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Thermodynamic research of coal mining waste gasification processes

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Abstract

Purpose. Research aims to study the thermodynamic patterns of coal mining waste gasification process and the formation of a theoretical basis for carbon conversion processes with the production of synthesis gas with a high hydrogen content.

Methods. Thermodynamic calculations are based on the main carbon conversion reactions in the temperature range of 500-1100°C and pressures of 1-10 atm. To assess the probability of the flow of processes, the values of Gibbs energy, equilibrium constants and equilibrium conversion degree were determined, which made it possible to predict the composition of the gas phase and determine the optimal gasification conditions. The method of least squares was used to ap-proximate the obtained dependences.

Findings. It has been determined that coal mining waste dumps pose a significant source of environmental hazard, since they lead to pollution of soil, water resources and atmospheric air. Traditional methods of utilization focus mainly on localization, but do not provide complete neutralization of harmful components. The conducted thermodynamic calculations confirmed the expediency of using the gasification process, which is effective at temperatures above 860°C. The autothermal nature of this process is achieved through the partial oxidation of carbon to carbon monoxide (CO), which compensates for heat loss. It has been found that increasing pressure reduces the equilibrium degree of carbon conversion. The obtained thermodynamic dependences make it possible to predict the composition of synthesis gas and, subsequently, to assess the prospects for the implementation of technologies for complex recycling of coal mining waste.

Originality. For the first time, a comprehensive thermodynamic assessment of coal mining waste gasification reactions has been conducted, and thermodynamic dependences of Gibbs energy change, equilibrium constants, and equilibrium conversion degree have been obtained over a wide range of temperatures and pressures. This made it possible to determine the optimal conditions for the process flow and confirm its technological feasibility at temperatures above 860°C.

Practical implications. The results of the research form a theoretical basis for creating effective technologies for complex recycling of coal mining waste to produce synthesis gas, which can serve as a promising energy source, ensuring compliance with modern principles of sustainable development and rational nature management.

Keywords: *mining waste, gasification, coal, pyrolysis, conversion, synthesis gas, temperature*

1. Introduction

The mining industry, while stimulating the country's economic development, is at the same time the cause of significant environmental problems. One of the major consequences of mineral mining is the accumulation of mine waste dumps, also known as tailings dams or waste heaps. These waste dumps cause soil, water and air pollution, as well as landscape degradation [1]-[3].

Therefore, in order to achieve sustainable development that combines economic growth with environmental protection and social justice, it is necessary to introduce innovative approaches to the processes of mine waste utilization [4]-[6].

At the UN Climate Change Conference in Glasgow (COP26) in autumn 2021, world leaders agreed to achieve carbon neutrality by 2060, gradually phasing out coal-fired power and switching to alternative energy sources. Under the agreement, Ukraine committed to close all state-owned coal-fired power plants by 2035, reduce methane emissions by 30% by 2030, and stop deforestation [7]. At the same time, according to the International Energy Agency data, at the current rate of consumption, proven cost-effective oil reserves will be sufficient for 30-40 years, gas – until the middle of the century, coal – for 300-400 years, and nuclear fuel – up to 120 years using thermal neutrons and up to 1000 years using fast neutrons. That is, in the near future, hydrocarbons will remain the main energy sources [8].

Until recently, hard coal accounted for more than 80% of all fossil fuel sources. Coal is still the world's main source of electricity generation, but its share in the energy balance is gradually decreasing: the current figure (35%) is the lowest since the creation of the International Energy Agency in 1974. In 2024, global demand for coal increased by 1.2%,

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mainly due to rising consumption in Asia. China and India, the largest coal consumers, have provided a major increase, driven by increased demand for electricity. Developed economies, particularly the US and the EU, continue to reduce their use of coal [9]. At the same time, global demand for energy has increased significantly as a result of population growth and the desire to improve quality of life. Despite limited resources and environmental hazards, fossil fuels, particularly oil (31.7%), coal (28.1%) and natural gas (21.6%), remain the mainstay of the global energy supply, providing over 81% of total primary energy [10].

The critical need for sustainable and cleaner alternative energy sources has brought hydrogen to the forefront. Recent studies also highlight the importance of hydrogen-oriented energy technologies and advanced ceramic materials resistant to irradiation, which are considered in the context of sustainable energy systems [11]. The use of H_2 as an energy source has a number of advantages: energy conversion produces non-toxic products (water), hydrogen can be produced from domestic and industrial waste, and it has high thermal characteristics. Therefore, thermochemical conversion becomes a key method of industrial production of H_2.

Ukraine has the largest coal reserves in Europe (140.8 billion tons). This is enough for 250-300 years of mining and in the long run, provided that innovative mining technologies and complex processing are used, coal can become a raw material for the production of high-tech materials. It should be noted that coal mining in the Donetsk Basin, the largest in Ukraine (97.6% of all coal reserves), has been conducted for more than 300 years. This resulted in the formation of waste heaps: 1130 of them are located in Luhansk and Donetsk Oblasts, with a total volume of 1 billion m^3 and an area of 5500 hectares. There are also similar dumps in the Western Donbas and in the Lviv-Volyn Basin, so the scale of their technogenic impact is enormous [12], [13]. Similar studies emphasize that the negative consequences of mining are not limited to waste heaps, but also include the long-term geological transformations of ore deposits, the stability of surrounding rock masses, and the need for advanced extraction technologies [14]-[16].

The approximate percentage composition of coal dumps (waste heaps) may vary depending on the specific deposit and coal mining technology. However, the following average values of the content of the main components can be given:

1) rock – 70-80% (sandstone, shale, limestone and other inorganic materials);

2) residual coal – 10-20% (in some cases, the content reaches 30%);

3) sulphur compounds, typically pyrites – 1-5%;

4) polluted water, in particular acid mine drainage, formed from the oxidation of sulphide minerals, resulting in the formation of acidic waters that can carry heavy metals into rivers, lakes and groundwater – 5-10%;

5) organic and other impurities – 1-3% [13], [17].

In addition, these wastes contain quite a significant amount of metal compounds, including heavy and rare-earth metals, and can serve as raw materials for their industrial extraction [18]-[21].

Coal dumps are easily self-igniting, resulting in prolonged burning. Inside the waste heaps, temperature can reach 1200°C, resulting in the emission of greenhouse gases and hazardous substances (sulphur oxides, nitrogen, carbon, hydrogen sulphide, ammonia, hydrocarbons, etc.) [12]. Water erosion washes away toxic substances, polluting soil and groundwater. Wind erosion spreads dust hundreds of kilometers, polluting the air. Thus, waste heaps lead to the degradation of natural landscapes in coal-mining regions, threaten human health and pose a risk of technogenic catastrophe. Thus, waste heaps lead to the degradation of natural landscapes in coal-mining regions, threaten human health and pose a risk of technogenic disaster [22]. Similar environmental challenges are also emphasized in studies devoted to underground coal gasification, where design and technological solutions significantly influence the intensity of gas release and the formation of thermal fields [23]-[25].

To date, these environmental problems have not been fully solved, therefore, research aimed at developing new and intensifying existing methods for the reclamation of coal waste heaps and the recycling of valuable components from them is extremely relevant.

The coal mining process generates a significant amount of waste that accumulates in mine dumps. Effective management of these dumps is crucial for sustainable development and environmental protection. Various methods for repurposing coal mine waste dumps have been explored and implemented, with the main objectives of reducing environmental impact and obtaining economic benefits. The main recycling methods include: mechanical, biological and physical-chemical technologies. Geotechnical use (land filling and reclamation). Backfilling involves the use of coal mine overburden material to fill underground mine cavities, reclaim land and create technogenic landscapes. This method stabilizes the soil, prevents subsidence and rehabilitates the land, reducing the environmental impact of mining operations [26]-[30].

A logical extension of the preceding method is the methods of environmental and ecosystem restoration. Reforestation and ecological restoration projects use coal mine waste dumps to create wildlife habitat and restore ecosystems. This approach prevents biodiversity loss and increases the resilience of natural landscapes. This also includes the use of soil in agriculture. Recycled coal mine waste can be used as a soil amendment to improve its quality and fertility [31].

Coal beneficiation waste is also used as structural materials in construction. Coal mine waste can be recycled into building materials such as bricks, tiles and aggregates for road construction. This not only conserves natural resources, but also reduces waste [32], [33]. The above-described methods localize waste and reduce its impact on the environment. But these methods fail to completely detoxify toxic components and extract useful components from waste.

Biological remediation is a promising method for decontamination of coal mining waste dumps: use of bacteria, fungi [34], [35], or plants (phytomining and phytoremediation). Phytomining involves the cultivation of hyperaccumulator plants that absorb heavy metals from the soil. These plants can then be harvested and processed to extract metals [36]. Phytoremediation focuses on using plants to stabilize or remove pollutants from the environment to neutralize and remove harmful substances from waste [37]. These methods are cost-effective and environmentally friendly as they use natural processes to remove and stabilize pollutants. They also have the added benefit of revegetating mine dump areas, contributing to landscape restoration. The main limitation is the relatively low concentration of metals that can be extracted, making the process suitable only for certain types of pollutants and specific economic conditions. Nor are these methods suitable for rapid remediation of waste dumps. In parallel, innovative concepts based on underground coal gasification are proposed as integrated technologies that combine waste utilization with energy recovery, providing both environmental and economic benefits [38], [39].

Conversion of coal mining waste into energy. Given that coal mining waste contains up to 30% of coal, it can serve as an unconventional energy source. A technologically feasible method to utilize it is the pyrolysis and coal gasification [40]-[43]. In general, pyrolysis is understood as high-temperature thermolysis of organic substances (wood, petroleum products, coal, peat, etc.) in the absence of oxygen or an oxygen-deficient atmosphere. In a narrower sense, pyrolysis (low-temperature pyrolysis) is the thermal decomposition of carbon-containing substances without air access at a temperature of 450-600°C with the formation of the target product – a mixture of carbon and ash (semi-coke), as well as associated liquid and gaseous products. The semi-coke obtained in the pyrolysis process can be marketed as a commercial product, but it is more expedient to use it as a raw material for high-temperature (800-1600°C) gasification to produce synthesis gas. Main advantages of turning coal mining waste into energy:

1) toxic substance neutralization: this method can be used to decompose hazardous organic compounds such as polycyclic aromatic hydrocarbons (PAH) found in waste dumps;

2) activated carbon production: solid residues after pyrolysis and partial gasification can be further processed to obtain activated carbon, which is used as an adsorbent;

3) conversion of semi-coke into synthetic gas (producer gas, “water gas”, etc.), the main components of which are carbon monoxide (CO) and hydrogen (H_2): it can be used as a raw material for chemical synthesis, as well as an efficient fuel for electricity generation, thereby reducing greenhouse gas emissions into the environment.

Coal gasification is recognized as a major technology for the clean use of coal, which has significant advantages in producing hydrogen-rich synthesis gas and reducing CO_2 emissions [44]-[47]. The properties of the raw material, in particular the coal grade, largely determine the thermodynamics and kinetics of the pyrolysis process. Therefore, it is important to understand how different types of coal behave during thermochemical processing to optimize process conditions and enhance the yield of valuable products. According to experimental research [48], bituminous coal and anthracite begin to decompose at higher temperatures (350-500°C), while brown coal decomposes at temperatures as low as 250-300°C. Research [49] has shown that heating to 600°C causes a change in coal structure. In [50], bituminous coal and brown coal were studied in the temperature range of 600-1100°C. The graphite-like microcrystalline carbon content (degree of orderliness) initially decreased from 600 to 900°C, and then increased with an increase in temperature to 1100°C. It has been found that the specific structure of coal also changes: with an increase in temperature (600-1100°C), the average pore size increases, and the content of functional groups ($C = O$, COOH) decreases. According to the results [51], during pyrolysis at 1000°C, the gas phase yield (H_2, CO, CH_4, CO_2) from brown and bituminous coal is significantly higher than from anthracite; the porosity and pore area are the largest in brown coal, which contributes to its gasification. Therefore, based on the analysis, it can be concluded that brown coal is best for obtaining volatile chemical products, bituminous coal is best for resins and medium-temperature coke, and anthracite is best for solid energy carrier and premium coke. In addition, in order to achieve high yield and the desired composition of the final materials, it is technologically expedient to select pyrolysis modes experimentally depending on the type of coal.

However, the use of pyrolysis technologies for the utilization of coal industry waste faces a number of challenges. The heterogeneous nature of waste can lead to inconsistent yield, variable quantitative and qualitative composition of processed products. In addition, the presence of pollutants such as heavy metals in the waste can hinder the pyrolysis process and produce hazardous by-products.

The use of two-stage schemes increases the efficiency and environmental friendliness of these processes, making them technologically feasible and economically attractive options for the utilization of industrial coal-containing waste. The first stage involves low-temperature pyrolysis (550-600°C) with the separation of volatile vapor-gas products and solid carbon-containing products. The vapor-gas mixture is fed to combustion to maintain the temperature regime, and the solid phase is fed to maintain gasification [44], [45], [53], [54]. This process organization makes it possible to extract the majority of harmful volatile impurities during pyrolysis process, oxidize them and utilize them [59]. The second stage receives a carbon-containing product, which, to a first approximation, can be considered as a mixture of coal and ash. The carbon content in the solid phase is determined by the composition of the raw material and the technological conditions of pyrolysis.

The choice of gasification agent (air, oxygen or water vapor) has a significant impact on the gasification process efficiency. The use of air reduces the calorific value of the resulting synthesis gas due to its high nitrogen content (about 79%), which, without reacting, only dilutes the gas mixture. On the other hand, water vapor gasification usually demonstrates better results compared to oxygen, since the latter oxidizes combustible components (H_2, CO), reducing their concentration and heat of gas combustion [51]. In turn, vapor stimulates the formation of these combustible gases, which positively affects both the qualitative composition of the synthesis gas and its energy value [53], [54].

The economic feasibility of implementing large tonnage pyrolysis technologies for coal industry waste management is still being studied, and current researches are focused on improving the efficiency and scalability of the process. In particular, there are no clear temperature parameters for conducting the process, which in the above-described studies vary significantly from 600 to 1600°C. Thus, pyrolysis and coal gasification is a promising method for sustainable coal mining waste management with potential environmental and economic benefits. However, further research is needed to address the technical and economic challenges associated with its implementation.

The technologies described above focus on extracting valuable minerals from waste dumps, reducing waste and mitigating environmental impact. All of which have their own advantages and disadvantages. The combination of these technologies will make it possible to recover residual coal, rare-earth elements and other valuable minerals from the waste dumps, turning waste into a resource [55]-[58].

Comprehensive reviews and experimental works underline that underground coal gasification remains one of the most effective integrated technologies for both energy generation and waste utilization, with promising prospects for climate neutrality and co-utilization of solid wastes [59]-[62].

In our opinion, a promising technology for mine waste utilization should provide for an integrated approach: at the first stage – low-temperature pyrolysis, at the second – conversion of coal into synthesis gas with maximum content of CO and H_2, at the third – extraction of valuable metals from the residue of pyrolysis and coal gasification processes [63], [64], with subsequent use of purified and stabilized rock in construction. In addition, it is imperative to provide for effective purification of gas emissions from pyrolysis and coal gasification [65], [66], as well as disposal of acidic drainage wastewater [67], [68]. An integrated approach to mine waste management fits well with the principles of a circular economy, where waste is minimized and resources are reused and recycled. The economic attractiveness of coal mining tailings processing is therefore enhanced by two advantages: natural resource recovery and environmental management [69], [70]. That is, reducing costs associated with waste management and creating additional sources of income [71].

To develop the scientific basis for the complex recycling of coal mining waste, it is expedient to perform thermodynamic calculations of the main chemical reactions occurring during the carbon conversion process. The data provided in the literature are incomplete; calculations are usually made for a limited number of reactions in a narrow range of temperatures and pressures and without theoretical substantiation of the technological process parameters [72]-[74].

Therefore, the purpose of this research is to study the thermodynamic patterns of the gasification process of coal mining waste and to form a theoretical basis for carbon conversion processes with the production of synthesis gas with a high hydrogen content. To achieve this purpose, it is necessary to solve the following objectives:

– assess the probable direction of the course of decisive carbon conversion processes, which will give an idea of the thermodynamic probability of gasification processes;

– determine the value of equilibrium constants of the main chemical reactions, which will serve as the basis for determining the equilibrium gas composition of the system;

– determine the influence of system parameters on the completeness of chemical transformations, in particular the influence of temperature on the equilibrium degree of coal gasification.

2. Materials and methods

The gasification process of coal-containing waste, as shown above, is complex and depends on many factors that are difficult to model mathematically. Therefore, thermodynamic calculations were performed for the ideal case, assuming that pure carbon undergoes high-temperature vapor gasification.

The carbon conversion process is described by a significant number of reactions, which significantly complicates its calculation and analysis. Therefore, the subject of research is the main endothermic reactions describing the processes of formation of fuel gases, hydrogen H_2 and CO (1)-(3) and the dynamic equilibrium between gas products (4), as well as exothermic reactions that can provide the energy needs of production (5)-(8). Theoretical research was conducted in the most interesting temperature range from a practical point of view – 500-1100°C and non-high pressures of 1-10 atm.

$$C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)}; \tag{1}$$

$$C_{(s)} + 2H_2O_{(g)} \leftrightarrow CO_{2(g)} + 2H_{2(g)}; \tag{2}$$

$$C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}; \tag{3}$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)}; \tag{4}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}; \tag{5}$$

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}; \tag{6}$$

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}; \tag{7}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}. \tag{8}$$

The formation of hydrocarbons, particularly methane, can be neglected because the conditions of high-temperature vapor gasification promote their decomposition. Reactions involving methane formation are exothermic $\Delta H < 0$ and proceed with a decrease in the volume of the gas phase:

$$CO_{(g)} + 3H_{2(g)} \leftrightarrow CH_{4(g)} + H_2O_{(g)}; \tag{9}$$

$$C_{(s)} + 2H_{2(g)} \leftrightarrow CH_{4(g)}. \tag{10}$$

Therefore, at high temperatures and low pressures, the equilibrium shifts to the left, that is, the CH_4 decomposition process proceeds.

The probable direction of the processes is assessed by changing the isobaric-isothermal potential (ΔG, Gibbs energy) of the system. Spontaneous flow of the process is possible only in the direction in which the Gibbs energy decreases ($\Delta G < 0$) under the condition of constant temperature and pressure (T = const, P = const).

Some of these processes are equilibrium processes, and therefore the equilibrium constant is an important quantitative characteristic for them. Equilibrium constant is the ratio of the product of reaction product concentrations to the product of concentrations of the initial substances. In this case, the concentrations of all reaction participants are written in exponents corresponding to the stoichiometric coefficients in the chemical process equation. For a conditional reaction that occurs in the gas phase:

$$aA + bB \Leftrightarrow dD + cC. \tag{11}$$

The equilibrium constant value can be written in terms of partial pressures:

$$K_p = \frac{p_D^d \cdot p_C^c}{p_A^a \cdot p_B^b}, \tag{12}$$

where:

p_A, p_B, p_D, p_C – the partial pressures of the corresponding gas participants of the reaction;

a, b, c, d – the stoichiometric coefficients in reaction equation.

The equilibrium constant is a very important value to characterize chemical equilibrium, as it:

– links the partial pressures of all reaction participants so that a change in at least one leads to a change in all the others, while the value of K_p remains unchanged;

– the equilibrium constant depends only on the nature of reacting substances;

– is a temperature function.

What is important is that by changing the concentration, or partial pressures of gases, the direction of reaction can be shifted in one side or another. For the studied C-H_2O-O_2-CO-CO_2 system, the equilibrium constant is a function of temperature only.

Knowing the value of the equilibrium constant is very important, as it allows us to calculate the concentrations of reacting substances in a state of equilibrium (equilibrium concentrations), product yield and the degree of conversion of the initial substances (Eq. (10)). The calculation of K_p is based on the laws of chemical thermodynamics. Thus, at constant pressure, K_p can be found based on the following dependence:

$$\Delta G = -RT \ln K_p, \tag{13}$$

where:

ΔG – the Gibbs energy variable;

R – the universal gas constant.

The depth of reactions during the research is expressed through the degree of conversion (X_A) – which is the fraction of the initial reagent that has entered the chemical reaction. It is determined by the ratio of the amount (mass) of the reagent (kg, kmol, etc.) that has entered the reaction to its initial amount (mass) ($m_{A\text{o}}$):

$$X_A = (m_{A\text{o}} - m_A) / m_{A\text{o}}, \tag{14}$$

where:

m_A – the amount (mass) of a reagent that did not enter into a chemical reaction.

For reversible reactions, an indicator such as the equilibrium degree of conversion (X_A^*) is used, which is equal to the ratio of the amount (mass) of the reagent converted before reaching the equilibrium state to the initial amount of this reagent:

$$X_A^* = (m_{A\text{o}} - m_A^*) / m_{A\text{o}}, \tag{15}$$

where:

m_A^* – the mass of unreacted reagent in a state of equilibrium.

To calculate the heat capacity of reacting substances (C_p) in the studied temperature range, the Kirchhoff equation is used in the following form:

$$C_p = a + bT + c' / T^2, \tag{16}$$

where:

T – the temperature, K;

a, b, c' – coefficients.

The values of the coefficients a, b and c' are taken from reference literature [75] and are given in Table 1.

Table 1. Thermodynamic values

Compound	ΔH_{298}, kJ/mol	ΔS_{298}, J/(mol·K)	Coefficients in the Kirchhoff equation		
			a	$b \cdot 10^3$	$c' \cdot 10^{-5}$
O_2	0	205.04	31.46	3.39	-3.77
H_2	0	130.52	27.28	3.26	0.50
CO	-110.53	197.55	28.41	4.10	-0.46
CO_2	-393.51	213.66	44.14	9.04	-8.54
H_2O	-241.81	188.72	30.00	10.71	0.33
C	0	5.74	17.15	4.27	-8.79

The enthalpy (ΔH_T) and entropy (ΔS_T) values for each substance at a certain temperature are calculated using the Equations:

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p dT ; \tag{17}$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^{T} \frac{\Delta C_p dT}{T} . \tag{18}$$

The values of thermal effects (ΔH) and entropy changes for reactions 1-8 in the studied temperature range are calculated for each temperature according to the Hess's law:

$$\Delta H = \sum H_{fin} - \sum H_{init}; \tag{19}$$

$$\Delta S = \sum S_{fin} - \sum S_{init}, \tag{20}$$

where:

$\sum H_{fin}$, $\sum H_{init}$, $\sum S_{fin}$, $\sum S_{init}$ – the sum of enthalpies and entropies of initial and final substances, respectively, that enter into chemical interaction.

The Gibbs energy value for each reaction in the studied temperature range is calculated using the Equation:

$$\Delta G = \Delta H - T\Delta S; \tag{21}$$

and the equilibrium constant by the formula derived from Equation (13):

$$K_p = e^{-\frac{\Delta G_T}{RT}} . \tag{22}$$

At a certain temperature, the equilibrium constant for each reaction is a constant value. Therefore, having the value of K_p, it is possible to calculate the amount of reacting substances at equilibrium moment, and from here – the equilibrium degree of conversion (Eq. (15)), which is maximal for these conditions. Formula (12) is used to calculate the degree of conversion (X^*, %). In this form, with four unknowns, the equation of the law of mass action cannot be solved. However, according to Dalton's law, the following ratio is confirmed for ideal gases:

$$p = N_i P = \frac{n_i}{\sum n_i} P , \tag{23}$$

where:

N_i – the i-th component mole fraction;

n_i – the i-th component substance amount, mole;

$\sum n_i$ – the total substance amount for all reaction participants, mole;

P – the total pressure in the system.

Substituting (22) into (12), obtain:

$$K_p = \frac{N_R^r N_S^s}{N_A^a N_B^b} P^{\Delta v} = K_N P^{\Delta v} , \tag{24}$$

where:

K_N – the equilibrium constant if the concentration of reacting substances is expressed in mole fractions, and in the case of gases – in volume fractions;

Δv – the sum of stoichiometric coefficients in reaction Equation (11):

$$\Delta v = r + s - a - b. \tag{25}$$

To solve Equation (24), the mole fractions of reaction mixture components are given through one unknown value using stoichiometric reaction Equation (11), that is, the mole fraction of each component in the equilibrium state is expressed through the mole fraction of any arbitrarily selected reaction component. This provides an opportunity to determine a functional dependence between the degree of conversion and the equilibrium constant.

The analysis and processing of the experimental results obtained were performed using standard Microsoft Office 365 programs. To derive mathematical dependences, the method of least squares was used with approximation of values by corresponding functions that most accurately describe these dependences. The equations and values of approximation probabilities (R^2) are shown in the figures.

3. Results and discussion

The influence of temperature on thermodynamic parameters of reactions (1)-(8) and equilibrium constants is shown in this section. Within the studied temperature range, for all endothermic equilibrium reactions (Eqs. (1)-(4)), the change in the Gibbs energy values (ΔG) and equilibrium constants (K_p) is typical: as the temperature increases, the Gibbs energy decreases and the equilibrium constant increases (Fig. 1).

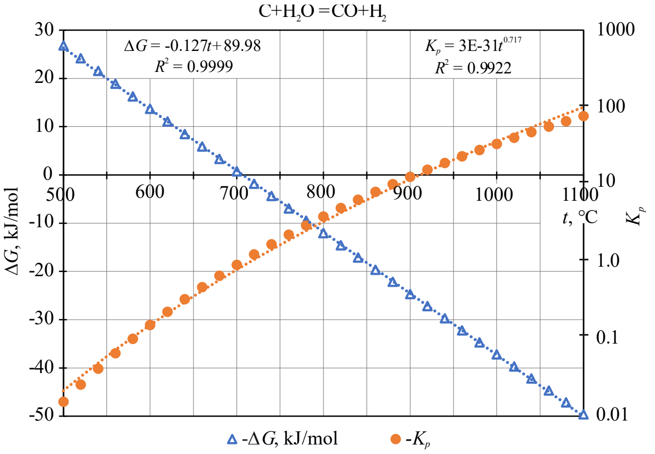

Figure 1. Dependence of thermodynamic parameters of the system $C + H_2O_{(g)} = CO + H_2$ on temperature (at temperature 707°C, $\Delta G = 0$, $K_p = \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}} = 1$)

At relatively low temperatures, the Gibbs energy value will be positive ($\Delta G > 0$), which means that the partial pressures of the final reaction products in the system are greater than they could be in the equilibrium state, and accordingly the reaction can only proceed in the opposite direction (from right to left). This is explained by the fact that the thermal effect of the reaction ΔH is positive and (3) orders of magnitude higher than the entropy value ΔS. That is, at low temperatures, the enthalpy factor has a decisive influence on the process (Eq. (21)). As the temperature increases, the influence of the entropy component $T\Delta S$ increases (Eq. (21)) and at a certain temperature value, $\Delta H = T\Delta S$.

Accordingly, at this temperature, $\Delta G = 0$, $K_p = 1$. That is, this is the "point of dynamic equilibrium" at which the rate of direct and reverse reactions is equal. The equilibrium temperature values for reactions (1)-(4) are in the range of 658-860°C (Table 2). At higher temperatures, the ΔG value becomes negative, and accordingly, the direct reaction rate increases and the equilibrium shifts to the right. All exothermic processes (Eqs. (5)-(8)) in the studied temperature range occur at very low negative values of ΔG (Fig. 2, Table 2), that is, the reaction equilibrium is almost completely shifted to the right.

Based on the value of ΔG, a conclusion is drawn about the direction and depth of the chemical process. If the value of $\Delta G < 0$, then based on Equation (22), it is possible to conclude that there is a high probability of thermodynamic feasibility of the process, since the value of the equilibrium constant in this case will be higher than 1. A positive value of ΔG indicates that $K_p < 1$. It should be noted, however, that these conclusions are only valid for the stoichiometric mixture. That is, if, for example, a gas mixture of stoichiometric composition containing one mole of H_2O, CO, H_2, is brought into contact with coal (Eq. (1)) at a temperature of < 707°C (Fig. 1, Table 2), then the reaction will occur in the direction to the left, that is, towards the consumption of CO and H_2 until a state of equilibrium is reached.

Table 2. Summary table of the dependence of C-H2O-O2-CO-CO2 system thermodynamic parameters on the temperature

No.	Equations	Parameters	t, °C							
			660	700	760	800	860	900	960	1000
1	$C + H_2O \leftrightarrow CO + H_2$, $T_{Eqs.} = 707°C$	ΔH, kJ/mol	132.4	132.0	131.6	131.2	130.7	130.4	129.8	129.5
		ΔS, J/mol	135.6	135.0	134.1	133.5	132.7	132.2	131.4	131.0
		ΔG, kJ/mol	5.9	0.7	-6.9	-12.0	-19.6	-24.7	-32.2	-37.2
2	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$, $T_{Eqs.} = 659°C$	ΔH, kJ/mol	97.4	97.4	97.5	97.5	97.5	97.5	97.5	97.4
		ΔS, J/mol	104.6	104.4	104.0	103.8	103.4	103.1	102.7	102.4
		ΔG, kJ/mol	-0.2	-4.1	-10.0	-13.8	-19.6	-23.4	-29.2	-32.9
3	$C + CO_2 \leftrightarrow 2CO$, $T_{Eqs.} = 737°C$	ΔH, kJ/mol	167.3	166.7	165.6	164.9	163.9	163.2	162.2	161.6
		ΔS, J/mol	166.5	165.5	164.1	163.3	162.0	161.3	160.2	159.5
		ΔG, kJ/mol	12.0	5.6	-3.9	-10.3	-19.7	-25.9	-35.3	-41.5
4	$CO_2 + H_2 \leftrightarrow CO + H_2O$ $T_{Eqs.} = 860°C$	ΔH, kJ/mol	35.0	34.6	34.1	33.7	33.2	32.9	32.4	32.1
		ΔS, J/mol	31.0	30.6	30.1	29.8	29.3	29.1	28.7	28.5
		ΔG, kJ/mol	6.1	4.9	3.0	1.8	0.0	-1.3	-3.1	-4.3
5	$C + O_2 \rightarrow CO_2$	ΔH, kJ/mol	-395.1	-395.3	-395.6	-395.7	-395.9	-396.0	-396.1	-396.2
		ΔS, J/mol	0.0	-0.3	-0.6	-0.8	-1.0	-1.1	-1.1	-1.1
		ΔG, kJ/mol	-395.1	-395.0	-394.9	-394.9	-394.8	-394.8	-394.8	-394.8
6	$2C + O_2 \rightarrow 2CO$	ΔH, kJ/mol	-227.8	-228.7	-230.0	-230.8	-232.0	-232.8	-233.9	-234.6
		ΔS, J/mol	166.5	165.3	163.5	162.4	161.0	160.2	159.1	158.4
		ΔG, kJ/mol	-3831	-389.5	-3989	-405.1	-414.5	-420.7	-430.0	-436.3
7	$2CO + O_2 \rightarrow 2CO_2$	ΔH, kJ/mol	-562.4	-562.0	-561.2	-560.7	-559.9	-559.3	-558.4	-557.7
		ΔS, J/mol	-166.5	-165.8	-164.8	-164.1	-163.1	-162.4	-161.3	-160.6
		ΔG, kJ/mol	-407.1	-400.6	-391.0	-384.6	-375.1	-368.8	-359.5	-353.3
8	$2H_2 + O_2 \rightarrow 2H_2O$	ΔH, kJ/mol	-492.5	-492.8	-493.1	-493.3	-493.5	-493.5	-493.6	-493.6
		ΔS, J/mol	-104.6	-104.7	-104.7	-104.6	-104.4	-104.2	-103.8	-103.5
		ΔG, kJ/mol	-394.9	-390.9	-385.0	-381.0	-375.2	-371.3	-365.6	-361.8

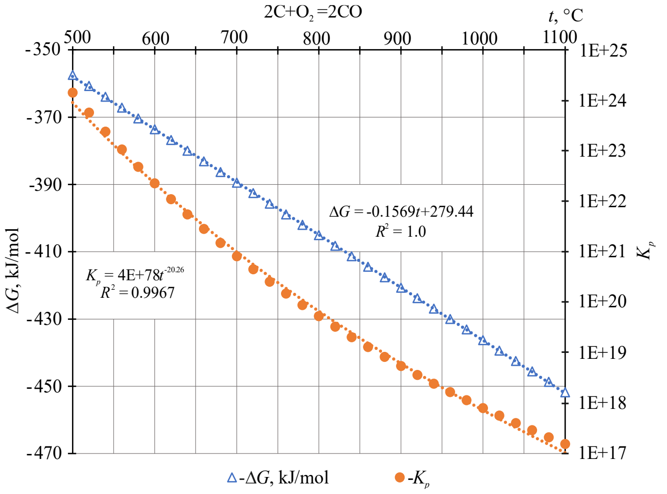

Figure 2. Dependence of thermodynamic parameters of the system $2C + O_2 = 2CO$ on temperature (in the entire studied temperature range $\Delta G < 0$, $K_p = \dfrac{P_{CO} \cdot P_{H_2}}{P_{H_2O}} = 1$)

However, if water vapor comes into contact with coal at the same temperature, the reaction will proceed to the right until equilibrium state is reached. Therefore, a positive value of ΔG indicates that the equilibrium constant of the studied reactions is less than unity, and not a fundamental impossibility of the process. Theoretically, a reaction with a positive ΔG value can be carried out to completion by constantly removing the resulting products from the reaction zone.

For all endothermic reactions (Eqs. (1)-(4)), the K_p value increases with increasing temperature (Fig. 3). The increment in the equilibrium constants of reactions (3) and (1) is particularly intense. At a temperature of 1000°C, their values are $K_{p3} = 50.32$ and $K_{p1} = 33.63$, respectively. An order of magnitude increase in the equilibrium constants for reactions (1)-(3) occurs in the temperature range of 860-890°C. That is, it can be argued that at temperatures of > 860°C, the content of inerts in the gas mixture (CO_2 and H_2O) will be minimal, and therefore the carbon conversion process is technologically feasible to conduct at temperatures above 860°C.

Reaction (4) (Fig. 3) characterizes a change in the equilibrium gas composition of a system formed in the process of carbon conversion.

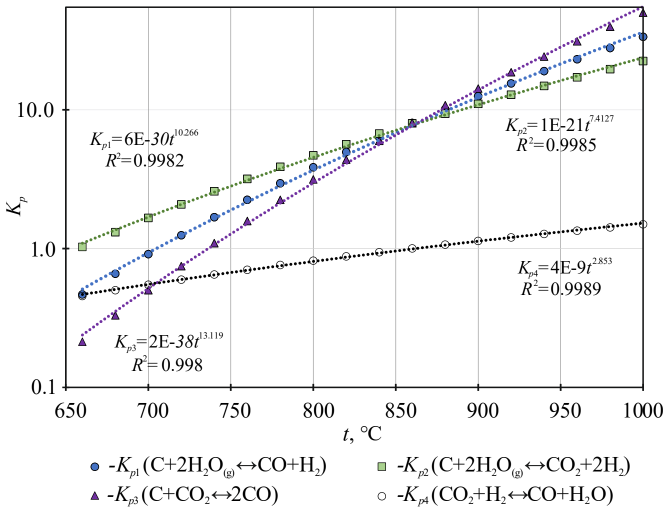

Figure 3. Dependence of equilibrium constants of endothermic reactions (K_p) on temperature

As the temperature increases, the CO content increases and the H_2 content decreases by an equivalent amount. CO has slightly better energy performance, since the low calorific values of CO and H_2 are 12.64 and 10.79 MJ/m³, respectively. However, under identical conditions, hydrogen has 14 times less mass and is a valuable raw material for chemical syntheses. In addition, the process of converting H_2 into CO requires additional energy inputs, which in practice are not compensated by the higher calorific value of CO due to heat losses to the environment. Consequently, this reaction has a decisive influence on the gas composition, but a negligible effect on its energy characteristics.

For all exothermic reactions (Eqs. (5)-(8)), the K_p value decreases with increasing temperature (Fig. 4).

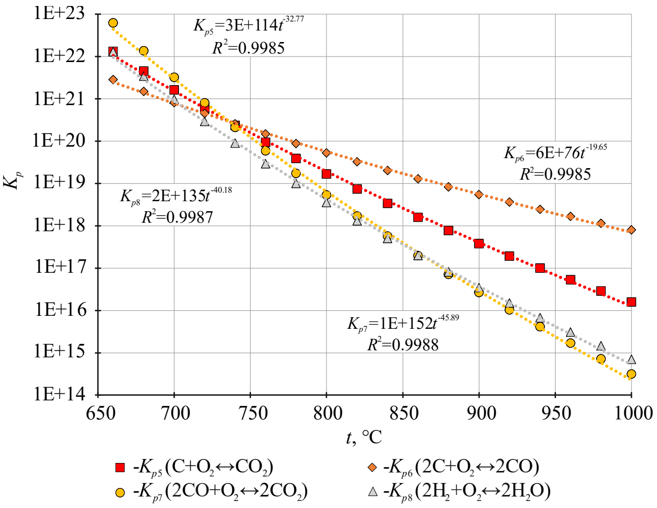

Figure 4. Dependence of equilibrium constants of exothermic reactions (K_p) on temperature

Therefore, from a practical point of view, when hydrogen is the target product of the carbon gasification process with water, it is necessary to conduct the process at the lowest possible temperatures to shift the equilibrium of reaction (4) (≤ 860°C). This can be achieved by using a catalyst, an excess of water vapor relative to stoichiometry, or by removing CO_2 from the reaction zone, in particular as a result of its sorption [76]-[78].

However, in the studied temperature range, the equilibrium constant values are very high and vary from $33.1 \cdot 10^{14}$ to $6.2 \cdot 10^{22}$ (record 3.1E+14 and 6.2E+22). That is, the reaction equilibrium is practically completely shifted to the right and in the entire studied temperature range there is a complete (100%) conversion of initial substances into reaction products. Such results are well consistent with theoretical concepts. The dependence of the equilibrium constant on temperature at constant pressure is determined by the Van't-Hoff isobar equation:

$$\frac{\Delta H}{RT^2} = \frac{d \ln K_p}{dT}, \tag{26}$$

where:

R – the gas constant.

From Equation (26) it follows that in the case of endothermic reactions ($\Delta H > 0$), the derivative always acquires positive values $\dfrac{d \ln K_p}{dT} > 0$.

Therefore, an increase in temperature leads to an increase in the value of K_p, that is, it has a positive effect on the endothermic process. For exothermic reactions ($\Delta H < 0$), the value of the derivative is negative, and therefore, an increase in temperature has a negative effect on the exothermic process.

For ease of practical use, the results obtained on the temperature influence on ΔG and K_p for the observed reactions were mathematically processed using the least squares method with approximation of the values corresponding to the functions. The approximation equation and coefficient of determination (R^2) are given in Table 3.

Table 3. Equation for calculating values ΔG and K_p

No.	Equations	Regression equation and coefficient of determination			
		ΔG, kJ/mol	R^2	K_p	R^2
1	$C + H_2O \leftrightarrow CO + H_2$	$\Delta G_1 = -0.127 \cdot t + 89.978$	0.9999	$K_{p1} = 2.551 \cdot 10^{-31} \cdot t^{10.717}$	0.9922
2	$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	$\Delta G_2 = -0.097 \cdot t + 63.606$	0.9999	$K_{p2} = 1.513 \cdot 10^{-22} \cdot t^{7.731}$	0.9932
3	$C + CO_2 \leftrightarrow 2CO$	$\Delta G_3 = -0.158 \cdot t + 116.350$	0.9999	$K_{p3} = 4.301 \cdot 10^{-40} \cdot t^{13.703}$	0.9914
4	$CO_2 + H_2 \leftrightarrow CO + H_2O$	$\Delta G_4 = -0.031 \cdot t + 26.372$	0.9999	$K_{p4} = 1.686 \cdot 10^{-09} \cdot t^{2.986}$	0.9960
5	$C + O_2 \rightarrow CO_2$	$\Delta G_5 = 0.001 \cdot t - 395.786$	0.9493	$K_{p5} = 9.976 \cdot 10^{117} \cdot t^{-33.961}$	0.9969
6	$2C + O_2 \rightarrow 2CO$	$\Delta G_6 = -0.157 \cdot t - 279.435$	1.0000	$K_{p6} = 4.291 \cdot 10^{78} \cdot t^{-20.258}$	0.9967
7	$2CO + O_2 \rightarrow 2CO_2$	$\Delta G_7 = 0.159 \cdot t - 512.136$	0.9998	$K_{p7} = 2.319 \cdot 10^{157} \cdot t^{-47.664}$	0.9980
8	$2H_2 + O_2 \rightarrow 2H_2O$	$\Delta G_8 = 0.098 \cdot t - 459.391$	0.9998	$K_{p8} = 6.594 \cdot 10^{139} \cdot t^{-41.693}$	0.9975

For carbon conversion reactions, the thermal effects of the reaction are almost temperature-independent (Fig. 5). The overall autothermicity of the coal gasification process can be achieved by a combination of endothermic (1)-(3) and exothermic (5)-(6) reactions.

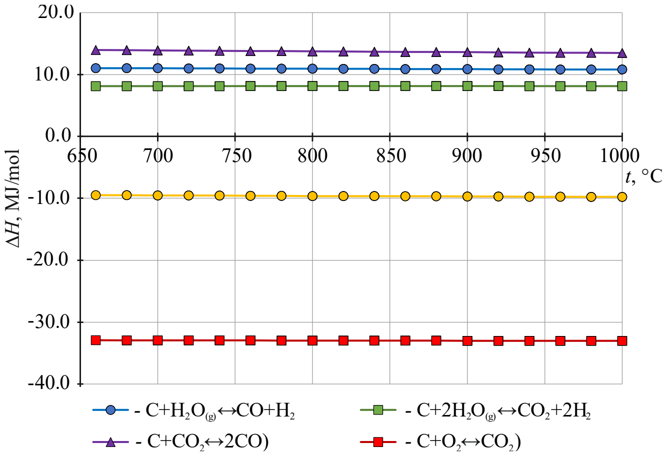

Figure 5. Dependence of thermal effect of reactions on temperature

To compensate for the heat of endothermic reactions, it is reasonable to use the heat of the exothermic reaction of incomplete carbon oxidation $2C + O_2 = 2CO$, since as a result of its occurrence, a combustible gas is formed – CO, in contrast to the complete oxidation reaction, where the product is an inert substance – CO_2. At the same time, to compensate for the endothermic decomposition of 1 kg of carbon by reaction (1), 1.10-1.16 kg of carbon should be oxidized by reaction (6) and only 0.33-0.34 kg of C by reaction (5). The main disadvantage of this approach is the dilution of conversion gases with an inert gas – nitrogen, which enters the process with oxygen from the air.

According to general concepts and the results of theoretical research, the determining reaction for the development of efficient coal gasification technology is the process described by Equation (1). As a result of its course, it is theoretically possible to obtain a synthesis gas consisting of 50% of CO and 50% of H_2. This product has the best consumer properties and energy performance. Provided that the reaction products (CO and H_2) are removed from the system, there will be an excess of coal and water vapor in the reactor, and therefore, according to Le Chatelier's principle, the process equilibrium will shift to the right. Under these conditions, the process (2) is unlikely to occur, since the reaction is trimolecular and occurs due to the interaction between one C molecule and two H_2O molecules, and reaction (3) is possible only in the presence of CO_2 in the system – the product of complete carbon oxidation.

The total pressure in the system will influence the depth of the process, that is, the equilibrium degree of carbon conversion (X^*). Therefore, the influence of pressure on X^* for the determining carbon conversion reaction $C + H_2O \leftrightarrow CO + H_2$ has been studied. The obtained results are presented in the graph (Fig. 6).

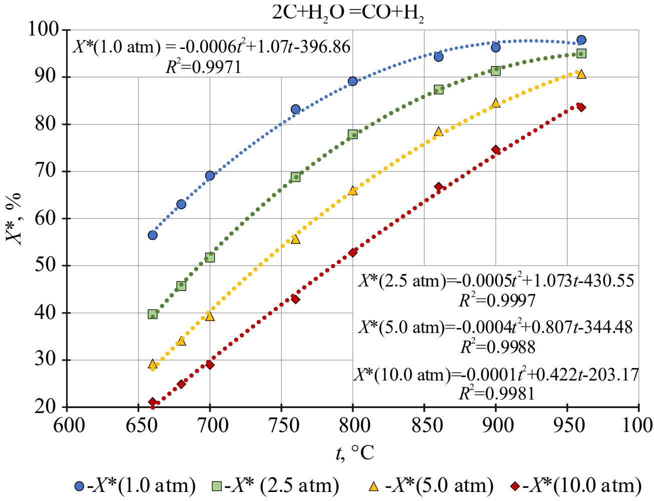

Figure 6. Dependence of the equilibrium conversion degree for the reaction $C + H_2O_{(g)} = CO + H_2$ on the total pressure in the system

In general, an increase in pressure has a negative effect on the equilibrium parameters of the carbon conversion process, which is in good agreement with Le Chatelier's principle. The influence of pressure on the equilibrium constant value is determined by the second Van't-Hoff equation:

$$\frac{d \ln K_N}{dP} = -\frac{\Delta V}{RT}, \tag{27}$$

where:

ΔV – the change in mole volume of the reaction mixture, in our case $\Delta V = 1$.

Analyzing the above-mentioned equation, it can be concluded that for reactions that occur with increasing gas volume ($\Delta V > 0$), the derivative ($d \ln K_N / dP$) is a negative value. That is, an increase in pressure will result in a decrease in K_N value and vice versa – for reactions that occur with a decrease in gas volume ($\Delta V < 0$), the derivative will be positive, that is, the equilibrium constant increases.

At the same time, it is not necessary to speak unambiguously about the negative influence of increased pressure, since the basis for theoretical research are thermodynamic calculations, which give an idea of the fundamental probability of processes, but do not give time frames, that is, an understanding of how long it takes to conduct the process to reach a certain depth of processing or equilibrium state. These questions are studied by chemical kinetics, and this will be the subject of further experimental research. In addition, technological and economic factors are also taken into account in real production processes, in particular, increased pressure makes it possible to reduce the volume of reaction apparatus.

4. Conclusions

Coal mine waste dumps pose a significant environmental problem due to their potential to pollute soil, water and air. Traditional approaches to managing these wastes often focus on their localization, but the principles of sustainable development require more innovative technologies. In particular, this research proposes an integrated approach to solve this problem, which is based on the process of gasification of coal residues from waste dumps with subsequent extraction of valuable metals, as well as the use of purified and stabilized rock in construction.

Based on thermodynamic calculations, it has been determined that the coal gasification process is advisable to be conducted at temperatures above 860°C, and to use water vapor as a coal oxidizer. To ensure the autothermicity of the process, heat losses can be compensated by the exothermicity of the reaction $2C + O_2 \rightarrow 2CO$. An increased pressure in the system has a negative impact on the equilibrium degree of carbon conversion, but at the same time it can be an intensifying factor when introducing the technology into production.

The obtained thermodynamic dependences, reflecting changes in Gibbs energy, equilibrium constants and conversion degree, make it possible to predict the composition of synthesis gas with a high content of hydrogen and carbon monoxide, form the scientific-theoretical basis for creating effective technologies for the integrated coal mining waste management, while complying with modern principles of sustainable development and rational nature management.

The prospect for further research is a comprehensive study of the processes of extracting rare and rare-earth elements from gasification and pyrolysis products, optimizing the conditions for their extraction and purification, as well as research into the possibilities of practical application of ash residues as secondary raw materials. The implementation of these measures will contribute to improving the efficiency of integrated waste management in coal mining, while providing additional environmental and economic benefits.

Author contributions

Conceptualization: NL, VP, PS; Formal analysis: NL, AH, OD; Funding acquisition: VP, PS; Investigation: NL; Methodology: NL, AH, OD; Project administration: VP; Resources: NL, AH; Supervision: AH, VP; Validation: NL, PS; Visualization: OD; Writing – original draft: NL, AH, PS, OD; Writing – review & editing: NL, VP. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

Author PS declared that he was an editorial board member of the Mining of Mineral Deposit journal at the time of submission. This had no impact on the peer review process and the final decision. The remaining authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Термодинамічні дослідження процесів газифікації відходів видобутку вугілля

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Мета. Дослідження термодинамічних закономірностей процесу газифікації відходів вуглевидобутку та формування теоретичного підґрунтя для процесів конверсії вуглецю з одержанням синтез-газу з високим вмістом водню.

Методика. Основою термодинамічних розрахунків є основні реакції конверсії вуглецю в діапазоні температур 500-1100°C та тисків 1-10 атм. Для оцінки ймовірності перебігу процесів визначали значення енергії Гіббса, констант рівно-ваги та рівноважного ступеня конверсії, що дозволило спрогнозувати склад газової фази та визначити оптимальні умови газифікації. Для апроксимації отриманих залежностей застосовано метод найменших квадратів.

Результати. Встановлено, що відвали відходів вуглевидобутку становлять значне джерело екологічної небезпеки, оскільки призводять до забруднення ґрунтів, водних ресурсів та атмосферного повітря. Традиційні методи їх утилізації зосереджуються переважно на локалізації, проте не забезпечують повної нейтралізації шкідливих компонентів. Проведені термодинамічні розрахунки підтвердили доцільність застосування процесу газифікації, який є ефективним за температур понад 860°C. Автотермічність цього процесу досягається за рахунок часткового окиснення вуглецю до оксиду вуглецю (CO), що дозволяє компенсувати теплові витрати. Встановлено, що підвищення тиску знижує рівноважний ступінь конверсії вуглецю. Отримані термодинамічні залежності дають змогу прогнозувати склад синтез-газу та, у подальшому, оцінювати перспективність впровадження технологій комплексної переробки відходів вуглевидобутку.

Наукова новизна. Вперше проведено комплексну термодинамічну оцінку реакцій газифікації відходів вуглевидобутку та отримано термодинамічні залежності зміни енергії Гіббса, констант рівноваги й рівноважного ступеня конверсії у широкому діапазоні температур та тисків, що дало змогу визначити оптимальні умови перебігу процесу та підтвердити його технологічну можливість при температурах понад 860°C.

Практична значимість. Результати дослідження формують теоретичне підґрунтя для створення ефективних технологій комплексної переробки відходів вуглевидобутку з отриманням синтез-газу, який може слугувати перспективним енергоносієм, забезпечуючи відповідність сучасним принципам сталого розвитку та раціонального природокористування.

Ключові слова: *відходи вуглевидобутку, газифікація, вугілля, піроліз, конверсія, синтез-газ, температура*

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