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(RESEARCH ARTICLE)

How to control reactions of syngas

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Abstract

As is known, syngas containing a mixture of carbon monoxide and hydrogen is used to synthesize various products such as methanol, artificial methane, and gasoline. In this research, a complete thermodynamic analysis was performed in a wide range of temperatures and pressures to predict the most probable direction of the synthesis reactions. It was shown that in the case of methanol synthesis at normal pressure, an increase in the reaction temperature above 400 K leads to the positive value of the Gibbs potential, as a result of which this reaction is blocked. An increase in pressure to at least 3 MPa is necessary to implement the methanol synthesis reaction. Under this pressure, the methanol synthesis can be carried out in the temperature range from 480 to 530 K. In addition, to enhance the alcohol yield, this process requires the use of a special catalyst. Artificial n-octane is mainly formed at 3 MPa in the temperature range from 530 to 600 K along with the use of a catalyst to improve the reaction selectivity. Selective methane synthesis may occur at a syngas pressure of 3 MPa but at high reaction temperatures, between 900 and 1200 K. To reduce the upper temperature of this process and increase the yield of the final product without significantly changing the reaction rate, a special catalyst is used. The reactions of syngas cease at normal pressure when the temperature increases above 900 K. At a syngas pressure of 3 MPa the synthesis reactions should cease if the temperature rises above 1200K,

Keywords: Syngas; Synesis products; Methanol; Methane; Octane; Synesis conditions; Thermodynamic analysis

1. Introduction

As is known, synthesis gas, or shortly syngas is a mixture of carbon monoxide (CO) and hydrogen (H_2) [1]. Syngas got its name because it can be used to synthesize some valuable products such as methanol, artificial methane, and gasoline, as follows [2]:

$$CO + 2\ H_2 \rightleftharpoons CH_3OH \quad \ldots\ldots\ldots\ldots\ (1)$$

$$CO + 3\ H_2 \rightleftharpoons CH_4 + H_2O \quad \ldots\ldots\ldots\ldots\ldots(2)$$

$$n\ CO + (2n + 1)\ H_2 \rightleftharpoons C_nH_{2n+2} + n\ H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

A typical component of gasoline is normal octane with n=8, the synthesis of which can be expressed by the reaction (4):

$$8\ CO + 17\ H_2 \rightleftharpoons C_8H_{18} + 8\ H_2O \quad \ldots\ldots\ldots\ldots\ (4)$$

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 590-720 K using a zinc-chromium catalyst [3]. Since then, the technology of methanol production has been improved. A modern industrial method provides

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methanol production from syngas on a copper-zinc oxide catalyst under temperatures of 550-580 K and pressures of 5-6 MPa [3-5].

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/m^3) is 450 times higher than methane and more than 1000 times higher than hydrogen [6]. Moreover, the octane number of methanol is higher than that of gasoline. Methanol is considered environmentally friendly since the combustion of this fuel generates 2.3–2.7 times less CO_2 than the combustion of the same amount of fossil fuel. In addition, methanol is the main feedstock for producing a large variety of chemicals [7].

The production of artificial methane from syngas requires temperatures of 600-800 K and pressures of 2-4 MPa, as well as the presence of a catalyst, Ni, or Ru/Al_2O_3 [8]. The Fischer-Tropsch reaction (3) to produce artificial gasoline is usually carried out at temperatures of 550-600 K under normal or moderate pressure using a metal catalyst, Co, Fe, etc. [9]. Higher temperatures lead to higher conversion rates but are accompanied by the formation of methane.

There are several sources of starting syngas and its components. The syngas is produced usually by steam reforming of natural gas or coal gasification through reactions [6, 10]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

$$C + H_2O \rightleftharpoons CO + H_2 \quad \ldots\ldots\ldots\ldots\ldots (6)$$

The component of syngas, carbon monoxide, can be produced by reducing carbon dioxide with coal:

$$C + CO_2 \rightleftharpoons 2CO \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

An additional method for obtaining carbon monoxide is the reduction of carbon dioxide in electrochemical cells [11, 12].

However, natural gas and coal are non-renewable fossil fuels, and their reserves are gradually depleted. Renewable sources of syngas and its components can be plant biomass and its based biochar [7, 13, 14]. The process of biochar gasification proceeds according to eq. (6) and (7). Steam gasification of plant biomass and its waste having formula $C_xH_yO_z$ produces H_2, CO, and CO_2, as follows:

$$C_xH_yO_z + a\,H_2O \rightarrow b\,H_2 + k\,x\,CO + (1-k)\,x\,CO_2 \quad \ldots\ldots\ldots\ldots\ldots (8)$$

where $a = x\,(2 - k) - z$; $b = x\,(2 - k) - z + 0.5y$; and coefficient k can vary from 0 to 1.

The obtained gas mixture can be purified from CO_2 using various methods such as pressure swing adsorption, capture with sorbents, chemisorption with sodium hydroxide, etc. [15-17].

As is known, plant biomass is formed from carbon dioxide and water by photosynthesis, absorbing solar energy. When the biomass is burned, the accumulated solar energy is released as heat along with the emission of carbon dioxide and other biogases. Therefore, plant biomass is considered a carbon-neutral and renewable source [18].

Typically, the hydrogen content in the syngas is lower than of carbon monoxide, so an additional amount of hydrogen must be introduced into the syngas to implement the synthesis reaction. This additional “green” hydrogen can be obtained, e.g., by water electrolysis using renewable energy [19]:

$$2H_2O \rightleftharpoons 2H_2 + O_2 \quad \ldots\ldots\ldots\ldots \quad (9)$$

Since the syngas extracted from renewable sources is “green”, the products of its synthesis can also be called “green”.

It is amazing that syngas containing the same components, CO and H_2, can synthesize various products such as methanol, artificial methane, and artificial gasoline, e.g., n-octane. To understand how it is possible and to predict the most probable synthesis direction, in this research a complete thermodynamic analysis of the reactions (1), (2), and (4) was performed in a wide range of temperatures and pressures.

2. Objects and methods

The objects of this study were products of syngas reactions such as methanol, artificial methane, and artificial n-octane. The main characteristics of these products such as molecular mass (M), boiling point (T_b), calorific value (Q), and density of thermal energy (ED) are shown in Table 1.

Table 1 Characteristics of synthesis products

Products	M	T_b, K	Q, MJ/kg	ED, MJ/m^3
Methanol	32	337.8	22.7	1.8×10^4
n-Octane	114	398.6	47.8	3.4×10^4
Methane	16	111.7	55.5	39.6

To study the synthesis reactions of these products from syngas, the methods of chemical thermodynamics were used [20-22]. The standard thermodynamic characteristics (TDCs), such as formation enthalpies ($\Delta_f H^o$) and entropies (S^o) of the gaseous reagents (CO and H_2) and products (CH_3OH, CH_4, n-C_8H_{18}, and H_2O) of the reactions are presented in Table 2.

Table 2 Standard TDCs of gaseous substances

Substances	-$\Delta_f H^o$, kJ/mol	S^o, J/mol K
CO	110.5	197.4
H_2	0	130.6
CH_3OH	201.2	239.7
CH_4	74.85	186.19
n-C_8H_{18}	208.5	465.0
H_2O	241.84	188.74

If the reaction temperature, T, is higher than the standard temperature, T_o = 298.15 K, then the following equations are used to calculate the TDCs [20]:

$$\Delta_f H(T) = \Delta_f H^o + \int_{To}^{T} Cp\, dT \quad \ldots\ldots\ldots\ldots\ldots (10)$$

$$S(T) = S^o + \int_{To}^{T} (Cp/T)\, dT \quad \ldots\ldots\ldots\ldots (11)$$

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

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

$$C_p = a + bT + c/T^2 \quad \ldots\ldots\ldots\ldots (12)$$

On the other hand, the temperature dependence of C_p for methane, gaseous methanol, and n-octane is calculated by the following equation:

$$C_p = k + mT + nT^2 + pT^3 \quad \ldots\ldots\ldots\ldots (13)$$

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

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 the stoichiometric coefficients [21, 22]:

$$\Delta_r H = \sum n_p \, \Delta_f H_p - \sum n_r \, \Delta_f H_r \text{ .... } (14)$$

The change in the entropy ($\Delta_r S$) of a chemical reaction can be found using an equation similar to the Hess equation [21, 22]:

$$\Delta_r S = \sum n_p \, S_p - \sum n_r \, S_r \quad \text{............ } (15)$$

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 P_o can be calculated, as follows:

$$\Delta_r G(T) = \Delta_r H - T \, \Delta_r S \qquad \text{............ } (16)$$

If the process is carried out at temperature T and elevated pressure P, the Gibbs potential of the reaction is calculated using the equation [6]:

$$\Delta_r G(T, P) = \Delta_r G(T, P_o) + \Delta n \, RT \ln(P/P_o) \text{............ } (17)$$

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 $\Delta_r G < 0$, the reaction can be implemented. This is facilitated by a decrease in the enthalpy ($\Delta_r H$) 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.

After determining the Gibbs potential, the equilibrium constant (K_{eq}) of the reaction can be calculated:

$$\ln K_{eq} = -\Delta_r G/RT \text{ .,......}(18)$$

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3. Results and Discussion

The standard thermodynamic functions (TDFs) of reactions (1), (2) and (4) are shown in Table 3.

Table 3 Standard TDFs of reactions (1), (2) and (4)

TDFs	Reaction (1)	Reaction (2)	Reaction (4)
$\Delta_r H^o$, kJ/mol	-90.70	-206.19	-1259.22
$T_o \Delta_r S^o$, kJ/mol	-65.26	-63.88	-543.97
$\Delta_r G^o$, kJ/mol	-25.44	-142.31	-715.25

As follows from Table 3, under standard conditions, T_o=298.15 K and P_o=0.1 MPa, the Gibbs potential of all the studied reactions has a negative value, i.e., $\Delta_r G^o < 0$. Thus, these reactions can theoretically be carried out under normal temperature and pressure. However, experiments have shown that under these conditions the reaction rates are very low [3, 8, 9]. To overcome kinetic obstacles and increase the reaction rates, it is necessary to enhance the temperature to 450-470 K, at least [8, 9, 23]. On the other hand, all these reactions are exothermic; therefore, an increase in the temperature should reduce the negative values of the Gibbs potentials.

To study the temperature impact on the Gibbs potential of various reactions, graphs similar to Ellingham diagrams [24] were drawn (Figures 1, 3, and 4). These graphs show that with increasing temperature the negative value of the Gibbs potential really decreases. Thus, although the temperature rise causes an increase in the synthesis reaction rate, the equilibrium constant and the yield of the final product decrease. Therefore, it is advisable to carry out the reaction in the middle temperature range to maintain a balance between the reaction rate and the equilibrium constant. On the other hand, the enhancement of syngas pressure at a certain temperature causes an increase in the negative value of the Gibbs potential, which contributes to a higher value of the equilibrium constant and yield of the final product.

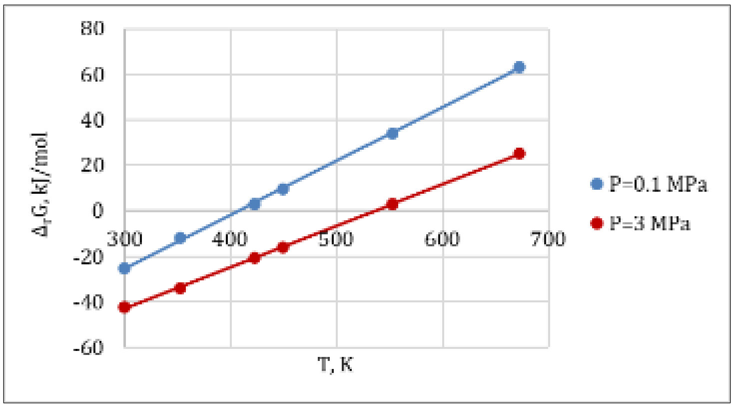

Figure 1 Temperature dependence of Gibbs potential for methanol synthesis reaction at normal and moderate pressures

In the case of methanol synthesis at normal pressure, an increase in the reaction temperature above 400 K leads to the positive value of the Gibbs potential, as a result of which reaction (1) is blocked (Figure 1). To implement this reaction, an increase in pressure is necessary to compensate for the negatory effect of temperature.

To study the reaction conditions, a P-T graph was drawn, reflecting 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.

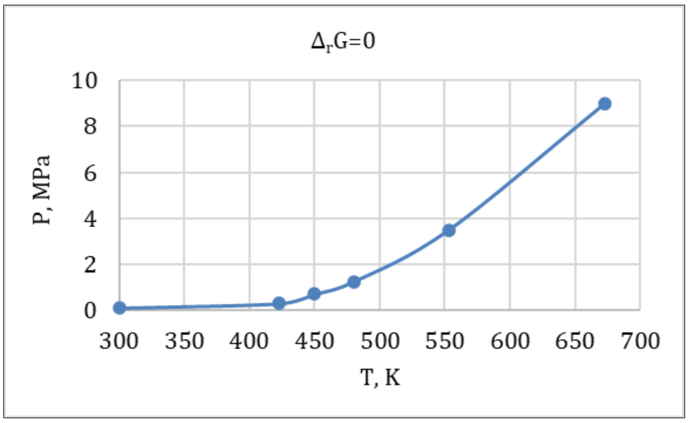

Figure 2 Temperature-pressure relationship for the equilibrium state of methanol synthesis reaction, where $\Delta_r G = 0$

From these results, it follows that at a pressure of 3 MPa the methanol synthesis reaction can be implemented but it is carried out only in a narrow temperature range from 480 to 530 K. To further expand the temperature range in which the reaction (1) is feasible, it is necessary to significantly increase the pressure of syngas, which can create technical problems.

Unlike methanol synthesis, the reaction of methane synthesis can be carried out at normal pressure in a wide temperature range, from 480 to 900 K, where $\Delta_r G < 0$ (Figure 3). An enhancement in syngas pressure is favorable for this reaction because it increases the equilibrium constant (Table 4) and shifts the reaction equilibrium to the right.

Table 4 Equilibrium constants of reaction (2) at T=800 K and various pressures

P, MPa	ln K_{eq}
0.1	3.6
3.0	10.4

If the pressure of syngas is increased to 3 MPa, then the temperature range of feasibility for reaction (2) expands by 280 degrees and reaches 1180 K. A problem is that a rise in the reaction temperature leads to a decrease in the equilibrium constant and yield of methane. Therefore, it is advisable to reduce the upper temperature of methane synthesis.

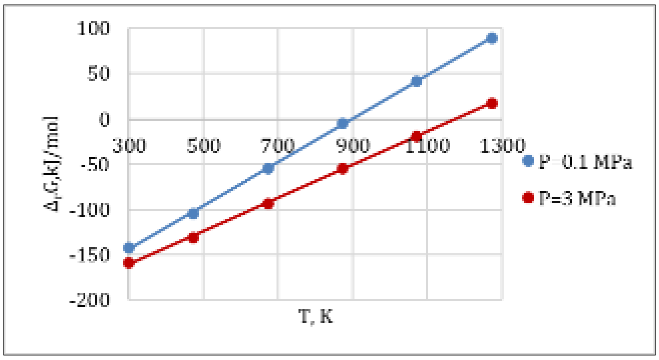

Figure 3 Temperature dependence of Gibbs potential for methane synthesis reaction at normal and moderate pressures

The synthesis of n-octane from syngas at normal pressure occurs at temperatures from 480 to 680 K (Figure 4). This temperature interval is 220 degrees narrower than that for methane synthesis. An increase in syngas pressure for this reaction is also favorable since it increases the equilibrium constant (Table 5). In addition, at a pressure of 3 MPa, the temperature range of reaction feasibility can be extended by 400 K.

Table 5 Equilibrium constants of reaction (4) at T=600 K and various pressures

P, MPa	ln K_{eq}
0.1	29.1
3.0	83.4

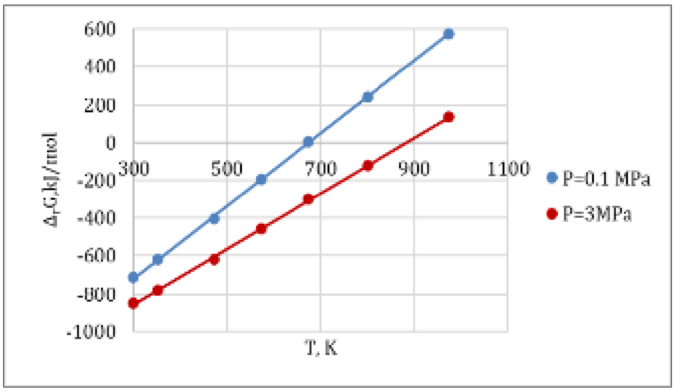

Figure 4 Temperature dependence of Gibbs potential for n-octane synthesis reaction at normal and moderate pressures

Analysis of the obtained results showed that at normal pressure and high temperatures from 680 to 900 K, selective synthesis of only methane from syngas is possible. At temperatures from 400 to 680 K, two products, methane, and n-octane, can be formed from syngas in different ratios, which depend on the equilibrium constants.

For example, if at normal pressure the temperature of reactions is 600 K, then after calculating the equilibrium constants it can be shown that under these conditions mainly n-octane will be synthesized (Table 6). When the temperature of these reactions increases to 670 K, on the contrary, methane will be predominantly formed.

Table 6 Equilibrium constants of reactions (2) and (4) at normal pressure

T, K	ln K_{eq}	
	Reaction (2)	Reaction (4)
600	14.4	29.1
670	11.0	2.0

However, at normal pressure of syngas, the yield of final reaction products is usually low. To increase the yield of these products, their synthesis from syngas should be performed at elevated pressures.

Thermodynamic studies have shown that at a syngas pressure of 3 MPa and reaction temperatures between 900 and 1200 K, only methane synthesis occurs. However, in the temperature range from 530 to 900 K, at such pressure, the n-octane is mainly formed along with a certain amount of methane. Once cooled below the boiling point of n-octane, this artificial gasoline can be isolated, while methane evaporates under these conditions. Lowering the reaction temperature increases the equilibrium constant and the yield of the n-octane (Figure 5). In addition, the presence of a special catalyst, iron or cobalt, significantly improves the reaction selectivity and the purity of the resulting n-octane.

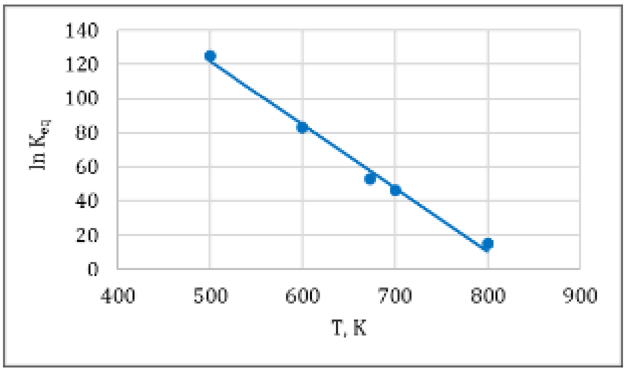

Figure 5 Temperature dependence of equilibrium constant for n-octane synthesis reaction at a pressure of 3 MPa

A more complex picture can be observed at a syngas pressure of 3 MPa when the temperature drops below 530 K. Under these conditions, the resulting methanol may contain impurities of methane and n-octane, from which it can be purified, e.g., by distillation. In addition, the selectivity of the reaction (1) and the production of sufficiently pure methanol can be ensured by using a specific catalyst such as copper-zinc oxide [3].

4. Conclusions

In this research, a complete thermodynamic analysis was performed to predict the most probable direction of reactions involving syngas. This analysis showed that at normal pressure and temperature above 400 K, the Gibbs potential of the reaction of methanol synthesis has a positive value, therefore, this alcohol is not formed under these conditions. Unlike this case, the Gibbs potentials of the synthesis reactions of methane and n-octane at normal pressure are negative above 400 K. Thus, these products can be obtained even at normal syngas pressure in a certain temperature range, but probably with insufficient yield.

An enhancement in syngas pressure, e.g., to 3 MPa, is favorable for all studied reactions because it increases the equilibrium constant and shifts the reaction equilibrium to the right. Under this pressure, the methanol synthesis can be implemented if the reaction temperature ranges from 480 to 530 K. However, under these reaction conditions, the resulting methanol may contain impurities of methane and n-octane, from which it should be purified. In addition, the selectivity of this reaction and the production of sufficiently pure methanol can be ensured by using a special catalyst.

Artificial n-octane is mainly formed at 3 MPa in the temperature range from 530 to 900 K, along with a certain amount of methane. Since the equilibrium constant of the reaction increases at lower temperatures, it is recommended to reduce the upper temperature to 600 K along with using a catalyst to improve the reaction selectivity.

Selective methane synthesis may occur at a syngas pressure of 3 MPa but at high reaction temperatures, between 900 and 1200 K with decreased methane yield. To reduce the temperature of this process and increase the yield of the final product without significantly changing the reaction rate, a special catalyst is used in the chemical industry.

At normal pressure, the reactions of syngas cease when the temperature increases above 900 K. If the pressure of syngas is 3 MPa and the temperature rises above 1200 K, then the equilibrium of reactions shifts to the left, and all synthesis reactions should cease.

Thus, to adjust the direction of the syngas reaction, the pressure and temperature must be controlled. In addition, to ensure the reaction selectivity, it is necessary to use specific catalysts.

Compliance with ethical standards

Disclosure of conflict of interest

The author of this paper declares that there is no conflict of interest.

References

[1] Speight JG. Chemical and Process Design Handbook. McGraw-Hill: New York, 2002; 566 p.

[2] Ioelovich M. Thermal energy of plant biomass, its components, and secondary biofuels. World J. Adv. Res. Reviews 2024; 24: 2786-2794.

[3] Bozzano G, Manenti F. Efficient methanol synthesis: perspectives, technologies and optimization strategies. Progress in Energy and Combustion Sci. 2016; 56: 71-105.

[4] Lange J-P. Methanol synthesis: a short review of technology improvements. Catalysis Today 2001; 64: 3-8.

[5] Jadhav SG, Vaidya PD, Bhanage BM, Joshi JB. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. Chem. Eng. Res. and Design 2014; 92: 2557-2567.

[6] Ioelovich M. Thermodynamic analysis of methanol synthesis. Chem. Res. Prac. 2025; 2: 1-6.

[7] Reschetilowski W. Alternative resources for the methanol economy. Chemical Reviews, 2013; 82: 624-634.

[8] Schmider D, Maier L, Deutschmann O. Reaction kinetics of CO and CO_2 methanation over nickel. Ind. Eng. Chem. Res. 2021: 60: 5792–5805.

[9] Dry ME. The Fischer–Tropsch process: 1950–2000. Catalysis Today 2002; 71: 227–241.

[10] Vita A, Cristiano G, Italiano C, Pino L, Specchia S. Syngas production by methane oxy-steam reforming on Me/CeO_2 (Me=Rh, Pt, Ni) catalyst lined on cordierite monoliths. Appl. Catalysis B: Environmental 2015; 162: 551-563.

[11] Ma M, Bartek J, Trześniewski BJ, Xie J, Smith WA. Selective and efficient reduction of carbon dioxide to carbon monoxide on oxide-derived nanostructured silver electrocatalysts. Angewandte Chemie, 2016; 55: 9748-9752.

[12] Proietto F, Li S, Loria A, Hu X-M, Galia A, et al. High-pressure synthesis of CO and syngas from CO_2 reduction using Ni–N-doped porous carbon electrocatalyst. Chem. Eng. Journal 2022; 429: 132251.

[13] Lu Z, Wei W, Yongjie Z, Xianchao Z. Clean synthesis gas production from municipal solid waste via catalytic gasification and reforming technology. Catalysis Today 2018; 318: 39–45.

[14] Sasidhar N. Carbon neutral fuels and chemicals from standalone biomass refineries. Indian J. Env. Eng. 2023; 3: 1–8.

[15] Sanz-Pérez ES, Murdock CR, Didas SA, Jones CW. Direct capture of carbon dioxide from ambient air. Chemical Reviews 2016; 116: 11840–11876.

[16] Nikulshina V, Ayesa N, Gálvez ME, Steinfeld A. Feasibility of Na-based thermochemical cycles for the capture of CO_2 from air. Thermodynamic and thermogravimetric analyses. Chem. Eng. Journal, 2008; 140: 62-70.

[17] Stolaroff J, Lowry G, Keith D. Using CaO-and MgO-rich industrial waste streams for carbon sequestration. Energy Conversion and Manag. 2005; 46: 687-699.

[18] Saidur R, Abdelaziz E, Demirbas A, Hossain M, Mekhilef S. A review on biomass as a fuel for boilers. Renew. Sustain. Energy Review, 2021; 15: 2262–2289.

[19] Franco A, Giovannini C. Recent and future advances in water electrolysis for green hydrogen generation: critical analysis and perspectives. Sustainability 2023; 15: 16917.

[20] Ioelovich M. Application of thermodynamic methods to the study of plant biomass and its components - a review. Appl. Biosci.2024; 3: 577–616.

[21] Koper GJM. An Introduction to Chemical Thermodynamics. 2nd ed. VSSD: Leiden, 2008; 212 p.

[22] Klotz IM, Rosenberg RM. Chemical Thermodynamics, Basic Concepts and Methods. 7th ed. Whiley & Sons Inc.: Hoboken, 2008; 588 p.

[23] Gallucci F, Basile A. Theoretical analysis of methanol synthesis from CO_2 and H_2 in a ceramic membrane reactor. Int. J. Hydrogen Energy 2007; 32: 5050-5058.

[24] Epifano E, Monceaux D. (2023). Ellingham diagram: A new look at an old tool. Corrosion Sci. 2023; 217: 111113.