

PAPER • OPEN ACCESS

Modeling of pyrolysis process of high-moisture coals

To cite this article: M. V. Pyatygina *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **288** 012112

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the **collection** - download the first chapter of every title for free.

Modeling of pyrolysis process of high-moisture coals

M. V. Pyatygina, A. A. Galkeeva, G. R. Mingaleeva

Kazan State Power Engineering University, Russia, Kazan, Krasnoselskaya Str., 51

pmv_83@mail.ru, prujinka1990@mail.ru, mingaleeva-gr@mail.ru

Abstract. The research is aimed at solving the fundamental scientific task of creating scientific fundamentals, deep processing of hydrocarbon raw materials (preliminary gasification, conversion, pyrolysis of solid minerals and renewable combustible resources) to produce liquid and gaseous fuels and a total increase in efficiency.

Modern lines of research in the field of thermal processing of solid fuels

In order to create efficient technological schemes and productions from the point of view of energy and resource saving, as well as increasing efficiency through the integrated use of the obtained products of processing hydrocarbon fuels, it is necessary to investigate the physico-chemical processes of decomposition of the organic mass of solid fuels, which depend to a large extent on its structure, range of temperatures, the stages of decay of compounds that make up the organic mass of raw materials and the assessment of the effect of these or other intermediate substances on the final quality and quantitative composition of the products obtained.

Investigation of the physicochemical basis for the deep processing of hydrocarbon raw materials will allow to create a methodology for calculating the technological schemes that realize these processes and to increase the energy efficiency of hydrocarbon processing.

Thermal and thermochemical processing of organic fuels is realized through such processes as gasification, pyrolysis (coking and semi-coking), hydropyrolysis, hydrogenolysis and others.

The phase and elemental compositions of brown coal and peat are studied with a wide application of such complex analysis methods as X-ray diffractometry, X-ray fluorescence and ICP-MS spectrometry supplemented with thermal gravimetry, elemental analysis of organic matter (OB) and scanning electron microscopy, Fourier transform, extraction organic solvents of different polarity, cryoscopy [1, 2]. In [3, 4], the authors noted the effect of the coal composition on structural parameters such as the presence of oxygen-containing groups, the hydrogen content in coal, and the results of thermal studies of coal and the effect of such methods of its processing as alkylation, solubility and mechanical activation on thermal degradation of coal.

Based on the obtained model of the average statistical unit (CCE) using different density and basis functionals and additional study of different CCE, calculation of IR spectra, total energy values and reactivity parameters, allowing comparison with experimental data [5, 6], the author compared on the structural characteristics of the 3D model of the so-called CCE organic mass of coal (OMC) $C_{29}H_{28}O_2$ with the molecular model of coal $C_{100}H_{79}O_7NS$. Thus, a volumetric molecular model of coal was obtained, which describes in more detail the structure of real coal, and takes into account, in contrast to the CCE OMC model, the presence in coal of such chemical elements as nitrogen and sulfur. The author also noted that, in spite of the lack of complete coincidence in the elemental composition with any of the technical coal grades given, the concentration of chemical elements in the 3D model of



$C_{100}H_{79}O_7NS$ is within the limits typical for coal, and as a result, this model in terms of structural composition best corresponds to the known experimental data for coals.

The authors of the research [7] present mathematical dependencies between the indicators characterizing the electronic and molecular structure of the organic mass of solid fuels of the series: wood - peat - brown coal - coal - anthracite. These equations are a theoretical tool for studying the processes of deep processing of solid fuels. The electronic structure of coals largely determines the variety of their properties and reactivity, as well as the features of the mechanisms of various reactions. It is shown that the parameters characterizing the electronic structure of coals have a close relationship with their molecular structure.

Confirmation of the dependence of the yield of polycyclic aromatic hydrocarbons (PAH) and phenol on the structure of coal was obtained by the authors of [8] when investigating the yield of two organic compounds (PAH and phenols) liberated during the pyrolysis of coals of various classes. So PAHs are formed not only by thermal destruction of the coal structure, but also by the combination of various low-molecular compounds with each other.

According to the author of the paper [9], in order to understand the mechanism of transformations of the organic mass of coals (OMC) and to assess the changes in their properties during the modification, an analysis of the initial stages of destruction, the most informative by the methodology of nonisothermal kinetics, which allows controlling the process from the initial stages to deep OMC conversions. The author studied the influence of methods based on the principles of chemistry of extreme effects (plasma chemistry, mechanoactivation, radiolysis, supercritical extraction, etc.) on the fuel structure change, and models of structural fragments of the investigated coals were constructed.

Thus, to date, a sufficient amount of experimental data on the composition of fuels obtained by various methods of physical and chemical analysis has been accumulated in order to obtain volumetric models of the molecular structure of fuels, as well as to find mathematical relationships between the initial fuel composition and the resulting products as a result of its pretreatment and further deep processing. Experimental data obtained by methods such as Raman spectrometry, thermogravimetry, gas-liquid chromatography, etc., are used as a basis for modeling and isolating groups of compounds, and for the mathematical description it is proposed to use numerical methods of quantum chemistry that allow obtaining a three-dimensional model of a specific fuel and structural parameters of the incoming in its composition of compounds.

The model of distributed activation energy, used for the pyrolysis of a number of materials (including coal, biomass, residual oils and kerogen), considered in [10], suggests that the thermal decomposition of numerous components is described by the distribution of activation energies.

In [11], the authors investigated the process of low-temperature pyrolysis using the Raman spectroscopy method. The change in the composition curves of different types of fuel after the pyrolysis process in a given temperature range is shown.

The author's work [12] is the closest to the concept of research. It shows a scheme for the usual pyrolysis of coal with the possible use of intermediate products. Optimal models of coal structure are considered, in the form of structural fragments and in the form of blocks of molecules of certain groups of compounds. The mechanism of pyrolysis from the point of view of molecular composition is explained. The kinetic parameters of the coal decomposition process are given, and the curves of the dependence on the process temperature are constructed. It is indicated the selection of the main products by temperature ranges.

On the basis of the analysis of the methods for studying decomposition processes of solid fuels for energy production and various chemical products, it can be concluded that attention is not sufficiently paid to the study of the chemical nature of the mechanism for the formation of groups of compounds, since the data are given only with respect to the influence of various components on the yield of the final product and general methods for calculating associated models of evaporation and combustion.

At the present stage of research in this field, not only the physicochemical aspects of thermal decomposition of hydrocarbons are revealed, but attempts are also being made to describe the mathematical and create the appropriate calculation methods.

Thus, the enthalpy of dissociation of the homolytic bonds of various bonds (CH, CC, CO and OH) for model coal compounds, which are characteristics of the functional components present in coal, were calculated in [13] using the numerical method of quantum chemistry of the two-hybrid method mPW2PLYP. The authors confirm the hypothesis of splitting the bonds of CO and CC with the formation of phenoxy radicals or benzyl radicals at the stage of initiation of coal pyrolysis.

A mathematical model based on the equations of chemical thermodynamics, which make it possible to calculate the composition of combustion products under conditions of a non-optimal fuel-oxidizer ratio, and the computational method for determining the composition of the fuel in the combustion process, were proposed in [14].

On the basis of the thermodynamic analysis of the efficiency of the use of various types of fuel and the calculation of the thermal efficiency, useful work, and the introduction of a fuel energy utilization factor, the authors of [15] obtained a result showing that low-calorie fuels, from the point of view of thermodynamics, are much more effective at steam turbine power plants, than high-calorie.

Modeling of the process of pyrolysis of water-coal suspension (WCS)

Analysis of the current state of scientific research in the field of thermal processing of hydrocarbon fuels shows that any raw material containing organic substances can be studied by the same methods as for solid fuel, since the structure also contains the basic elements - carbon and hydrogen. The difference will be only in the set of decomposition reactions and the applied regime parameters.

The physicochemical regularities of pyrolysis of water-coal suspensions of the most widespread brown coal - Irsha-Borodinsky, having the following composition: $W^r=33\%$; $A^r=9,98\%$; $S^r=0,29\%$; $C^r=41,2\%$; $H^r=2,89\%$; $N^r=0,6\%$; $O^r=12,1\%$. The ratio of water to fuel: 40% - water, 60% - coal.

Pyrolysis of water-coal suspension

The principal difference between the construction of the thermal decomposition model of the water-coal suspension is that the reaction of water vapor with organic compounds of coal containing oxygen, nitrogen and sulfur is considered. According to the WCS decomposition model, moisture is first released, then products (moisture, volatile components, coke residue) are released from the WCS with a dried membrane. From the coke residue with further heating, coke is released, loose products from the heating surface, mono- and carbon dioxide.

Further, the possibility of decomposition reactions of these compounds was calculated on the basis of Gibbs energy values taking into account the bond breaking energy:

a) Primary disintegration:

Oxygen-containing: $E = 230 \text{ kJ} / \text{mole}$ - decomposition of acid carboxylic with the release of benzene, phenol, derivatives of toluene, naphthalene, and oxide carbon and water (collateral);

$E = 296 \text{ kJ} / \text{mole}$ - decomposition of i-propylphenol to form phenol and propane (collateral);

$E = 377 \text{ kJ} / \text{mole}$ - decomposition of 1,1-biphenylmethanol with the formation of biphenylmethane and water (collateral);

$E = 384 \text{ kJ} / \text{mole}$ - decomposition of crezols with the formation of phenol and methane (collateral);

$E = 460 \text{ kJ} / \text{mole}$ - decomposition of naphthols with the formation of naphthalene and water (collateral);

Sulfur-containing: $E = 230 \text{ kJ} / \text{mole}$ - decomposition of bibenzysulphide with the formation of bibenzyl and hydrogen sulphide (collateral);

Azot-containing: $E = 356 \text{ kJ} / \text{mole}$ is the degradation of 9H-carbazole, 2,3-bimethyle-1H-indole, pyrrole derivatives with the formation of biphenyl, 3-methylpropylbenzene, 1,2,4-trimethyl-3-ethylbutane, benzobutane and ammonia (collateral).

b) Second disintegration:

$E=384 \text{ kJ/mole}$ – decomposition of derivatives of toluene, naphthalene, benzene, benzobutane with the formation of benzene and methane, butane, water (collateral).

Further, for the obtained reactions according to the model (Fig. 1), the rate constant and the decomposition time are determined (Fig. 2), the yield of the components - coke, gas, tar - is estimated.

Calculation of the yield of decomposition products of organic WCS was carried out. The calculated yield of coke was 58%, coke oven gas - 38.9%, coal tar - 1.8%, crude benzene - 0.8%, ammonia - 0.1%, while for ordinary coal particles these yields are 82 %, 15%, 2.5%, 1.2% and 0.2%, respectively.

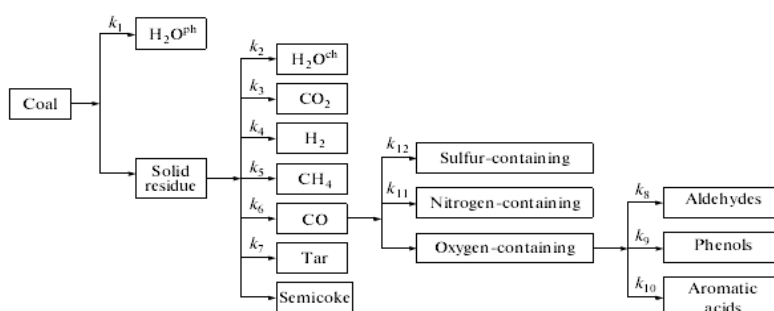


Fig. 1. Model of the kinetic parameters of the thermal decomposition (pyrolysis) of WCS

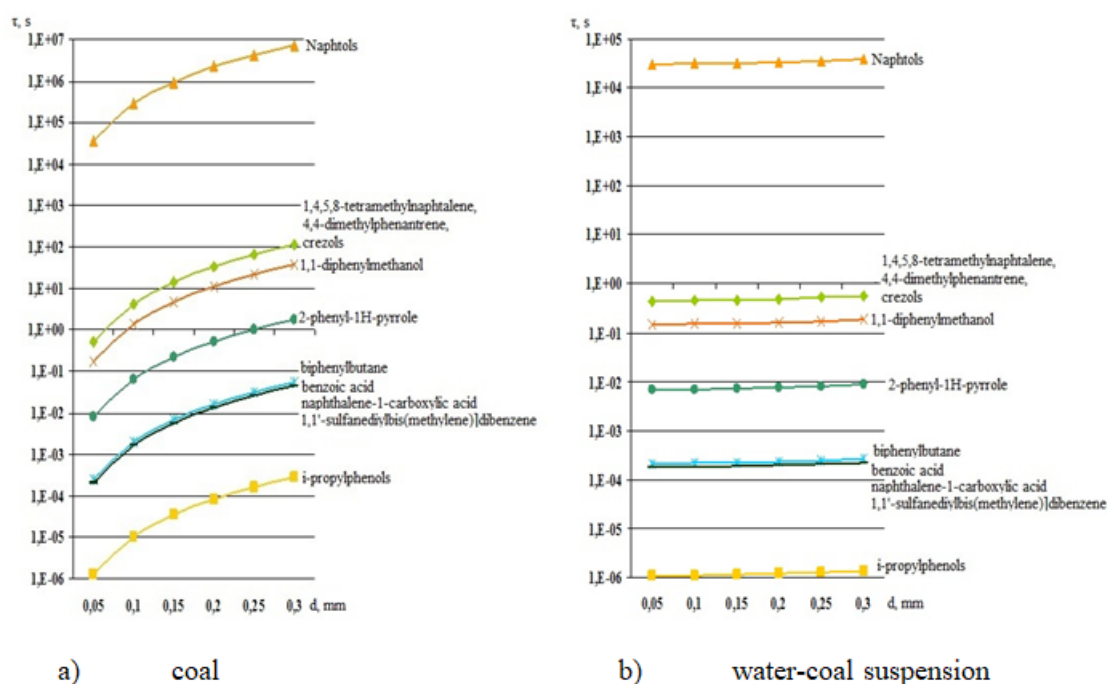


Fig. 2. Decomposition time of OMC compounds

Conclusions

The presence of certain substances in the mixture forming the organic mass of the fuel was revealed, modeling of the decomposition of the water-coal mixture during heat treatment was carried out.

The decomposition time of OMC for the diameter of the coal particle ($d = 0.05-0.3$ mm) is established, which increases with increasing diameter of the coal particle.

The greatest value of the endothermic effect is the reaction with allowance for di- and tetramethylarenes, as a result of which it is allowed to allow their withdrawal at 400°C and after

cooling to 300 ° C of decomposition to another part of the coal organic mass to 550 ° C. And at the same time, there is a gas of methane. The first to dissociate compounds containing COOH and -S-groups.

The obtained data on the mechanism of decomposition of a drop of a coal-water suspension allow to carry out the pyrolysis process more efficiently and to regulate the yield of the target products due to the variation of the water content in the WCS and the regime parameters of the process.

References

- [1] Podgaeczkij A.V., Vorob`eva I.M., Petrenko D.B., Samojlova E.K. Sostav i texnologicheskie svojstva e`nergeticheskix uglej Pavlovskogo mestorozhdeniya (Primor`e) // Otechestvennaya geologiya. №3. 2016. S. 13-20.
- [2] Poloveczkaya O.S., Bojkova O.I. Ximicheskij sostav organicheskoy massy` torfa Yaroslavskoj oblasti // Uspexi sovremennogo estestvoznaniya. №2-0. 2016. S. 61-64.
- [3] Kulikova M.P. Issledovanie svojstv uglya Ulug_Xemskogo bassejna // Vestnik Tuvinskogo gosudarstvennogo universiteta. №2 Estestvenny`e i sel'skoxozyajstvenny`e nauki. 2015. S. 108-118.
- [4] Kulikova M.P. Issledovanie fiziko-ximicheskix svojstv Ulug-Xemskix uglej // E`nergetik. №8. 2014. S. 29-32.
- [5] Poroxnov A.N. Model` srednestatisticheskoy strukturnoj edinicy OMU: analiz struktury` // Sbornik statej mezhdunarodnoj nauchno-prakticheskoy konferencii «Rol` i mesto informacionny`x texnologij v sovremennoj nauke». Saransk. 03 fevralya 2016g. S. 3-4.
- [6] Poroxnov A.N. Molekulyarny`e modeli organicheskoy massy` uglya: sravnenie strukturny`x xarakteristik // Sbornik statej Mezhdunarodnoj nauchno-prakticheskoy konferencii «Nauchny`e issledovaniya i razrabotki v e`poxu globalizacii». Kirov. 05 fevralya 2016g. S. 12-14.
- [7] Moskalenko T.V., Mixeev V.A. Matematicheskoe modelirovanie e`lektronnoj struktury` uglej // Vestnik Irkutskogo gosudarstvennogo texnicheskogo universiteta. №6 (89). 2014. S. 158-161.
- [8] Correlation between coal structure and release of the two organic compounds during pyrolysis. Yan L., Bai Y., Zhao R., Li F., Xie K. Fuel. 2015. Vol. 145. P. 12-17.
- [9] Patrakov Yu.F. Fiziko-ximicheskie prevrashheniya uglej v neizotermicheskix usloviyax i metody` ix aktivacii: avtoref. dis. ... d-ra xim. nauk. Kemerovo, 2005.
- [10] Approximations to the distributed activation energy model for the pyrolysis of coal. Please C.P., McGuinness M.J., McElwain D.L.S. Combustion and Flame. 2003. Vol. 133. Issues 1-2. P. 107-117.
- [11] FT-Raman spectroscopic characterisation of chars from the pyrolysis of coals of varying rank. Li Xiao-jiang, Li Chun-zhu. Journal of Fuel Chemistry and Technology. 2005. Vol. 33. Issue 4. P. 385-390.
- [12] Pyrolysis of Coal. Radenovic A. Journal of Chemists and Chemical Engineers. 2006. 55. (7-8). P. 311-319.
- [13] A theoretical study on bond dissociation enthalpies of coal based model compounds. Li L., Fan H., Hu H. Fuel. 2015. Vol. 153. P. 70-77.
- [14] Brunetkin A.I., Bondarenko A.V., Ly`syuk A.V. Opredelenie kolichestvennogo sostava neizvestnogo gazoobraznogo topliva i produktov sgoraniya na osnove izmerenny`x texnologicheskix parametrov // Trudy` Odesskogo politexnicheskogo universiteta. №1. 2014. S. 127-136.
- [15] Nesenchuk A.P., Beglyak A.V., Ry`zhova T.V., Shklovchik D.I., Yarmol`chik M.A., Kachar L.I. K ocenke e`ffektivnosti ispol`zovaniya organicheskix topliv v cikle parosilovy`x ustanovok // Izvestiya vy`sshix uchebny`x zavedenij i e`nergeticheskix ob`edinenij SNG. E`nergetika. №1. 2013. S. 56-60.