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MECHANISMS OF GAS-COAL THERMAL PREPARATION IN ELECTROMAGNETIC FIELD

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Abstract. The article deals with the structure of low-metamorphosed coal vitrain macromolecules. The mechanism of thermal preparation in gas coal electromagnetic field is shown.

Keywords: macromolecule, chemical bonds, polarization, mechanism, hydrogenation.

1. Introduction

The present-day notions of the model of coal matters structure are various. However, it is accepted to consider as common the model of statistically average vitrain macromolecule structure as one of the main microelements of low-metamorphosed black coal [1]. This model of structure was presented by V. Fuks-D. Van-Krevelene. The macromolecule structure gives an ability to consider it as a condensed aromatic system, *i.e.* as a ring surrounded with molecules connected to it by chemical bonds [2].

Condensed aromatic ring is thermally stable as it has strong chemical bonds C_{ar}–C_{ar} (dissociation energy 836.0 kJ/mol). The bonds such as C_{ar}–H (dissociation energy 425.7 kJ/mol) are also thermally stable. Therefore, carbon bonds in the aromatic ring, and also with hydrogen atoms which are situated in the periphery, are quite strong, so they are the most stable fragments in the macromolecule [3].

Ether oxygenated and sulfur-containing bonds of bridge type C–O–C and C–S–C in macromolecule are weakened and dissipation of a molecule into components will occur by these bonds. Thus, all kinds of thermal treatment and chemical transformations of the organic vitrain matters in low-metamorphosed coal will proceed by detaching of side chains (hydrogen- and oxygen-containing) in the area of their connection with the ring (Fig. 1), dissipation of a macromolecule into components

through ether bonds, and further interaction between all formed radicals and a ring particle.
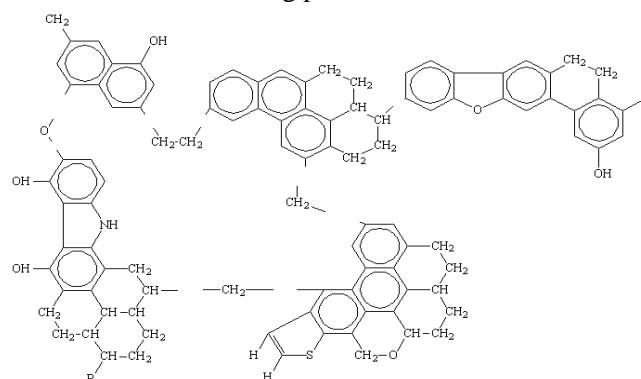

Fig. 1. A variant of dissipation of vitrain macromolecule in low-metamorphosed coal which undergoes thermal treatment

Since the article [4] deals with thermal pretreatment of low-metamorphosed low-caking coal using high-frequency electromagnetic energy as heating agent, it is necessary to consider the way in which conversion of energy into heat happens.

2. Results and Discussion

Coal heating as well as dielectric materials heating by using electromagnetic field of high frequency as heat carrier, is based on the polarization effect [5]. In its turn polarization contributes to occurrence of oscillating, pulsing, and rotary movement in electric dipoles, charges, and electrons. If particles in dielectric are linked hard enough the forces seeking to return the charges displaced by electric field to the starting position have quasi-elastic character. The occurring displacements are usually insignificant and this kind of polarization is called elastic or deformational.

In case of deformational polarization particles displacement occurs almost inertiallessly (elastically) and heat evolution in dielectric will not occur as energy is not spent for particles displacement [6].

If in the coal macromolecule structure there are side radicals, which have weak bonds with condensed aromatic ring [3] the process of polarization will show their thermal movement. Side radicals cover some distance under the influence of electric field by means of thermal energy during displacement. The system comes back (relaxes) to a starting position more slowly ($\tau_p = 10^{-10}-10^{-6}$ s), when there is no field due to disorienting influence of thermal movement, comparatively with elastic polarization ($\tau_p = 10^{-17}-10^{-12}$ s). Such kind of polarization is called thermal (relaxation polarization) [6].

The relaxation (delayed) types of polarization in the process of coal matters heating occur in gaseous, liquid, and solid phase, as they consist of polar molecules, dipoles, or molecules, which have separate radicals or parts (segments) with their own electric moments appertain.

The process of relaxation polarization is settled by placing a coal sample in a high-frequency electromagnetic field. As coal macromolecule is a complex bonded structure the result of increasing common energetic system state is opening of ether and weakened bonds. Oxygen- and hydrogen-containing bonds split out from the main condensed ring part of macromolecule and as a result take on the properties of radicals and turn into active separate molecular-kinetic units [7]. Therefore, newly-formed active centres take on the properties of separate bonds that means different influence of electromagnetic energy on them.

There are several types of relaxation polarizations: the dipole relaxation, the ion relaxation, the electron relaxation, and the interlayer polarization.

The dipole relaxation polarized substances are the ones with an asymmetrical structure of molecules (H_2O, CO, SO_2, *etc.*). The molecules of these substances are polar since they have a permanent dipole moment in the absence of an external electric field and are oriented under its influence.

When the external field is discharged, the polarization disappears and molecules regain to their original position. Due to the rubbing of molecules their rotational motion contributes to generation of heat. The relaxation time of the dipole relaxation polarization is $10^{-10}-10^{-4}$ s.

The ion relaxation polarization ($\tau_p = 10^{-8}-10^{-4}$ s) is observed in the mineral part of the coal substance [7] and inherent in the compounds with ionic bonds. Being under the influence of an applied electric field, weakly bound ions among the random thermal motion get an excessive movement in the direction of the field, and shifted in a distance substantially greater than the value of the ions displacement from the elastic ionic polarization. After the disappearance of the external field, ions are slowly returning to the balance centers. At the same time, the irreversible dissipation of energy in form of heat is observed.

The electronic-relaxation polarization ($\tau_p = 10^{-7}-10^{-2}$ s) is typical of molecules with a symmetric structure (methane, benzene, paraffin) and radicals formed as a result of bond opening with the free valences, *i.e.* the compounds that are able to trap electrons. In the absence of an electric field these trapped electrons can move from one position to another under the influence of thermal vibrations. In an external electric field such conversions will be accomplished mainly in the direction of the field and in the volume of coal substance electric dipole moment is induced, *i.e.*, the thermal electron polarization occurs.

The migration polarization arises because of the heterogeneity of the structure with macroscopic irregularities and the presence of mineral impurities. The reasons for its occurrence are conductive and semi-conductive inclusions and the presence of layers of different conductivity. In general, the process of migration polarization is similar to ion relaxation polarization ($\tau_p = 10^{-5}-10^{-4}$ s), with the difference that the movement of the charge occurs at much greater distance.

It follows from the preceding that the heat emission in the volume of coal particle which has been placed in a high-frequency electromagnetic field is connected with the rotation of dipoles, ionic and electronic oscillating (vibrational) motion, causing the dissipation of energy spent on the polarization of the dielectric in the form of heat. Therefore, as a result of volumetric heating temperature of the inner portion of the carbon grain will be slightly higher than the outer one.

Using the scheme of pyrogenetic conversion of coal into coke [3], proposed by N. Gryaznov, it can be assereted that the changes in carbon grain are characterized by phases G1, S1, and L1, which correspond to the temperature of 623 K. Nevertheless, the surface of coal is unchanged and the coal particle integrity is not disturbed.

In connection with this, the mechanism of the thermal preparation of metamorphic low-caking coal using high-frequency electromagnetic energy as heat carrier can be divided into two main stages:

I – from the start of heating to 423 K. The process is accompanied by detachment of the oxygen- and hydrogen-containing compounds to the places of their links with the condensed aromatic bars – deep drying;

II – from 423 to 523 K. The collapse of the macromolecule into the links by ester bonds – the thermal preparation.

As a result of the coal macromolecule splitting by the weak bonds active radicals are formed, which undergo the relaxation polarization with converting high-frequency electromagnetic energy to the heat. Rising of the temperature will promote the removing of moisture, containing in the coal.

Due to the fact that the coal is heated comprehensively during the high-frequency processing the movement of heat flows from the center to the periphery is unidirectional with the movement of moisture [8], thus providing favorable conditions for the hydrothermal conductivity (Fig. 2). The steam pressure, which grows inside the particle, is also promoting the moisture removal since it reduces the total pressure from the inside to the outside.
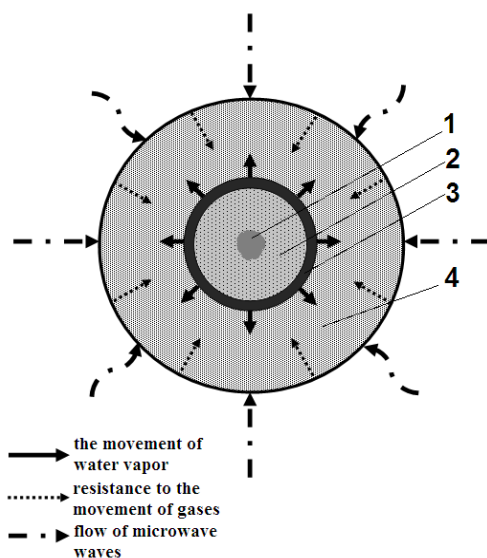

the movement of water vapor

resistance to the movement of gases

flow of microwave waves

Fig. 2. The influence mechanism of the high-frequency electromagnetic energy on the coal particle in the process of the thermal preparation: mesophase (the formation of amorphous carbon) (1); liquid-plastic mass (2); the condensation zone of tarry substances in microcracks and pores in the coal particles (3) and input coal material (4)

The thermal preparation stage is characterized by a significant change in the properties of the prepared coal (Fig. 2). Since the heat in this period largely occurs at the expense of the electron relaxation, migration, and ion relaxation polarizations, the emission of low molecular weight gases (CO_2, O_2, N_2) takes place. The gap of hydrogen bonds promotes the forming of organic complex compounds (free radicals) that can significantly affect the properties of the organic mass, as well as contribute to the formation of free (atomic) hydrogen. Naphthenic compounds may serve as donors for hydrogen because of dehydrogenation, which leads to the formation of stable aromatic compounds [9, 10].

The resulting free radicals are molecular fragments of aromatic, aliphatic, and naphthenic nature. In an effort to stabilize the atoms may rearrange within the molecular fragments, condensing or attaching atomic hydrogen to them.

While the temperature of thermal preparation is approximately 473–523 K, in the inside of the coal particles at high-frequency heating it can reach the temperature of about 573–623 K. As a result, liquid-plastic and steam products are formed in the center of the particle.

Internal wetting liquid products are characterized by solid work of adhesion [11]:

$$W_A = S_{S-G} + S_{L-G} + S_{L-S}$$

where S_{S-G} – the surface energy at the interface between the solid-gas; S_{L-G} – the surface energy at the liquid-gas; S_{L-S} – the surface energy at the liquid-solid body.

The value of the work of adhesion characterizes the full range of intermolecular and interatomic interactions occurring at the contact boundary between liquid-plastic mass and solid carbon.

The value of the contact angle (θ) is a measure of liquid-plastic mass wetting and coal solid phase surface wettability. The dependence of θ on the work of adhesion and surface energy of the liquid follows from the formula [11]:

$$\cos q = \frac{W_A - S_{L-G}}{S_{L-G}}$$

Mechanical filling of the pores and micro cracks is described by the equation which characterizes the rate of impregnation for a single capillary [11]:

$$L = \sqrt{\frac{S_{L-G} \cdot \cos q \cdot r \cdot t}{a \cdot h}}$$

where L – length of the wetting layer, m; r – the effective radius of the capillary, m; η – viscosity of the plastic mass, N·s/m^2; τ – time, h.

The formulas give insight into the factors affecting the rate and terms of the processes of the solid phase surface wetting by liquid products. The better the liquid products moisten the hard surface and the lower their viscosity, the more effective the impregnation processes. Impregnation rate increases with increasing temperature since the viscosity of the plastic mass largely depends on the temperature.

While reaching higher temperatures in the center of the coal particle the process is accompanied by the formation of mesophase, *i.e.* an increase in liquid-plastic mass liquidity increases the relative orientation of planar aromatic molecules, which combine into blocks and form solid products.

Formation of liquid-plastic mass occurs with the release of steam and gas products. Consequently, the gas emitted from the coal tends from the center of coal particle to its periphery. This creates an internal gas pressure, the interfacial solid-gas promotes primary tar compounds condensing in the pores and micro cracks (which include naphthalene, phenanthrene, indene, fluorene, and others) thereby forming a diffusion layer (Fig. 2).

3. Conclusions

As a result, during caking coals microwave pre-treatment the whole complex of reactions takes place, involving the rupture of carbon bonds and joining of the formed hydrogen atoms to them (so-called partial hydrogenation) [12-14]. The pressure of the gases inside the coal particle promotes the process [15].

It is in the process of the steam and gas products movement that redistribution and connection of the atomic hydrogen from free gas phase takes place. During this hydrogen redistribution free radicals formed are blocked by it, which favors the emergence of low molecular weight plasticizing agents, which are capable of moving in a plastic state.

Thus, thermal preparation of low-metamorphosed caking coals using high-frequency electromagnetic energy allows reaching more profound changes in the intermolecular organic matter of coal. While the process of partial hydrogenation practically does not affect the appearance of the coal particles, it dramatically affects their thermoplastic characteristics and strength properties. Therefore, such non-standard way of pre-heating allows modifying gas caking coals on their genetic level [4].

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МЕХАНІЗМ ТЕРМІЧНОЇ ПІДГОТОВКИ ГАЗОВОГО ВУГІЛЛЯ В ЕЛЕКТРОМАГНІТНОМУ ПОЛІ

Анотація. *Розглянуто будову макромолекули вітрену малометаморфізованого вугілля. Наведено механізм термічної підготовки в електромагнітному полі газового вугілля.*

Ключові слова: *макромолекула, хімічні зв'язки, поляризація, механізм, гідрування.*