Thermodynamic Analysis of Methanol Synthesis

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Abstract

In this research, the synthesis reactions of such promising e-fuel as methanol by hydrogenation of syngas were studied using methods of chemical thermodynamics. The standard enthalpy and entropy of the starting reagents (CO_2, CO, and H_2) and products (CH_3OH, and H_2O) of the reactions were found. Using these thermodynamic characteristics, the enthalpy ($\Delta_r H$), entropy ($\Delta_r S$), and Gibbs potential ($\Delta_r G$) of the hydrogenation reactions were determined. It was established that the hydrogenation of carbon dioxide at temperatures above 473 K may create a problem since high pressures above 20 MPa are required to implement this reaction. On the other hand, the hydrogenation reaction of carbon monoxide at temperatures above 473 K can be carried out even under moderate pressures. Since the presence of carbon dioxide in the synthesis gas is a negatory factor hindering methanol synthesis, it is desirable to use synthesis gas pre-purified from carbon dioxide. As a result, the following optimal conditions for the synthesis of methanol from syngas consisting of carbon monoxide and hydrogen were proposed, T = 483-503 K, P = 2-3 MPa.

Keywords: E Fuel, Methanol, Syngas Hydrogeneration, Reaction Conditions, Thermodynamic Analysis

1. Introduction

Most experts and scientists do not doubt that in recent years the Earth's climate has changed significantly due to global warming [1,2]. One of the causes of global warming is the increased use of fossil fuels such as coal, oil, and natural gas for intensive energy generation. These energy sources account for about 80% of the world's annual energy consumption [3]. The combustion of these fossil fuels leads to the release of carbon dioxide, the accumulation of which in the Earth's atmosphere creates a greenhouse effect. Many different ways have been proposed to reduce carbon dioxide concentrations and address climate change, one of which is the increased production and use of e-fuels such as methanol [4].

Methanol is an important substance that has received much attention in recent years. This simple alcohol can be used as a promising energy source, the energy density of which (18 GJ/m³) is 450 times higher than methane and more than 1000 times higher than hydrogen [5]. Besides, it is easier to store in liquid form than hydrogen or methane. Methanol is much cheaper than gasoline or kerosene, and this alcohol is much less harmful to the environment. The volume of carbon dioxide formed during the combustion of 1 ton of methanol is 700 m3, which is 2.3 times less than the CO_2 volume released during the combustion of 1 ton of liquid or gaseous fossil fuel and 2.7 times less than the CO_2 volume released during the combustion of 1 ton of coal [6]. Due to its high-octane number, methanol is used as an anti-explosion additive to gasoline. In addition, methanol-air mixtures increase engine power. As a result, racing car engines running on high-octane methanol fuel have a compression ratio of 1.5 times higher than gasoline engines [7]. Fuel cells are also known,
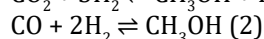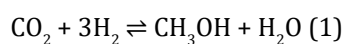
the operation of which is based on the catalytic oxidation of methanol into carbon dioxide.

Moreover, methanol is the main feedstock for the production of a large variety of chemicals such as formaldehyde, acetic acid, formic acid, methyl tert-butyl ether, dimethyl ether, methyl methacrylate, urotropine, dimethyl terephthalate, pesticides, and some other chemical products [8,9]. In addition, methanol is used for transesterification of vegetable oils to produce biodiesel fuel.
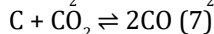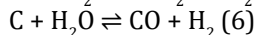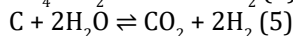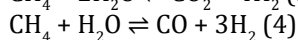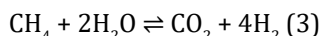
There are several lab and pilot methods for producing methanol such as wood pyrolysis, thermal decomposition of formic acid salts, and saponification of methyl chloride. Industrial methods of methanol production use the hydrogenation process of carbon dioxide and carbon monoxide with hydrogen [10].

The industrial technology of methanol production was first developed in Germany by BASF in 1923. This process was carried out under high pressures of 25-35 MPa and elevated temperatures of 593-723 K using a zinc-chromium catalyst [10].

Since then, the technology of methanol production has been improved. A modern industrial method provides methanol synthesis from syngas on a copper-zinc oxide catalyst under temperatures of 523-573 K and pressures 5-6 MPa by the following reactions [10-12].

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (1)$$
$$CO + 2H_2 \rightleftharpoons CH_3OH \quad (2)$$

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There are several sources of starting substances such as CO_2, CO, and H_2 used for methanol synthesis. The most common source is syngas obtained by steam reforming of natural gas or coal gasification through reactions [8,10-13].

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad (3)$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (4)$$
$$C + 2H_2O \rightleftharpoons CO_2 + 2H_2 \quad (5)$$
$$C + H_2O \rightleftharpoons CO + H_2 \quad (6)$$
$$C + CO_2 \rightleftharpoons 2CO \quad (7)$$

An additional method for the obtaining of CO is the reduction of CO_2 in electrochemical cells [14,15].

However, both natural gas and coal are non-renewable fossil fuels, and their reserves are gradually depleted. A renewable source of the starting substances can be plant biomass [9]. As is known, plant biomass is formed from carbon dioxide and water by photosynthesis absorbing solar energy. When the biomass is decomposed or burned, it releases the accumulated solar energy in the form of heat, along with the release of biogas containing hydrogen, carbon monoxide, and dioxide, as well as water vapor. Therefore, plant biomass is considered a CO_2-neutral source of renewable energy [16].

Steam gasification of plant biomass having formula $C_xH_yO_z$ produces CO, CO_2, and H_2, as follows:

$$C_xH_yO_z + a\ H_2O \rightarrow b\ H2 + kx\ CO + (1-k)\ x\ CO_2 \quad (8)$$
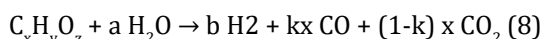
where a = x (2 - k) - z; and b = x (2 - k) - z + 0.5y; coefficient k can vary from 0.5 to 1.

The carbon dioxide required for methanol synthesis can also be extracted from air or flue gases using liquefaction, freezing, and sorption technologies or a combination of these. In addition, "green" CO_2 can be obtained by burning plant biomass, as follows:

$$C_xH_yO_z + (x + 0.25y - 0.5z)\ O2 \rightarrow 0.5y\ H_2O + x\ CO_2 \quad (9)$$
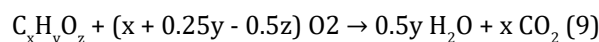
Hydrogen can be obtained also by water electrolysis using primary or alternative energy [17].

$$2H_2O \rightleftharpoons 2H_2 + O2 \quad (10)$$
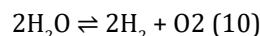
To produce 1 kg of hydrogen, this process theoretically requires 39.7 kWh of electricity. However, since the efficiency of electrolyzers is typically 60–65% the real electricity consumption reaches 61-66 kWh per 1 kg of hydrogen. In addition, "green" hydrogen can be isolated from biogas formed after biomass gasification [17-21].

Although methanol is currently synthesized at temperatures of 523-573 K and pressures of 5-6 MPa these conditions, selected experimentally, are probably not optimal. For this reason, this research performed a comprehensive thermodynamic analysis of the synthesis of methanol by hydrogenation of CO_2 and CO in a wide range of temperatures and pressures to find the optimal conditions for this process [10-12].

2. Objects and Methods

The object of this study was e-fuel, such as methanol. It is a simple aliphatic alcohol containing 50 wt. % of oxygen with the formula CH_3OH. Methanol has the following main characteristics: molecular mass M=32, density d=0.792 g/ml, boiling point T_b=337.8 K, melting point T_m=175.6 K, standard combustion enthalpy Δ_cH^o= -726.5 kJ/mol, calorific value Q=22.7 MJ/kg, and energy density ED= 18 GJ/m³.

To study the hydrogenation reactions of carbon mono- and dioxide, the methods of chemical thermodynamics were used [5,6,22,23]. The standard thermodynamic characteristics (TDCs), such as formation enthalpies (Δ_fH^o) and entropies (S^o) of the gaseous reagents (CO_2 or CO and H_2) and products (CH_3OH and H_2O) of hydrogenation reactions (1) and (2), are presented in Table 1.

Substance	$-\Delta_fH_o$, kJ/mol	So, J/mol K
CO_2	393.51	213.6
CO	110.5	197.4
H_2	0	130.6
H_2O	241.84	188.74
CH_3OH	201.2	239.7

Table 1: Standard TDCs of Gaseous Substances

If the reaction temperature T is higher than the standard temperature To = 298.15 K, then the following equations are used to calculate the TDCs [24].

$$\Delta_fH(T) = \Delta_fH^o + \int_{To}^{T} Cp\ dT \quad (11)$$

$$S(T) = S^o + \int_{To}^{T} (Cp/T)\ dT \quad (12)$$

where Cp is the specific heat capacity of the gaseous substance depending on temperature.

The temperature dependence of Cp for starting gaseous reagents and water vapor is described by the equation:

$$Cp = a + bT + c/T^2 \quad (13)$$

On the other hand, the temperature dependence of Cp for gaseous methanol is the following:

$$Cp = k + mT + nT^2 + pT^3 \quad (14)$$

where a, b, c, k, m, n, and p are coefficients, the values of which are given in reference books.

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The change in the reaction enthalpy ($\Delta_r H$) can be calculated using the Hess law according to which the enthalpy change of a chemical reaction is equal to the difference between the sums of the formation enthalpies ($\Delta_f H_p$) of the reaction products and the formation enthalpies ($\Delta_f H_r$) of the starting reagents, taking into account their stoichiometric coefficients [22,23].

$$\Delta_r H = \sum n_p\, \Delta_f H_p - \sum n_r\, \Delta_f H_r \qquad (15)$$

The change in the entropy ($\Delta_r S$) of a chemical reaction can be found using an equation similar to the Hess equation [22, 23]:

$$\Delta_r S = \sum n_p\, S_p - \sum n_r\, S_r \qquad (16)$$

where S_p and S_r are entropy values for obtaining products and starting reagents, respectively.

Finally, the Gibbs potential of a reaction at temperature T under standard pressure can be calculated, as follows:

$$\Delta_r G(T) = \Delta_r H - T\, \Delta_r S \qquad (17)$$

If the process is carried out at temperature T and elevated pressure P, the Gibbs potential of the reaction is calculated using the equation:

$$\mathbf{\Delta_r G}(T, P) = \Delta_r G(T, P_o) + \Delta n\, RT\, \ln(P/P_o) \qquad (18)$$

where P_o = 0.1 MPa is the standard pressure and Δn is the difference between moles of gaseous products of the reaction and starting gaseous reagents.

The Gibbs potential of the reaction characterizes the degree of non-equilibrium of the reaction system. The more negative its value is, the greater the deviation of the reaction system from equilibrium and the greater the probability of the reaction being feasible. Thus if $\Delta rG < 0$, the reaction can be implemented. This is facilitated by a decrease in the enthalpy (ΔrH) and an increase in the entropy factor ($T\Delta_r S$) of the reaction. On the other hand, if $\Delta_r G > 0$ then the reaction cannot be carried out.

3. Results

The standard thermodynamic functions (TDFs) of hydrogenation reactions (1) and (2) are shown in Table 2.

TDFs	Reaction (1)	Reaction (2)
$\Delta_r H^o$, kJ/mol	-49.5	-90.7
To $\Delta_r S^o$, kJ/mol	-52.7	-65.3
S_o, J/mol K	3.2	-25.4

Table 2: Standard TDFs of Hydrogenation Reactions (1) and (2)

The results showed that under standard conditions To=298.15 K and Po=0.1 MPa, the Gibbs potential of the CO_2 hydrogenation reaction (1) to form methanol has a positive value. Thus, under su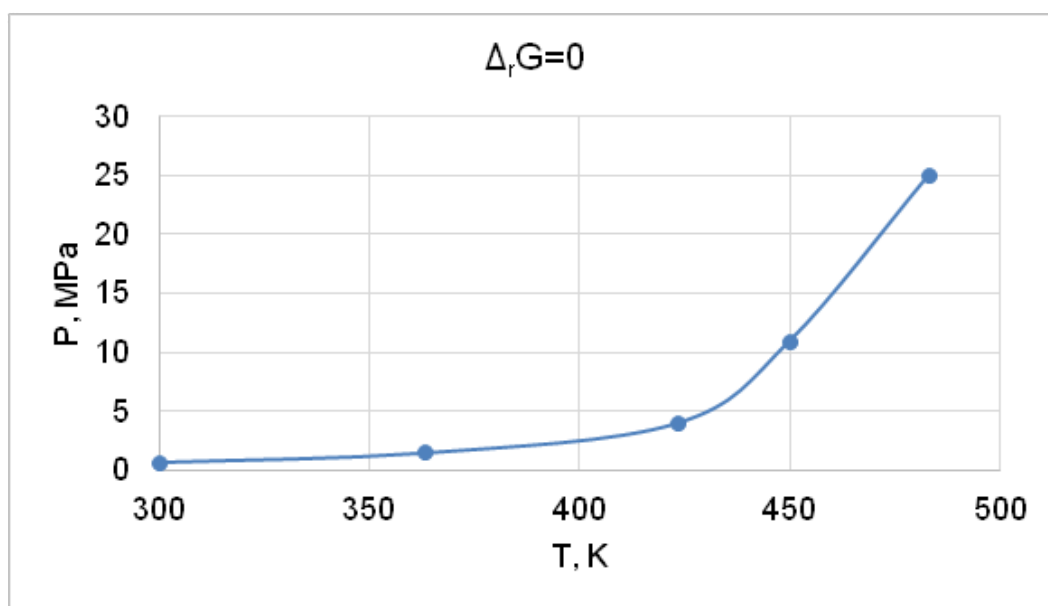ch conditions, this reaction cannot be implemented. Therefore, to carry out this reaction, it is necessary to find other conditions T and P. For this purpose, the temperature dependence of the reaction Gibbs potential was studied similarly to the Ellingham diagrams [25,26].
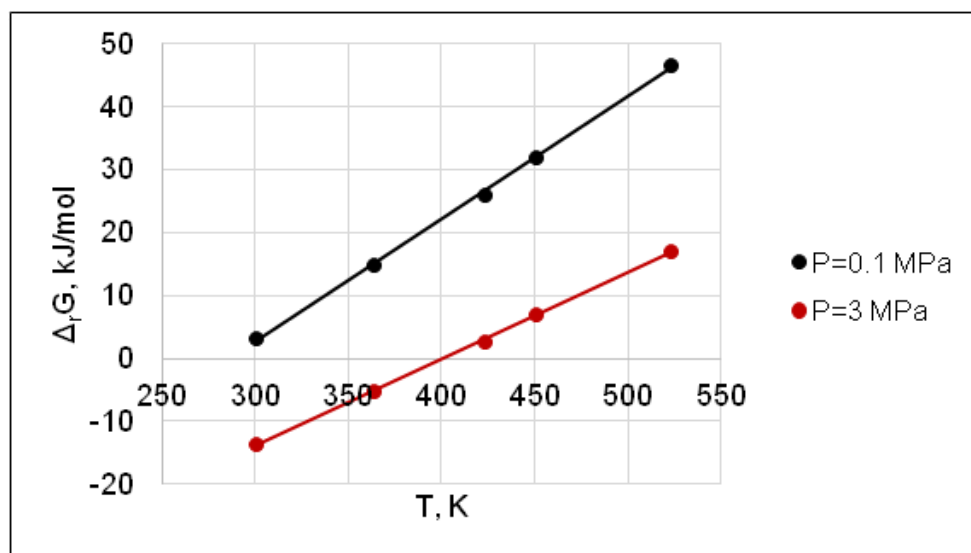
Figure 1: At Normal Pressure, an Increase in the Reaction Temperature Leads to an Increase in the Positive Value of the Gibbs Potential and Blocking of the Hydrogenation Reaction (1)

As can be seen from Figure 1, an increase in the reaction temperature leads to a decrease in the negative value of the Gibbs potential, and at elevated temperatures the value of the Gibbs potential becomes positive, which leads to the cessation of the hydrogenation reaction (1). To occur this reaction, an increase in pressure is necessary to compensate for the negatory effect of temperature.

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Figure 2: Temperature-Pressure Dependence for the Equilibrium State of Reaction (1), Where $\Delta_r G = 0$

To study the reaction conditions, a P-T graph was constructed that reflects the equilibrium state of the reaction system for which $\Delta_r G = 0$ (Figure 2). The peculiarity of this graph is that the reaction can be implemented only at P and T values located in the graph area above and to the left of the curve, since under these conditions $\Delta_r G < 0$. Conversely, at P and T values located in the graph area below and to the right of the curve, $\Delta_r G > 0$, and therefore under these conditions the reaction cannot be carried out.

Unlike reaction (1), the reaction of CO hydrogenation (2) can theoretically be carried out under standard T and P conditions because its $\Delta_r G_o < 0$ (Table 2). However, various studies [10-12] have shown that under standard conditions there are kinetic limitations to the implementation of the reaction (2). To overcome these limitations and increase the reaction rate, it is necessary to enhance the reaction temperature above 473 K [27].

Thermodynamic studies have shown that, similar to reaction (1), an increase in the temperature of reaction (2) also causes a decrease in the negative value of the Gibbs potential (Figure 3). However, at the same pressure for the reaction (2) the value of the Gibbs potential becomes positive at higher temperatures than for the reaction (1).

Such a feature is also confirmed by the analysis of the P-T graph of reaction (2) shown in Figure 4. Moreover, at the same temperature, the reaction (2) can be carried out at lower pressures than the reaction (1).
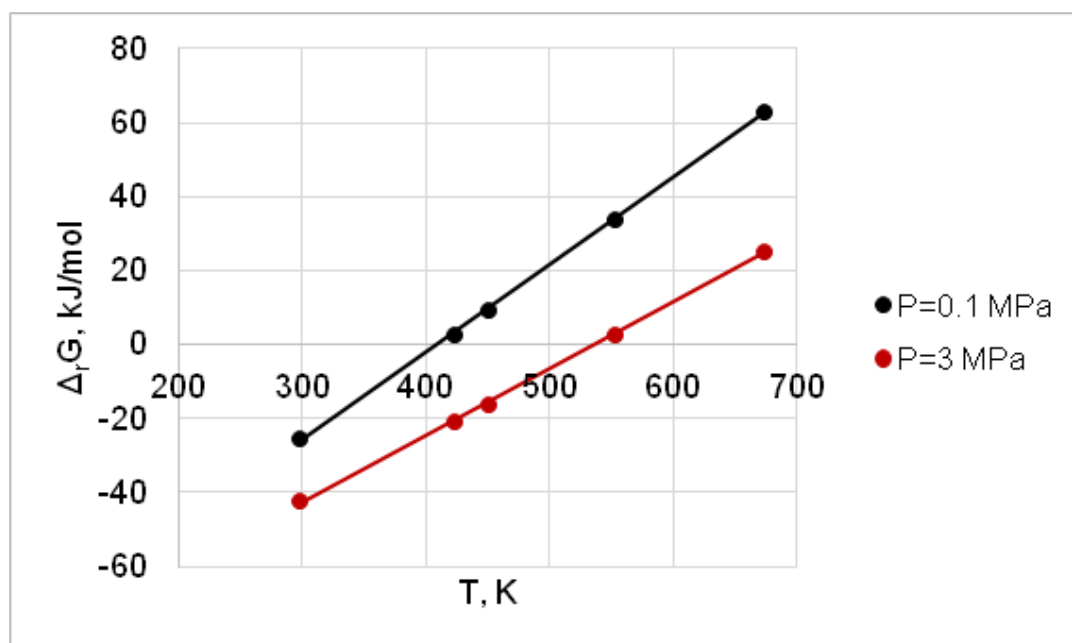
Figure 3: Temperature Dependence of Gibbs Potential of Reaction (2) at Two Different Pressures
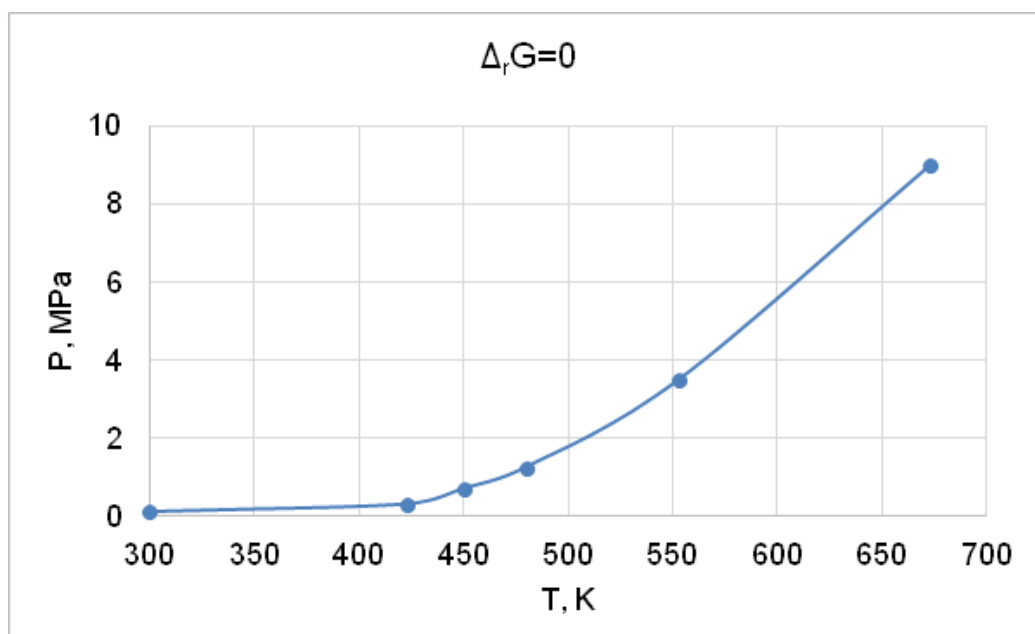
Figure 4: Temperature-Pressure Dependence for the Equilibrium state of Reaction (2), Where $\Delta_r G=0$

4. Discussion

The study of the hydrogenation reactions of carbon dioxide and carbon oxide to synthesize methanol has shown that at normal and moderate temperatures and pressures these reactions either do not occur at all since $\Delta_r G > 0$ (see e.g., Figures 1 and 2) or occur but at such a low rate that it is not possible to ensure the desired methanol yield [10-12]. To increase the reaction rate, its temperature should be above 473 K [27]. However, the hydrogenation of carbon dioxide at such a temperature may create a technical problem, since high pressures above 20 MPa are required to implement this reaction (Figure 2). On the other hand, the hydrogenation reaction of carbon monoxide at a temperature T above 473 K can be carried out even under moderate pressures of 2-3 MPa (Figure 4).

Thus, the presence of carbon dioxide in the synthesis gas is an unfavorable factor in methanol production. Therefore, for effective synthesis of methanol, it is desirable to use synthesis gas pre-purified from carbon dioxide. Various methods can be used to remove CO_2 from syngas, such as capture with sorbents, chemisorption with amines, calcium or magnesium oxides, and sodium hydroxide, etc. [28-31]. Among these methods, the most commercially profitable is the CO_2 chemisorption by sodium hydroxide with the formation of sodium carbonate, which after the causticizing process again turns into sodium hydroxide.

Based on the obtained results, the following optimal conditions for the synthesis of methanol from syngas consisting of carbon monoxide and hydrogen can be proposed, namely: T = 483-503 K, P = 2-3 MPa. These found optimal reaction conditions are "softer" than the conditions for the synthesis of methanol currently used in industry.

If syngas is obtained by gasification of renewable plant biomass using alternative energy sources, then CO_2-neutral methanol can be obtained.

5. Conclusions

A complete thermodynamic (TD) analysis of the reactions of synthesis of the promising e-fuel, methanol, by hydrogenation of carbon dioxide and carbon monohydride at different temperatures (T) and pressures (P) was carried out. The TD functions, such as enthalpy ($\Delta_r H$), entropy ($\Delta_r S$), and Gibbs potential ($\Delta_r G$) of the hydrogenation reactions were determined. To optimize the conditions of these reactions, two special methods were proposed: (1) plotting the temperature dependence of the Gibbs potential of the reaction at different pressures, and (2) plotting the P-T diagram at the value of $\Delta_r G = 0$. It was established that the hydrogenation of carbon dioxide at temperatures above 473 K may create a problem since high pressures above 20 MPa are required to implement this reaction. On the other hand, the hydrogenation reaction of carbon monoxide at temperatures above 473 K can be carried out even under moderate pressures. Since the presence of carbon dioxide in synthesis gas is a negative factor, for the synthesis of methanol it is desirable to use synthesis gas pre-purified from carbon dioxide. The following optimal conditions of the methanol synthesis from syngas consisting of carbon monoxide and hydrogen were proposed, T = 483-503 K, P = 2-3 MPa.

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