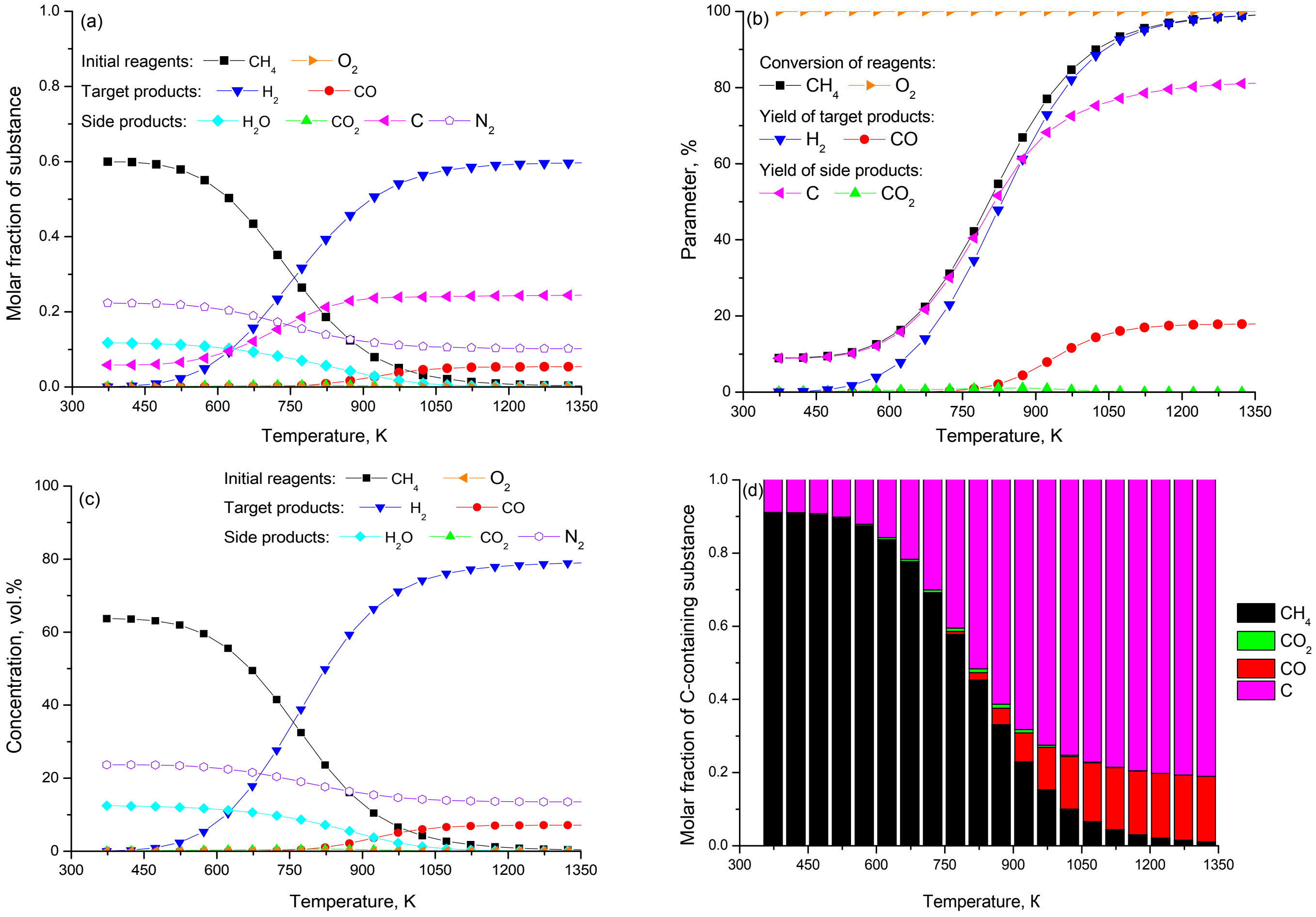

Fig. 9. Dependence of the equilibrium molar fractions of substances (a), reagent conversion and yield of products (b), gas mixture composition (c) and molar fraction of C-containing substances (d) on temperature for methane-air mixture of AMM type (70% CH_4, 6.3% O_2, 23.7% N_2).

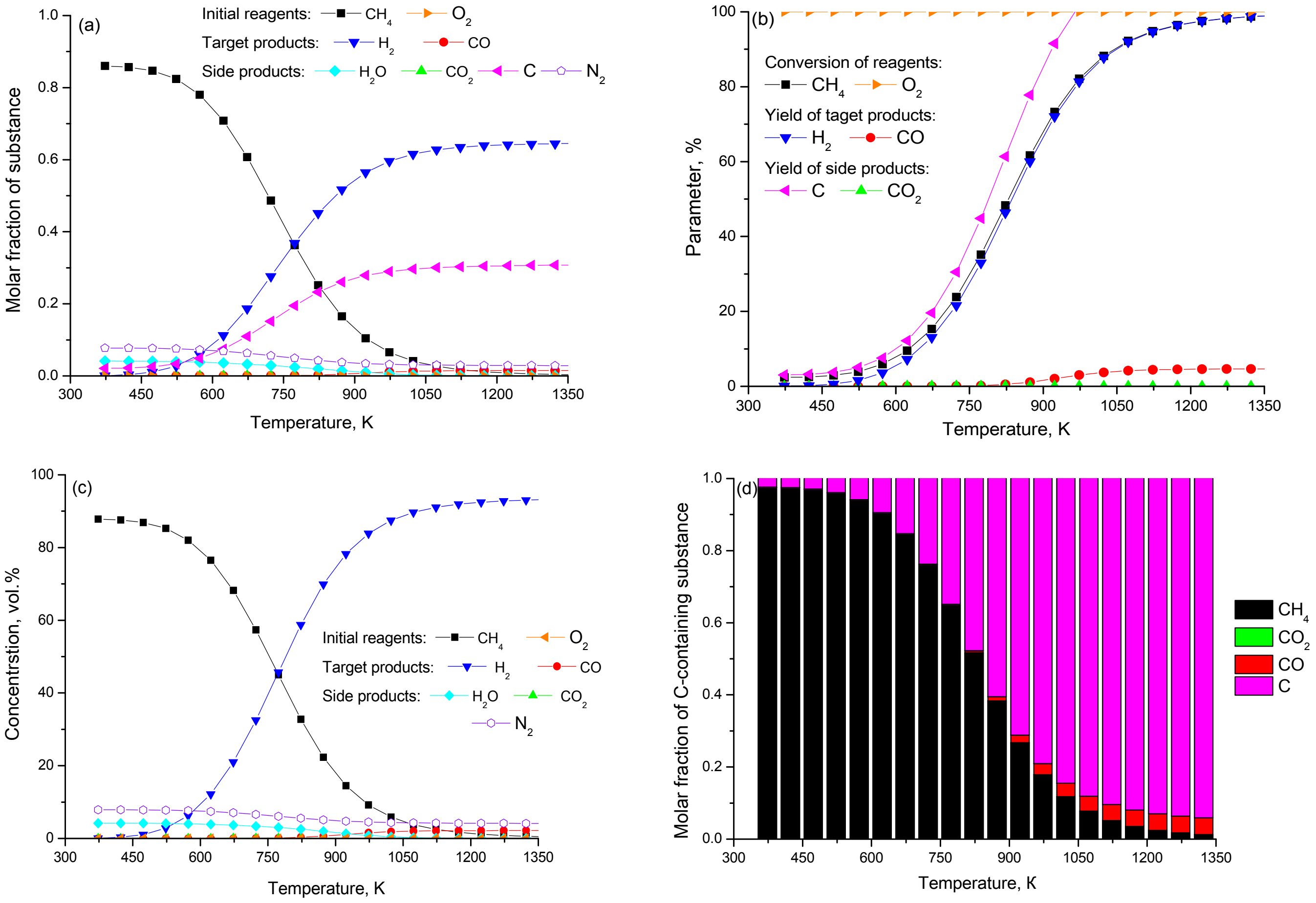

Fig. 10. Dependence of the equilibrium molar fractions of the substances (a), reagent conversion and product yields (b), gas mixture composition (c) and molar fraction of C-containing substances (d) on temperature for methane-air mixture of CBM type (90% CH_4, 2.1% O_2, 7.9% N_2).

also water and carbon dioxide. Their presence in CMM causes an increase in the yield of reforming products and, quite contrary, decreases the yield of pyrolysis products. The data for CMM mixture with the addition of H_2O and CO_2 (40% CH_4, 8.4% O_2, 31.6% N_2, 10% H_2O, 10% CO_2) are shown in Fig. 7e, f. One can see that at T = 1073 K the yield of carbon decreases from 56.4 to 10.9% due to the presence of additives (Fig. 7b, e). An increase in pressure has a negative effect on process parameters (Fig. 8a): methane conversion and the yield of target products decrease.

For methane-air mixture of AMM type containing methane of more than 70 vol.%, low values of methane conversion are observed in the low-temperature region; the products are carbon, CO_2 and H_2O (Fig. 9). With an increase in temperature, methane conversion increases, and the major components in the system become hydrogen and carbon, while CO is present in insignificant amounts. At T = 1073 K, the gas contains 76% H_2. With an increase in pressure, the parameters of methane conversion decrease (Fig. 8b).

For methane-air mixture of CBM type, in which methane concentration is the highest among the considered types, the regularities detected for mixtures of AMM type are conserved. The products of methane conversion are hydrogen and carbon (Fig. 10). Gas mixture with a high hydrogen concentration (90 vol.%) is formed.

For practical implementation, it is necessary to know not only the thermodynamic characteristics of the reaction but also its rate. In the case of kinetic hindrance, thermodynamically possible process is not implemented. The use of catalysts and the creation of the optimal process conditions ensure the practical feasibility of thermodynamically permitted processes and the achievement of the equilibrium parameters of the reaction [19–23].

4. Conclusion

Thermodynamic analysis of the main reactions going on in the multicomponent system CH_4–CO_2–H_2O–air is carried out. The temperature depends on changes in the standard Gibbs energy (ΔG^{o}_{T})

and enthalpy, the equilibrium composition of the mixture for the reactions of steam, dry, autothermal and steam- carbon dioxide reforming of methane, tri-reforming and partial oxidation of methane are calculated. Comparative analysis of methane conversion values, hydrogen yield, carbon yield is carried out; differences between the processes in the efficiency of methane utilization, the formation of target and by-products are determined.

The features of conversion are determined for methane-containing gases differing from each other in chemical composition and corresponding to different stages of coal production. It is determined that the composition of products depends on temperature and the molar ratio O/C in the mixture. In the high-temperature region at T > 1073 K, where the application of catalysts provides practical feasibility of thermodynamically permitted processes and achievement of the equilibrium reaction parameters, the equilibrium composition of products in the methane-air mixture of VAP type (1) VAM (CH_4 less than 1 vol.%) includes only the products of complete oxidation of methane. In the case of methane-air mixtures of CMM type (CH_4 25–60 vol.% or $0.3 < O/C < 1$), under the conditions of thermodynamic equilibrium the products will be H_2, CO and carbon, the amount of which decreases with an increase in the O/C ratio. For methane-air mixtures of AMM type (CH_4 60–80 vol.%) and CBM type (CH_4 more than 80 vol.%), the equilibrium composition practically corresponds to the composition of the products of methane pyrolysis and includes hydrogen and carbon. The possibility of 100% methane conversion is demonstrated, along with the possibility to obtain hydrogen-containing gas with the concentration from 40 to 90 vol.% using the methane-air mixture from coal production.

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