Research on the presence of coke oven gas in the chemical composition of Uzgen coal

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Annotation. One of the possible ways to use Kyrgyz coal, which is the subject of research in this work, is thermal processing for the production of coke, chemical coking products, gas and other products. To study KR coal, the process of high-temperature pyrolysis was used. The object of the study was coal from the Changet coal mine in the Uzgen region. The purpose of the research is to create a coke-chemical production; the composition of gaseous substances of high-quality coke gas from the Uzgen coal basin, the largest and most promising coal deposit basin in Kyrgyzstan, has been studied using the electrochemical method using gas analyzers. The result of the study showed that completely groups of chemical reactions occur in parallel; as a result of thermochemical changes, liquid gases and solid products are formed. The result of the research obtained shows that two main issues need to be resolved: assessing the quality of raw materials - providing an effective process for obtaining materials and target products. The peculiarity and scientific value of the results obtained during the study, the diversity of the structure and properties of coal strengthens the task of researchers to find ways to optimally use their energy potential, which in turn clarifies the area of scientific research aimed at coal processing processes for fuel and non-fuel purposes. The practical value of the study is that at 500-550°C the plastic mass of coal decomposes with the formation of primary products of gas and tar, consisting of paraffin and naphthene.

Key words: coke oven gas; gas analyzer; "Signal-4"; carbon monoxide; methane; hydrogen sulfide; nitrogen oxide; total hydrocarbons; indicator tubes; carbon dioxide; microanalysis; hydrogen;titrimetric.

1 Introduction

It is known that promising coal reserves in Kyrgyzstan are estimated at 25 billion tons. We know of 79 coal deposits, as well as areas where coal occurs. Of these, 24 deposits are included in the free balance sheet, 47 are in operation, and the remaining deposits are not being developed [1].

In the southern region of the Kyrgyz Republic, waste from coal deposits, in which up to 60% of pieces accumulate during processing, that is, substandard coal fines (deposits Sulukta, Kyzyl-Kiya, Almalyk, Kok-Zhangak, Tash-Komur, Uzgen, Alai group of deposits).

One of the possible ways to use coal from Kyrgyzstan is thermal processing to produce coke, chemical coking products, gas and other products [2].

For the creation of a coke-chemical industry, the largest and most promising coal deposit basin in Kyrgyzstan is the Uzgen coal basin. Because Uzgen coals are distinguished by their quality characteristics and can be used in the energy sector and metallurgy as raw materials. At the same time, in the chemical industry, a priority

direction for the development of coke chemistry in the Kyrgyz Republic may be the production of coke based on gas and other low-caking and non-caking coals of the Uzgen coal basin [3].

It has been established that coke obtained from a charge containing high-gas coals has a correspondingly increased reactivity, since it contains a small amount of anisotropic carbon, and the reactivity of coke is regulated using additives that increase the degree of softening of the coal mass during the transition to a plastic state [4].

The different structure of coals and different properties pose the task of researchers to find optimal ways to use the energy potential, which in turn determines the range of scientific research aimed at the process of processing coals for fuel and non-fuel purposes. In addition, any process development is based on theoretical knowledge, both about the process itself and about the raw materials undergoing processing, and some transformations that undergo at all stages of the process. Since the main tasks of theoretical research lead to the establishment of a connection between the structure and properties of coals, the identification of patterns of changes in the properties of coals and metamorphism, scientifically based interpretation of the results of physical and chemical studies of molecular and supramolecular structures based on modern ideas about the structure of matter and the formulation of chemical terms, which is decisive significance for the development of coal chemistry in general.

Coal science is intended to provide a scientific basis for coal processing processes to harness its energy and chemical potential, which can only be effectively realized based on a fundamental understanding of the structure and properties of coal. If the question is about what coal to use for a particular process or what products are appropriate to process this or that coal, then science assumes, from the standpoint of fundamental studies of structure and reactivity, the solution of two main problems: assessing the quality of raw materials and ensuring the efficiency and selectivity of the process with obtaining target products [5].

Currently, throughout the world, oil is the main source of organic raw materials, the limitation of its global reserves and the constant increase in the cost of production due to the involvement in the exploitation of hard-to-reach deposits, work on organizing new processes for the chemical processing of alternative organic raw materials. Coal, whose global reserves exceed those of oil and gas, can be considered in the future as one of the main types of raw materials for the production of motor fuels and organic synthesis products.

The increasing demand for fossil coal is accompanied by an increase in the environmental load on the environment, since the combustion and processing of coal produces harmful by-products than the by-products emitted by oil and gas.

The main disadvantages of the known technologies for the chemical processing of coal in comparison with oil refining and petrochemical technologies are the comparatively low productivity and difficult conditions for their implementation. To facilitate work in coal processing, catalysts and new catalytic processes are increasingly being used, which make it possible to obtain various products of fuel and chemical characteristics from coal [6].

Previously, most food products were used by pyrolysis and coking of coal. This process is based on heating coals without air access for the purpose of thermal destruction [7].

Such a process through the passage of all main groups leads to the following result: depolymerization of the organic mass of coal with the formation of detected molecules of molecular weight and ensures the implementation of secondary transformations that form products (condensation, polymerization, aromatization, alkylation, etc.). All two groups proceed in parallel, as a result of thermochemical transformations of liquid, gaseous and solid products [8].

Although it is known that this is one of the promising methods of coal processing, which is semi-coking in high-speed installations, which compare favorably in technical and economic indicators.

The main products of semi-coking of coals, tars and gas are good raw materials for obtaining a wide range of chemical products [9].

It is known that at temperatures from 500 to 600°C the hydrogen content increases and the CO_2 content decreases. The coal high-speed pyrolysis resin is a dark brown liquid.

In connection with the formulation of the problem - revealing the features of high-speed pyrolysis of coal, we examined the entire isolated material. With an increase in the process temperature from 600°C to 700°C, the yield of resin decreases, which significantly affects the yield of components: the content of phenols in the resin decreases, while an increase in the asphaltenes content is observed from 14% to 21% [10].

In laboratory conditions, in a furnace for pyrolysis of coal at a temperature of 500-600°C, processes were carried out with heating of coal without air access (Fig. 1).

By slowly and gradually heating components for physical and chemical transformations:
- up to 250°C, carbon monoxide and carbon dioxide are released and water evaporates;
- at a temperature of 300-350°C, tar vapors are released into the gas phase and pyrogenetic water is formed, and coal passes into a plastic state;

- at 500-550°C, the plastic mass of coal decomposes, forming primary products of gas and tar, which consist of paraffin, naphthenic unsaturated aromatic hydrocarbons, and the mass hardens, forming semi-coke, and such valuable products as volatile gas substances, coal resin, crude benzene, tar water, ammonia, etc.

2 Experimental part

In the study of the coal pyrolysis process in the Kyrgyz Republic, the high-temperature pyrolysis process is used. The object of study was coal from the Changet deposit in the Uzgen basin.

When studying the process of coal pyrolysis, it was necessary to use a special reactor (furnace) with a refrigerator, into which 1 kg of Changent coal was loaded and heated from 950 to 1000 ° C. The schematic diagram of a pyrogenetic installation looks
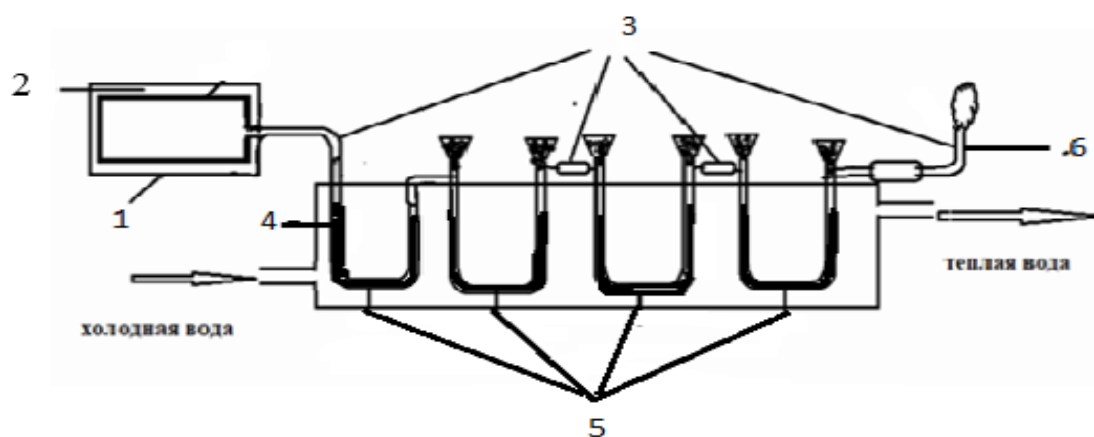like in Fig. 1.

Fig.1. Installation diagram for studying the coal coking process.
1-reactor, 2-thermopore, 3-steam gas line, 4-refrigerator, 5-sulfuric acid solution, pyrogenetic water, resin, 6-coke oven gas.

To study coke oven gas we used [11]:

1. Gas analyzer, "4M-SO_2 signal" for determining SO_2 and the amount of hydrocarbons.

2. Gas analyzer "Signal-4" for determining nitrogen oxide.

3. Gas analyzer "Signal-4" for determining carbon monoxide and methane.

The principle of operation and operation of the electrochemical gas analyzer in measuring the concentration (SO_2, $C1-C1_2$, CO, CH_4, CO) in the air is carried out in the device through the use of a sensor (SO_2, $C1-C1_2$, CO, - CH_4, NO). The conversion of the above substances in the air into an energy signal is carried out by an electrochemical cell of the type (SO_2/H_2O, Sixth sense eco-sune, NO/H_2) and the detected gases are adsorbed on the surface of the semiconductor sensitive element of the microprocessor and gives an intermittent sound signal and the electric display shows the content of the substance mg/ m^3.

1. Hydrogen sulfide content (H_2S)
   X_1=9.8 mg/m3.
   X_2=10.2 mg/m3. X_{av}=10 mg/ m^3.
   X_3=10.0 mg/m3.
2. Total hydrocarbon content (C1-C12)
   X_1=5.2 mg/m^3.
   X_2=4.9 mg/m^3. X_{av}=5.0 mg/ m^3.
   X_3=5.1 mg/ m^3.
3. Carbon monoxide (CO) content
   X_1=5.9 mg/ m^3.
   X_2=5.6 mg/ m^3. X_{av}=2.0 mg/ m^3.
   X_3=5.4 mg/ m^3.
4. Methane content (CH_4)

$X_1 = 25.0$ mg/ m³.
$X_2 = 24.8$ mg/ m³. $X_{av} = 25$ mg/ m³.
$X_3 = 25.2$ mg/ m³.

5. Nitric oxide (NO) content
$X_1 = 3.6$ mg/ m³.
$X_2 = 3.4$ mg/ m³. $X_{av} = 3.5$ mg/ m³.
$X_3 = 3.5$ mg/ m³.

6. Ammonia content in the absorption solution 1 mol/dm³, in a solution of sulfuric acid. The process of dissolving ammonia occurs according to the following reaction.

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + H_2O$$
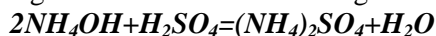
Add 2-3 drops of methyl orange (indicator) to the absorption solution under study. During the experiment, the ammonia yield was determined by the volume of a solution of a single sodium equivalent concentration (mol/dm³) used for titrating the absorption solution after extracting light, tarry, and oily substances from it.

The yield of ammonia (X1) in percent is calculated by the formula:

$$X_1 = \frac{(V - V_1) \cdot T \cdot 100}{m};$$ (1)

where: V - is the volume of sulfuric acid solution with a concentration equivalent to 0.1 mol/dm3 taken for the experiment, cm³;

V_1 - volume of alkali solution with a concentration equivalent to 0.1 mol/dm³, consumed for titration of excess sulfuric acid, which did not react, cm³;

T - is the titer of a sulfuric acid solution with a concentration equivalent to 0.1 mol/dm³, expressed as ammonia 2 cm³;

m - mass of coal sample.

Substituting the obtained data in formula (1), we have:

$$X_1 = \frac{(V - V_1) \cdot T \cdot 100}{m} = \frac{10 - 9,79 \cdot 0,960 \cdot 1000}{20} = 10,08\%$$ (2)

Determination of coke oven gas content using indicator tubes (express analysis).

Let's open the CO_2 indicator tube from both cones using the hole in the head of the sampling pump/aspirator, observing the direction of air pumping (indicated by the arrow on the surface of the indicator tube). We pump the volume of air required according to the instructions through the indicator tube, making the required number of swings with the sampler pump/aspirator.

Note the change in color and the length of the column of the reacted filler after pumping. We calculate the concentration of carbon dioxide on a scale (C_1% vol) marked on the indicator tube or by attaching it to the corresponding scale inside the package. If the boundary between the colors of the layers of the original and reacted indicator mass is blurred, we take the average value as the measurement result. Let's recalculate the CO_2

concentration from volume % mg/m³ using the formula: $C_2 = \dfrac{C_1 * M * 10^4}{22,4}$

where: C_1 - gas concentration in volume %;

C_2 – gas concentration in mg/m³;

M – molar mass of carbon dioxide (M=44);

10^4-conversion factor from volume % to mg/m³

$$C_2 = \frac{0,01 \times 44 \times 10^4}{22,4} = \frac{45,76}{22,4} = 2\%$$

The principles for the quantitative determination of carbon and hydrogen were developed by Liebig. Such methods have been preserved to this day. However, at the moment, microanalysis based on the same principles,

13

which was founded by F. Pregl, is more often used. Microanalysis requires 50 times less substance and is performed three times faster.

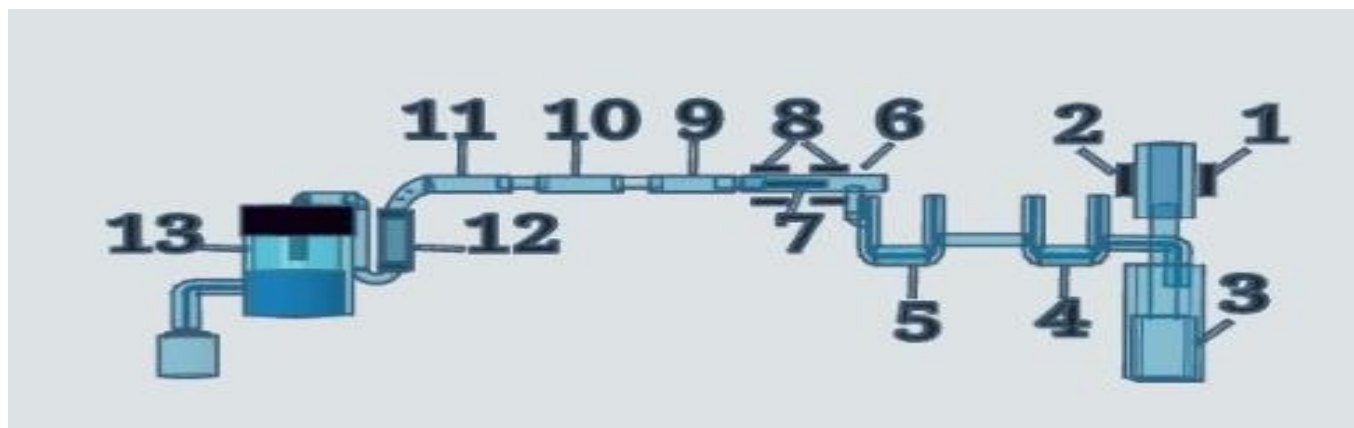The device for micro determination of carbon and hydrogen is shown in Fig. 2

Fig.2 1-nisel contact; 2.8-electric furnace; 3- coil;

4,5-absorbers; 6-tube for burning; 7-cup; 9-absorbent apparatus for water; 10-absorption apparatus for nitrogen oxides; 11-absorption apparatus for CO2; 12-final trumpet; 13-apirator.

After weighing 3-5 mg in a long narrow quartz glass (7) with an accuracy of 0.002 mg, pour it into a quartz tube 6 for combustion and, with the electric furnace 8 turned on (900°C), let it pass slowly for 3 minutes (35-50 ml/min) pass a flow of oxygen purified from hydrogen, water and CO2. Oxygen is purified from hydrogen and organic impurities by passing through a nickel contact heated to 800°C. Rough separation of the resulting water is carried out by condensation in coil 3, complete purification from water and CO2 absorbers H and S, each of which is filled with anhydrous magnesium perchlorate (anhydrone) and ascarite (asbestos impregnated with molten caustic soda) so that anhydrone is the first and the last filler and the path of gas passage. The combustion tube is connected to two series-connected absorbers, 9 for water and 11 for CO2, weighed on similar scales. The first absorber is filled with anhydrone (anhydrous magnesium perchlorate), and the second with ascarite. These tubes are weighed and attached immediately before burning. To regulate the pressure in the system, a Migunov aspirator is used. The burning process takes 10 minutes. It begins by piercing the open end of the combustion tube, in which a quartz beaker with a hanger is placed. After burning is completed, 2-3 minutes. The absorption apparatus is blown through with air, removed and weighed on analytical materials using the usual precautions. The weight gain of the first absorber corresponds to the amount of water from which the hydrogen content in a sample of the substance is calculated; the weight gain of the second absorber gives the amount of carbon dioxide, from which the carbon content in a sample of the substance is calculated. Calculations are carried out according to the formula:

To calculate we use the conversion factor where

1) $$fc = \frac{c}{CO_2} = \frac{12}{44} = 0{,}2729$$

2) $$\%C = \frac{fc \cdot \text{weight}\,CO_2 \cdot 100}{\text{coal weight}} = \frac{0{,}2729 \cdot 0{,}8 \cdot 10}{10} = 2{,}1\%$$

3) $$f\text{н} = \frac{H_2}{H_2O} = \frac{2}{18} = 0{,}1119$$

4) $$\%H_2 = \frac{fH \cdot \text{weight}\,H_2O \cdot 100}{\text{coal weight}} = \frac{0{,}1119 \cdot 35{,}7 \cdot 100}{10} = 39{,}9\%$$

3 Obtained experimental results

№	Research methods	Name of coke oven gas, % mg/m^3							
		Oxide carbon	Methane	Dioxide carbon	Hydrogen sulfide	Nitric oxide	Total hydrocarbons	Ammonia	Hydrogen
1	Electrochemical	5,6	25	-	10	3,5	5	-	-
2	Titrimetric	-	-	-	-	-	-	10	-
3	Express analysis (with inticator tube)	-	-	2	-	-	-	-	-
4	Microanalysis	-	-	2,1	-	-	-	-	39,9

Table 1. Results of experimental work.

4 Conclusion

1. The chemical composition of coke oven gas has been studied:

a) Electrochemical method, using a gas analyzer "Signal-4", "Signal-4", "Signal-4M SO$_2$ " the content of gaseous substances was studied: CO-5,6% mg/m^3, CH$_4$-25% mg/m^3, H$_2$S-10% mg/m^3, NO- $3,5 \cdot 10$ % mg/m^3, C$_1$-C$_{12}$-5% mg/m^3;

b) The titrimetic (chemical) method was used to study the ammonia content of 10% in the composition of coke oven gas;

c) Express analysis (with indicator tube) investigated CO_2-2% mg/m^3 in coke oven gas;

d) The contents were studied using the microanalytic method CO_2-2,1% mg/m^3, и H_2-39,9 % mg/m^3.

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