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# THERMODYNAMIC ANALYSIS OF THE PROCESS OF FORMATION OF SULFUR COMPOUNDS IN OXYGEN GASIFICATION OF COAL

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*A thermodynamic approach to the description of the behavior of the system fuel–oxidizer in oxygen gasification of coal is used to reveal the main mechanisms of the process of capture of sulfur by the mineral part of the coal and to determine the fundamental possibility of the process for coals from different coal fields.*

To design an environmentally nonpolluting thermal power plant (TPP) operating on solid fuel means to fulfill a number of requirements for the basic parameters: emission of nitrogen and sulfur oxides, effluent of fly ash, heat pollution of the environment, sewage disposal, and ash dumps. Practically all these parameters of a combined thermal power plant with intracyclic gasification of the fuel are better than the analogous parameters of a conventional coal-burning power plant [1].

The latest developments in the field of gasification of a solid fuel concern the use of an oxygen blast, a pulverized fuel, an increased pressure, a high-temperature regime, etc. [2]. The performance of the process at high temperatures allows one to remove the restrictions on the fuel quality, since in a vapor-oxygen medium in the region of temperatures of the order of 1800 K all hydrocarbons of the fuel turn to carbon oxides, hydrogen, and steam.

One of the directions in the work on the creation of "clean" coal technologies with previous gasification of the coal is the use of atmospheric-pressure gasification facilities [1]. In order to realize such a scheme on a thermal power plant, it is necessary to equip it with domestic devices that can be modified as needed, which decreases the cost of their introduction and maintenance. On the other hand, the energy efficiency of such power units is somewhat lower as compared to the power units in which high-pressure gasification facilities are used. The content of sulfur in power-generating coals varies from fractions of a percent to 10% of the dry ash-free mass [3]. In the process of oxygen gasification of coal, the main amount of the fuel sulfur is converted to the gas phase with the formation of $H_2S$ and small amounts of COS, $CS_2$, and $SO_2$. In this case, a large portion of the volatile sulfur can be bound by the alkali components of the ash, which is a powerful tool for decreasing the emission of sulfur compounds to the atmosphere [4]. The level of binding of sulfur by the ash is especially high for Kansk-Achinsk coals in which the number of calcium and magnesium compounds is larger by a factor of four than the stoichiometric ratio required for binding of sulfur [5]. Among the methods of mathematical modeling of such processes, of great importance are methods of thermodynamic analysis which allow one to perform a high-quality estimation of the efficiency of the sulfur redistribution between the gas and the condensed phases under different conditions of the process. In the present work, the thermodynamic approach to the description of the behavior of sulfur compounds in oxygen gasification of a solid fuel is used to reveal the main mechanisms of capture of sulfur by the mineral part of the fuel and determine the fundamental possibility of the process for different coals.

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1. Sulfur is contained in coals as sulfates, sulfides, and organic sulfur. Sulfate sulfur is presented for the most part by gypsum ($CaSO_4{\cdot}H_2O$). Sulfide sulfur occurs in the form of iron pyrite – iron disulfide $FeS_2$. The latter naturally has two forms of the crystal structure. Of them, pyrite (cubic structure) occurs more frequently in nature. At temperatures higher than 900 K, pyrite decomposes into FeS and S in the mineral part of the fuel. As the temperature increases further, FeS decomposes into Fe and S. In an oxidizing medium, Fe and S are oxidized to $Fe_2O_3$ and $SO_2$. In the case of an oxygen deficit, pyrite sulfur reacts with hydrogen and steam to form $H_2S$.

The behavior of organic sulfur is closely related to the breakdown of the organic mass of a coal at high temperatures. Recent models of the structure of the organic mass of a coal consider it as an ensemble of condensed aromatic, hydroaromatic, and heterocyclic structures (clusters) containing different functional groups (OH, COOH, $CH_3$, HS, and others) as substitutes, which are linked to each other by different bridge bonds [6]. As the coal particles are rapidly heated, the bonds connecting the functional groups to the ring clusters break with the formation of volatile gas components ($H_2O$, $CO_2$, $CH_4$, $H_2S$, and others). At the same time, the bridge structure of the coal breaks down to form large molecular fragments (of a resin). As a result of the breakdown of hydroaromatic structures, a great number of H atoms (donor hydrogen) appear. These atoms are used to stabilize free radicals formed in separation of the functional groups from the ring clusters. As the temperature increases further, the breakdown and regrouping of the aromatic and heterocyclic structures occur, and these processes are accompanied by the graphitization of the carbon residue and the release of $H_2$ from the aromatic hydrogen, $CS_2$ from thiophenes, and HCN from the ring nitrogen. Interaction of the main gas components ($O_2$, $CO_2$, and $H_2O$) with the carbon of the carbon residue in the process of gasification of the latter leads to the total release of sulfur from the heterocyclic structures of the organic mass of the fuel.

In the process of conversion of pyrite sulfur and the radicals of the functional group HS into the gas phase, prior to their stabilization to $H_2S$ molecules by the donor hydrogen, these active components can react with the carbon residue to form stable thiophene structures. The results of experimental investigations show [7] that when small pyrite crystals (of size 20 μm) embedded in the organic mass of the fuel break down, practically the entire amount of sulfur released in heating is absorbed by the carbon lattice. This points to the fact that in the process of gasification of coal, conversion of both pyrite sulfur and organic sulfur to the gas phase can be performed in several steps with partial transformation of the most volatile components to thermally more stable heterocyclic (thiophene) compounds.

As has been mentioned above, one of the advantages of the high-temperature gasification of a solid fuel is a practically total conversion of the organic mass of the fuel to the gas components. On the other hand, at temperatures of the order of 1800 K, the ash of the majority of coals is in the liquid state, which can lead to the envelopment of the particles of the nonreacted fuel by an ash film and the termination of the supply of a gasifying agent to it [2]. This decreases the gasification efficiency because of the increase in the unburned carbon. At the same time, the organic sulfur of the heterocyclic structures is confined in the coke particles, which increases the degree of binding of sulfur by the carbon-ash residue. As is shown in [8], in high-temperature gasification of coal, up to 80% of the sulfur of the carbon-ash residue can belong to the thiophene structures of the carbon lattice. By contrast, the liquid-phase state of the mineral part of the fuel slows down the process of binding of the gas-phase sulfur compounds, formed as a result of the release of volatile components, by the alkali ash components. These problems concern the purely kinetic features of the process and cannot be taken into account in its thermodynamic investigation.

The high content of sulfur compounds in gasification products deteriorates the environmental characteristics of the process. Recent systems for purification of a gas from $H_2S$ operate at temperatures lower than 600 K, which leads to energy losses in cooling of the gas. One of the effective ways of improving the efficiency of the process is the high-temperature (1100–1400 K) desulfurization of the gas by sorbents based on limestone and other natural materials [9].

TABLE 1. Composition and Enthalpy of the Combustion Products of Berezovskii Coal

| Component | $N_j$ (mole/kg of coal) | $h_j$ (kJ/mole) |
|---|---|---|
| $H_2O$ | 6.66104 | –241.814 |
| $SiO_2$ | 0.527259 | –910.700 |
| $Al_2O_3$ | 0.113926 | –1657.70 |
| $Fe_2O_3$ | 0.0595145 | –823.001 |
| CaO | 0.790879 | –635.090 |
| MgO | 0.157204 | –601.500 |
| $K_2O$ | 0.0134507 | –361.700 |
| $Na_2O$ | 0.0136337 | –414.570 |
| $SO_2$ | 0.0717405 | –296.810 |
| $CO_2$ | 45.7747 | –393.510 |
| $H_2O$ | 18.8014 | –241.814 |
| $N_2$ | 0.192764 | 0.0 |
| $O_2$ | – | 0.0 |

2. The thermodynamic analysis allows one to determine many characteristics of the process in the thermodynamic-equilibrium state, including the chemical composition of the multicomponent heterogeneous system, enthalpy, entropy, heat capacity, etc., although, as has been mentioned above, the kinetics of the process can be of primary importance in actual practice. In the present work, to find the thermodynamic characteristics of the high-temperature chemical transformation of coal in its oxygen gasification we used the TETRAN program complex [10] designed for automated calculation of the chemical composition, the thermodynamic properties, and the properties of the transfer of multiphase systems as applied to the products of combustion or conversion of organic fuels in the range of temperatures from 300 to 6000 K and pressures of up to 1000 atm. A distinguishing feature of the complex is direct calculation of heterogeneous systems without a previous analysis of the possibility of appearance of condensable materials.

As an example of the thermodynamic analysis of the process of formation of sulfur components in oxygen gasification of coal, we consider Berezovskii brown coal of the Kansk-Achinsk field, which has an increased ash content. The initial composition of the coal on a working-mass basis was taken to be as follows (%): $W$ = 12.00, $A$ = 10.56, C = 54.98, H = 3.79, O = 17.90, S = 0.23, and N = 0.54, where $W$ is the humidity and $A$ is the ash content. The composition of the mineral part was as follows: $SiO_2$ = 30.0, $Al_2O_3$ = 11.0, $Fe_2O_3$ = 9.0, CaO = 42.0, MgO = 6.0, $K_2O$ = 1.2, and $Na_2O$ = 0.8. The calculations were made in a two-phase approximation where all the condensed materials were presented in the form of an ideal solution of components in equilibrium with an ideal gas.

In calculating, we took into account 307 components, including 107 condensed components. The sulfur compounds in the gas phase are presented by the following components: S, $S_2$, $S_3$, SO, $SO_2$, $SO_3$, $S_2O$, COS, CS, $CS_2$, and $H_2S$. The condensed phase contains $CaSO_4$, $MgSO_4$, $K_2SO_4$, $Na_2SO_4$, CaS, MgS, SiS, $SiS_2$, FeS, and $FeS_2$. Numerical solution of the system of chemical equilibrium equations was carried out by the Newton method with the orientation of the system to a linearly independent basis of components maximum (dominant) with respect to the content using the matrix representation of the components' composition. The operation of the TETRAN program complex is provided by the initial thermodynamic data bank, which includes the larger part of the IVTANTERMO-85 bank of thermodynamic properties of individual materials [11], the data for a number of materials from the JANAF reference book [12], and some other data on condensed materials.

The process of oxygen gasification of coal can be considered as a process of combustion of a fuel with a low excess-oxidizer coefficient $\alpha$ determined as the ratio of the oxidizer mass to the oxidizer mass required for stoichiometric burning of the fuel. In this case, such notions as the combustion temperature $T$

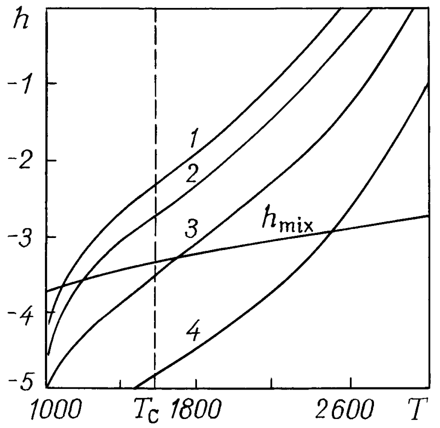


Fig. 1. Enthalpy of the oxygen–coal mixture vs. temperature $T$ with the mass ratio $m_O/m_C$: 1) 0.45; 2) 0.5; 3) 0.6, and 4) 0.8 for Berezovskii coal at $p = 0.1$ MPa. $h$, MJ/kg; $T$, K.

and the degree of conversion of the fuel sulfur to the gas phase $S_g/S$ can be used. The choice of the regime of the process is based on the consideration that a synthesis gas with a high yield of CO and $H_2$ should be produced.

The theoretical temperature of combustion $T$ was calculated on condition that in a closed adiabatic chemically reacting system at constant pressure the enthalpy of the system $h$ does not change during the process. In this case, at the temperature $T$ the enthalpy of the combustion products $h(T)$ is equal to the initial enthalpy of the fuel mixed with the oxidizer $h_{mix}$. For the quantity $h_{mix}$ we have

$$h_{mix} = [m_O h_O(298) + m_C h_C(298)]/(m_O + m_C)\,,$$

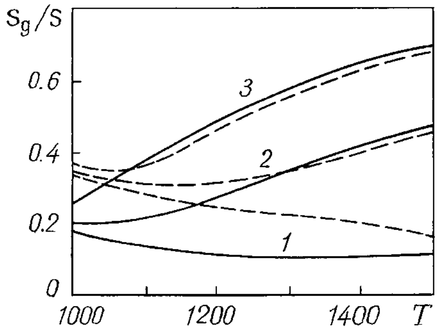
$$h_C(298) = \sum_j N_j h_j(298) + Q_i^r\,,$$

$$Q_i^r = Q_i^{daf}(100 - W_t^r - A^r)/100 - 24.4W_t^r\,,$$

where $h_O(298)$ and $h_C(298)$ are the enthalpies of oxygen and coal at $T = 298$ K. For the coal under consideration, $Q_i^{daf} = 26{,}460$ kJ/kg [3]; $N_j$ and $h_j$ are given in Table 1.

Figure 1 shows the results of calculating the enthalpy $h = h(T)$ of the products of oxygen gasification of Berezovskii coal for different values of the mass ratio $m_O/m_C$. The points of intersection of the calculated curves andh the lines $h_{mix} = h_{mix}(m_O/m_C)$ correspond to the theoretical values of the temperature $T$ of the process. It should be noted that, in general, the temperature of the process is not a constant value. For example, in oxygen gasification in a concurrent gas flow, it can reach a value of the order of 2500 K at the initial stage of the process and decrease to 1500 K at the exit from the reactor due to the endothermy of the reactions of interaction of $CO_2$ and $H_2O$ with the carbon residue [8]. It is also seen from Fig. 1 that for coal the temperature of the Berezovskii liquid-melt state of the ash is $T_C = 1580$ K [3].

3. Figure 2 shows the results of calculating the sulfur distribution between the gas and the condensed phases for Berezovskii coal for different temperatures and mass ratios $m_O/m_C$. The calculation was made in the temperature range from 1000 to 1500 K in which the coal ash is in the solid state. For this temperature interval, no difficulties concerning a decrease in the efficiency of heterogeneous chemical reactions in transition of the mineral part of the fuel to a liquid state arise. In this case, the results of the thermodynamic calculations describe the real characteristics of the process quite accurately in the appropriately chosen time interval which provides completeness of the chemical reactions.



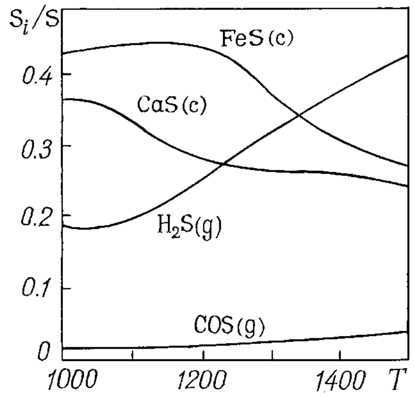


Fig. 2. Content of sulfur in the gas phase in oxygen gasification of Berezovskii coal. The mass ratio is $m_O/m_C$ = 0.45 (1); 0.50 (2), and 0.60 (3). The pressure in the system is $p$ = 0.1 MPa (solid lines) and 1 (dashed lines).

Fig. 3. Distribution of sulfur between the gas (g) and condensed (c) components in oxygen gasification of Berezovskii coal. The mass ratio is $m_O/m_C$ = 0.6. The pressure is $p$ = 0.1 MPa.

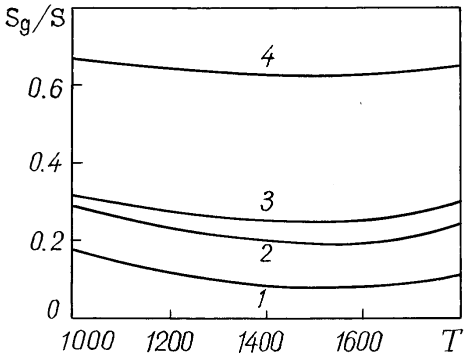


Fig. 4. Content of sulfur in the gas phase in oxygen gasification of Berezovskii (1), Kuznetsk (2), Pechera (3), and near-Moscow (4) coals. The ratio $m_O/m_C$ has been chosen to be stoichiometric for oxygen gasification of each coal. The pressure is $p$ = 0.1 MPa.

As is seen from Fig. 2, the degree of conversion of the fuel sulfur into the gas phase increases with increase in $T$ and the parameter $m_O/m_C$. On the other hand, for oxygen gasification of the given coal (the excess-oxidizer coefficient $\alpha = 0.283$) at a temperature of 1200–1500 K, a decrease in this parameter to the stoichiometric value 0.45 leads to the binding of 90% of the sulfur by the condensed components. An increase in the pressure in the system to 10 atm at temperatures of the order of 1000 K increases somewhat the degree of conversion of S into the gas phase.

Figure 3 shows the distribution of sulfur between the components of the system for Berezovskii coal. It is seen that $H_2S$ and COS are the main components in the gas phase and CaS and FeS are the main components in the condensed phase; the importance of the latter compound increases with decrease in the temperature. It should be noted that under oxygen-deficiency conditions where practically the entire amount of $O_2$ is used in gasification of the carbon residue, sulfur oxides are not formed in the gas phase. As the ratio $m_O/m_C$ increases to values of the order of unity, $SO_2$ becomes the main component containing sulfur.

Thus, the results of the thermodynamic analysis of the process of oxygen gasification of Berezovskii coal at temperatures lower than the temperature of the liquid-melt state $T_C$ show that in order that sulfur be

TABLE 2. Characteristics of the Coals under Study

| Index | Coal | | | |
|---|---|---|---|---|
| | Near-Moscow | Pechera | Kuznetsk | Berezovskii |
| *Composition of the coal, %* | | | | |
| $W$ | 7.5 | 2.5 | 1.8 | 12.0 |
| $A$ | 34.3 | 31.3 | 19.6 | 10.5 |
| C | 39.0 | 55.7 | 70.3 | 55.0 |
| H | 3.0 | 3.4 | 3.0 | 3.8 |
| O | 11.8 | 4.4 | 3.1 | 18.0 |
| S | 3.6 | 1.1 | 0.5 | 0.2 |
| N | 0.8 | 1.6 | 1.7 | 0.5 |
| *Composition of the ash, %* | | | | |
| $SiO_2$ | 48.2 | 62.6 | 55.4 | 30.0 |
| $Al_2O_3$ | 35.6 | 19.4 | 25.4 | 11.0 |
| $Fe_2O_3$ | 9.6 | 8.6 | 7.2 | 9.0 |
| CaO | 4.1 | 3.0 | 4.6 | 42.0 |
| MgO | 0.7 | 2.3 | 1.9 | 6.0 |
| $K_2O$ | 0.7 | 2.1 | 1.9 | 1.2 |
| $Na_2O$ | 0.3 | 1.0 | 0.7 | 0.8 |
| $TiO_2$ | 0.8 | 1.0 | 1.0 | 0.0 |
| $Q_i^{daf}$, MJ/kg | 25.33 | 33.49 | 34.0 | 26.46 |
| $T_C$, K | 1770 | 1630 | 1680 | 1580 |

effectively bound by the mineral part of the fuel, it is necessary to perform the process at a minimum possible value of the ratio $m_O/m_C$. If the remaining necessary conditions (a fairly high rate of binding, the total conversion of the carbon of the carbon residue, and others) are fulfilled, these conditions make it possible to decrease significantly the content of sulfur compounds in the gas phase.

4. Berezovskii coal is characterized by a small content of sulfur and a large amount of Ca and Fe in the mineral part. A different picture is observed for other coals. In particular, the sulfur content in near-Moscow coal is higher than that of Berezovskii coal by more than an order of magnitude, and the amount of Ca in the mineral part is small. Figure 4 shows the results of calculating the degree of conversion of the fuel sulfur to the gas phase for coals from different coal fields in Russia: near-Moscow (averaged over the field), Pechera (Vorkuta coal), Kuznetsk (lean coal of deep mining), and Berezovskii (brown coal) coals. The characteristics of the coals under study are presented in Table 2. The calculations were made for an $m_O/m_C$ ratio equal to the stoichiometric ratio for the process of oxygen gasification of a given coal: 0.45 for Berezovskii, 0.89 for Kuznetsk, 0.68 for Pechora, and 0.34 for near-Moscow coal.

Analysis of the calculation results shows that the higher the content of sulfur in the coal, the higher the degree of its conversion to the gas phase for a fairly wide range of variation of the ash content of the coal (see Table 2). For near-Moscow coal, the value of $S_g/S$ exceeds 60%. For such coals, one way of decreasing the degree of conversion of sulfur to the gas phase is performing the process of gasification for their mixture with a coal containing a large amount of Ca in the mineral part.

## NOTATION

$W$, humidity; $A$, ash content; $\alpha$, excess-oxidizer coefficient; $T$, temperature of the process; $T_C$, temperature of the liquid-melt state of the ash; $p$, pressure in the system; S, total sulfur content in the system;

$S_g$, sulfur content in the gas phase; $h$, enthalpy; $m$, mass; $N$, number of moles; $Q_i^r$, lowest combustion heat in the working state of the fuel; $W_t^r$, total humidity in the working state of the fuel; $A^r$, ash content in the working state of the fuel. Subscripts: O, oxygen, C, coal; mix, mixture; $j$, number of a component of the system.

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