Low-Temperature Pyrolysis of Coal

T. A. ROMANOVA, E. S. MIKHAILOVA, Z. R. ISMAGILOV

*Institute of Coal Chemistry and Material Science, Federal Research Center of Coal and Coal Chemistry,
Siberian Branch, Russian Academy of Sciences,
Kemerovo, Russia*

E-mail: t.weltdubroma@gmail.ru

Abstract

The present review is devoted to the study of the process for low-temperature pyrolysis of coal. The effect of genetic and technical factors (heating rate, microwave radiation effects, and catalyst) on the yield and composition of coal thermal decomposition products was assessed. As demonstrated by literature data analysis, low-temperature pyrolysis of coal contributes to an increase in the yield of semi-coke, tar, and gas in inert, reducing, and oxidizing media, respectively. The use of microwave radiation or low temperatures during coal pyrolysis leads to an increase in the yield of liquid products, and of catalysts – tar and light hydrocarbon fractions, correspondingly.

Keywords: coal, low-temperature pyro;ysis, coal thermal decomposition

INTRODUCTION

Currently, the efficient and rational use of natural resources is a relevant issue. Coal is valuable fossil fuel, the world reserves of which, as at the end of 2016, are 1139 billion t (according to British Petroleum (BP) in the Statistical Review of World Energy 2017 [1]), which more than 4.7 times exceeds the proven oil reserves. Coal remains a world leader; it is used in the fuel and energy complex and utilized to obtain metallurgical coke, peck, carbon materials, humic acids, raw materials for the chemical industry (benzene, toluene, *etc.*) [2–9]. Herewith, it is hard enough to isolate special individual substances not containing harmful impurities [10]. Beyond this, a large amount of greenhouse gases affecting climate change are generated during coal combustion. According to BP data [1], greenhouse gas emissions in the Russian Federation make up 4.5 % of the world, which is less than in China, the USA, and India. For example, carbon dioxide emissions have a big impact on the greenhouse effect; 30 % of their volume are generated by coal-fired plants in the USA [11]. In addition, thermal power plants emit other pollutants too, *e. g.* sulphur oxides (SO_2 and SO_3), to 680 t at the daily combustion of 20 000 t of coal [12]. Various technologies (chemisorption, adsorption, and filtration) [12, 13] are used to reduce emission, however, their use is not always economically profitable and efficient. Therefore, further development of the coal industry is directed at the search and the introduction of efficient environmentally clean technologies of deep processing and the integrated use of coal for the production of products with added value [2, 14–17].

Currently, a great number of papers [18–35] related to processes of coal thermal processing by coking [20, 21], gasification [24–26], hydrogenation [31, 32] processes *etc.* is known, the differences of which consist in technological methods, and properties of the resulting products [36].

Low-temperature pyrolysis of coal is one of the key coal processing methods with obtaining valuable products and raw materials for chemical synthesis. Modern research of this process is related to complex processing of coal, an increase in the yield of liquid and gaseous products, preparation of hydrocarbons, *e.g.* such, as benzene, toluene, and xylene, improvement of analysis methods, and also modelling of the pyrolysis process. Herewith, structure complexity and content inhomogeneity of petrographic components, mineral matter in coal, *etc.* are taken into consideration in the studies of the process [34, 42].

Low-temperature pyrolysis of coal is accompanied by complex processes related to coal organic mass decomposition and secondary pyrolysis reactions of the resulting products (condensation, polymerization, aromatization, alkylation, *etc.*) [43−45]. The main products of low-temperature pyrolysis are semi-coke, coal-tar resin, and gaseous products. Yield and composition of products formed depend on both genetic (the type of coal used, its composition and structure) and technological factors (heating rate, the degree of crushing, pressure, medium, and additives) [44, 46−52].

EFFECT OF GENETIC CHARACTERISTICS OF COALS ON THE YIELD AND COMPOSITION OF PRODUCTS OF THEIR THERMAL DESTRUCTION

Genetic characteristics of coal have a paramount impact on the yield and composition of products of low-temperature pyrolysis of coal due to the difference in chemical structure, petrographic composition, the structure of coal organic mass. Research is this area is aimed at identifying peculiarities of thermal decomposition of petrographic microcomponents of coal [53−55], coal in different degrees of reduction [56−59], and various metamorphic stages [60, 61]. From the data of thermogravimetric analysis of coal with a low metamorphic grade of the various genotype and petrographic composition, given in [56], it can be seen that the heat resistance, the rate of decomposition and mass loss increase in the following order: humic coal − liptobiolite − sapropelite. The molecular structure becomes more ordered, aromaticity of structural

fragments increases, while the number of functional group decreases with increasing metamorphic stages of coal, which affects a reduction in the yield and the rate of release of volatiles, and the temperature of maximum decomposition increases by shifting to higher temperatures (from 430 °C in long-flame coal to 590 °C in lean coal).

The study of primary tar as a potential source of liquid fuel, aromatic and aliphatic compounds and raw materials for carbon materials (peck, graphite, and carbon fuel) is of the greatest interest to researchers [27]. Thus, for instance, the Chinese author P. Liu and coworkers [62] studied the effect of coal structure on the formation of tar and liquid alkanes during low-temperature pyrolysis of coal by the NMR method. An increase of the fraction of aliphatic carbon and methylene structures in the coal structure leads to the formation of greater amounts of hydrocarbons during pyrolysis.

EFFECT OF TECHNOLOGICAL PARAMETERS OF COALS ON THE YIELD AND COMPOSITION OF PRODUCTS OF LOW-TEMPERATURE COAL PYROLYSIS

Technological parameters, especially the rate of heating of coal raw materials, the medium, microwave radiation, and the addition of a catalyst significantly affect the change in the yield and composition of products from low-temperature pyrolysis of coal. These parameters are used to vary the yield and composition of products, reducing the time of the pyrolysis.

Effects of the heating rate during low-temperature pyrolysis of coal

The heating rate variation allows to control the yield of products from thermochemical transformations of coal by changing the ratio of reactions of organic mass destruction and synthesis of final products [63]. Some authors studied the effect of heating rate on thermal decomposition of sapropelite coal [63], lignite [46, 47], coal of different metamorphic stages [53, 64−66]. The total mass loss of coal samples, tar yield (for brown coal, from 10 % at 3 °C/min to 14 % at 20 °C/min) and gaseous products

evolution (from 75 mL/g at 5 °C/min to 102 mL/g at 20 °C/min) increase with rising heating rate, as established [46, 66]. The researchers of [67] found similar changes in mass loss rate during pyrolysis of low-grade metamorphic coal with the higher heating rate from 15 to 60 °C/min, however, the trends in the formation of liquid and gaseous products were opposing. These authors explain an increase in the yield of liquid tar products by the fact that a high heating rate initiated the development of decomposition with higher activation energies, which contributed to a more intense removal of large fragments pieces of macromolecules of the coal's organic mass bypassing the secondary processes of pyrolysis [66, 68]. Whereas, during the pyrolysis of coal carried out at lower heating rates, there are processes that contribute to the formation of condensed structures and lower tar yield [46]. In the study of pyrolysis in an inert medium, vitrinite concentrates of coal with the reflection indicator $R_{o,r} = 0.63-1.41$ %, it was found that an increase in the temperature interval of the main thermal decomposition with increasing heating rate of 20 and 40 °C/min the value of this indicator decreased, especially for vitrinites of the medium metamorphic degree (coal vitrinite $R_{o,r} = 0.82$ % from 104 to 72 °C) at a rate of 10 °C/min [69].

Effects of gas media on the yield and composition of products of coal thermal destruction

The gas medium, in which low-temperature pyrolysis of coal is carried out, exerts a considerable impact on the yield and composition of volatile products [70]. Studies of coal pyrolysis in [46, 47, 71], reducing [66], and oxidizing (under the action of active oxygen, *i.e.* partial gasification) [48, 72, 73] media are being carried out. Herewith, the effect of the medium on the yield of primary tar at various pressures [74], the mechanism of methane formation in complex reducing media [75], and the semi-coke reactivity [76] is examined. For instance, the authors of [77] found that the medium of hydrogen, at supply of which in the amount of 60 mL/min, at low-temperature pyrolysis of coal briquettes tar yield was over 11 %, which by 26 % higher than in nitrogen medium,

contributed to the higher tar yield, but at the same time, a lower yield of gaseous products was noted in a hydrogen medium. The authors of this work explained an increase in tar yield through stabilization of hydrogen free radicals formed during pyrolysis resulting in suppression of polymerization reactions.

Hydrogen content in gaseous products increases, as demonstrated by the studies of the effect of the medium on the yield and composition of primary gas during low-temperature pyrolysis of coal briquettes [66]. There is an increase in methane content when using carbon monoxide and hydrogen as a gas atmosphere. Carbon dioxide medium contributed to a higher yield of carbon monoxide, and the yield of carbon dioxide was reduced by 5 %, unlike an inert medium.

In [77], the Chinese researchers studied the effect of various gas media (CH_4, N_2, CO, CO_2, and H_2) at low-temperature pyrolysis of briquetted coal on a change in textural characteristics of semi-coke formed on its basis. Micropores prevail in the structure of the resulting semi-coke, as established by the authors in nitrogen medium at −196 °C by the Brunauer−Emmett−Teller (BET) method. The specific surface area of samples according to the Dubinin−Astakhov method was significantly higher than that during polymolecular adsorption according to the BET method. Semi-coke obtained in methane medium had a higher specific surface (192 m^2/g), and the lower one (165 m^2/g) − in hydrogen medium. Semi-coke produced in CO, N_2, and CH_4 media have identical and uniform pore distribution. Whereas semi-coke obtained in CO and H_2 media mainly have micropores with a diameter of 0.6 nm. Micropore surface area is ordered as follows: $CH_4 = N_2 = CO > CO_2 > H_2$.

The studies of pressure effect on products yield of low-temperature pyrolysis of coal in inert and reducing media [74] demonstrated that an increase in pressure from 0.1 to 1.5 MPa in nitrogen medium led to a rise in the yield of liquid and gaseous products, and in carbon dioxide medium, these indicators decreased. Herewith, it is worth noting that the content of phenols increased in the composition of liquid hydrocarbon products. The authors explained the noted peculiarities by the fact that

pyrolysis at high nitrogen pressures consisted in the decomposition of methyl substituents in the aromatic ring and the generation of phenols with a lower number of these groups. A decrease in tar yield with increasing pressure occurred because of a more intense tar reforming with CO_2, and CH_3 radicals generated when forming volatile substances accelerated methyl substitution in the aromatic ring promoting the formation of phenols [74].

The Chinese researchers (S. Gao, J. Wang *etc*.) [75] found that the use of 50 % CO/50 % N_2 medium during pyrolysis in a fixed bed reactor with a heating rate of 1000 °C/s to a temperature of 600 °C contributed to developing specific surface area of semi-coke (S_{BET} = 99.95 m^2/g).

Effect of microwave radiation on the yield and composition of products of low-temperature coal pyrolysis

It is known that coal has a relatively low thermal conductivity. Pyrolysis under the influence of SHF-radiation, also known as microwave, also contributes to more efficient heating of materials with low thermal conductivity. Microwave radiation is widely used in research related to processing of coal by coking [78, 79] during improving of preparation of coal charges for coking [80], low-temperature pyrolysis [81−83], ore dressing [84], flotation of coal macerals [85], coal unfreezing [86], processes for preparation of benzene extracts of coal [87]. The use of SHF-radiation during coal pyrolysis leads to an increase in the yield of liquid products [81, 82, 88]. Microwave pyrolysis of coal carried out at 700 °C in an inert medium promoted tar yield to 18 %, and in the presence of methane − to 35 % [82]. During pyrolysis of coal under the action of microwave radiation, tar mainly comprises of 48.0 % of naphthalene and 41.8 % of polyaromatic compounds [83].

It is known [89, 90] that the mechanism of the interaction of microwave radiation is determined by dipole polarization, *i.e.* the penetration of waves into dipoles (polar molecules, groups of atoms with the selected polarization vector that have a certain freedom of movement) because of the Maxwell−Wagner effect, and also conductivity of aqueous solutions of salts; an electric current flows through a solution due to the migration of ions; herewith, internal heating occurs, which leads to a faster release of volatile matter. Herewith, coal (low metamorphic degree) weakly adsorbs microwaves and is heated only to a temperature of 367 °C. Therefore, carbon materials with a relatively large number of delocalized π-electrons (coke and semi-coke) or such additives as CuO, Fe_2O_3 that are able to absorb microwaves and transform them into heat energy, are mainly used [82]. The Chinese scientists in the paper [82] discussed the mechanism of microwave pyrolysis of coal. The introduction of semi-coke additive leads to fast heating of the reaction mixture to 180 °C due to water involvement into adsorption of microwaves, as noted by the authors. At a temperature above 470 °C, the authors found an increase in mixture temperature because of developing the semi-coke structure that led to a higher ability to absorb microwaves, which allowed for a reduction of the duration of coal pyrolysis. Thus, at a 10 % content of the additive, heating duration to a temperature of 900 °C was about 30 min during microwave pyrolysis, while an additive content in the amount of 20 % allowed for a reduction of heating time to 20 min.

Catalytic low-temperature pyrolysis of coals

To accelerate chemical transformations, a decrease in process temperature, and an increase in the yield of the valuable target products (aromatic and aliphatic) various catalysts are used [91].

Zeolite catalysts, the advantage of which lies in a high catalytic activity and relatively easy modifiability are mainly used for low-temperature pyrolysis of coal, as demonstrated by literature data analysis [49, 92−97]. Precisely this makes them suitable for industrial use. The use of NiO/ZSM-5 catalyst (15 mass % NiO) during pyrolysis of low-grade metamorphic coal [49] allowed a significant increase in the yield of liquid products to 38 % (18 % without catalyst), light fractions of tar (to 8 %), while the utilization of NiO/MgO-Al_2O_3 catalyst (6 mass % NiO) [96] contributed to an increase in

the yield of phenol (about 33 %) and light (to 49 %) fractions during the distillation of tar. Herewith, NiO/MgO-Al$_2$O$_3$ catalyst contributed to the transformation of heavy component and polycyclic aromatic hydrocarbons of tar into low-molecular-mass, single-ring aromatic compounds (20 % xylenes), as demonstrated by chromato-mass-spectrometric analysis.

To use coal-tar as a raw material for preparation of liquid fuel it is required to decrease the amount of oxygen in its composition. The authors of [94] found that the use of Co/HZSM-5, Mo/HZSM-5, and Ni/HZSM-5 catalysts led to an increase in gas yield, a decrease in the total yield of tar and oxygen content in its composition compare to catalytic pyrolysis, and also an increase in the content of aromatic compounds in tar composition — from 86.2 to 90.5, 88.4, and 94.2 %, respectively. The authors explain this by the fact that decarboxylation and dehydration reactions are intensified in the presence of catalysts.

Apart from this, there are studies of catalytic low-temperature pyrolysis of coal using alkali and alkaline earth metal salts [98], eutectic mixtures (Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$, Li$_2$CO$_3$–Na$_2$CO$_3$–Rb$_2$CO$_3$, Na$_2$CO$_3$–K$_2$CO$_3$) [99], inexpensive composite iron-sodium catalysts [10], semi-coke impregnated with nickel, cobalt, copper, and zinc salts [100], peroxide-type oxides [101], metal chlorides [102], magnetic catalysts during co-pyrolysis of low-grade metamorphic coal with biocoal [103], and alkali metals in coal with biomass [104]. From the data given in [100], it could be seen that the impregnation of initial coal raw materials with cobalt ions led to a decrease in the total yield of tar (from 9 to 5 %) but with a higher content of light hydrocarbon fractions in its composition. The use of eutectic mixtures of alkali and alkaline earth metal salts for steam gasification of low-metamorphic degree coal contributes to an increase in methane yield in the composition of the resulting gaseous products, as noted by the authors of [99].

It is known that mineral inclusions contained in coal may contribute to a change in the yield of products during thermal decomposition. Research in this area was aimed at studying the effect of coal mineral components on a change in properties of low-temperature tar

during pyrolysis with a solid heat carrier [105], and also the catalytic effects of minerals on the decomposition of oxygen-containing groups in pyrolysis products [106]. The metal cations К, Na, Ca, Mg promoted decomposition of carboxyl groups (COOH), which enhanced the formation of esters and anhydrides in liquid products, as found in [106]. At the same time, an elevated content of the mineral components with silicon and aluminium hindered the formation of esters preventing the interaction between oxygen-containing groups. Thus, catalyst additive promotes a change in the yield and composition of products of low-temperature pyrolysis of coal. However, there is a requirement for searching a more efficient catalytic system for low-temperature pyrolysis of coals that allows obtaining a greater yield of the target product, such as semi-coke or ensuring a high quality of primary tar and easily volatile gas components.

CONCLUSION

Summing up a review of contemporary data related to low-temperature pyrolysis of solid fossil fuels, several common regularities may be formulated.

Primary genetic (the type of coal used, its composition and structure) and technical factors (heating rate, medium, microwave radiation effects, and catalyst) affect the yield and composition of their thermal decomposition products during low-temperature pyrolysis of coals.

The presence of large amounts of aliphatic carbon and methylene structures in coal structure contributes to the formation of methane and naphthene hydrocarbons during low-temperature pyrolysis.

Carrying out low-temperature pyrolysis in an inert medium contributes to an increase in semi-coke yield, in reducing and oxidizing media — the yield of tar and gas products, respectively.

An increase in heating rate during low-temperature pyrolysis of coal leads to a higher yield of resinous substances and the total mass loss due to the intense removal of fragments of coal organic massbypassing secondary processes of thermal decomposition.

The use of the SHF energy during pyrolysis

of coal contributes to more efficient volume heating of species in coal, which is reflected in the composition of the resulting products; the amount of aliphatic and aromatic compounds in the composition of resinous substances increases.

The use of various catalysts during low-temperature pyrolysis of coal allows controlling the composition and the amount of the resulting target products. Currently, there is no optimal catalyst system for this process, therefore there is a need for searching for more efficient catalytic systems for low-temperature pyrolysis of coal that allows obtaining a greater yield of the high-value target products.

REFERENCES

1 BP Statistical Review of World Energy 2017 [Electronic resources]. URL: http://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf?wpisrc=nl_energy202&wpmm=1 (accessed 06.07.2017).

2 InfoMain. Obzor Tekhnologii i Rynkov Produktov Glubokoi Pererabotki Uglei. M., 2012. 121 p.

3 Mikhailova E. S., Ismagilov Z. R., Shikina N. V., *Khimiya Ust. Razv.* 2016. Vol. 24, No. 3. P. 369–377.

4 Kuznetsov P. N., Marakushina E. N., Buryukin F. A., Ismagilov Z. R., *Khimiya Ust. Razv.* 2016. Vol. 24, No. 3. P. 325–333.

5 Zherebtsov S. I., Malyshenko N. V., Smotrina O. V., Bryukhovetskaya L. V., Ismagilov Z. R., *Khimiya Ust. Razv.* 2016. Vol. 24, No. 3. P. 399–403.

6 Mikhailova E. S., Lyrshchikov S. Yu., Ismagilov Z. R., *Khimiya Ust. Razv.* 2014. Vol. 22, No. 3. P. 313–318.

7 Semenova S. A., Fedorova N. I., *Koks i Khimiya.* 2012. No. 1. P. 45–47.

8 Mikhailova E. S., Semenova S. A., Ismagilov Z. R., Aktual'nye voprosy uglekhimii i khimicheskogo materialoveden'ya: Sb. Tez. Dokl. II Konferentsii Molodykh Uchenykh, Kemerovo, 2013. P. 37.

9 Rokosova N. N., Kozlov A. P., Rokosov YU. V., Bodoev N. V., Khimiya Ust. Razv. 2003. Vol. 11, No. 2. P. 409–421.

10 Mikhailova E. S., Ismagilov Z. R., *Khimiya Ust. Razv.* 2017. Vol. 25, No. 2. P. 117–128.

11 Xu V., Lu W., Sun Z., He T., Goroncy A., Zhang U., Fan M., *Fuel Rroc. Technol.* 2017. Vol. 167. P. 334–344.

12 Shikina N. V., Khairulin S. R., Kuznetsov V. V., Rudina N. A., Ismagilov Z. R., *Khimiya Ust. Razv.* 2015. Vol. 23, No. 2. P. 199–208.

13 Zvereva E. R., Farakhov T. M., Iskhakov A. R., *Vestn. Kazan. Gos. Energeticheskogo Un-ta.* 2011. No. 1 (8). P. 39–44.

14 InfoMain. Obzor Rynka Polukoksa iz Burykh Uglei v Mire i Rossii. M., 2013. 67 p.

15 Programma razvitiya innovatsionnogo territorial'nogo klastera "Kompleksnaya pererabotka uglya i tekhnogennykh otkhodov" v Kemerovskoi oblasti. Kratkoe izlozhenie. Kemerovo, 2012. 46 p.

16 Proekt Energostrategii Rossiiskoi Federatsii na period do 2035 goda (redaktsiya ot 01.02.2017) URL: http://docplayer.ru/83702-Energeti-cheskaya-strategiya-rossii-na-period-do-2035-goda.html (accessed 17.12.2017).

17 Proshunin Yu. E., Shkoller M. B., *Koks i Khimiya.* 2016. No. 2. P. 10–16.

18 Jin L., Li Y., Feng Y., Hu H., Zhu A., *J. Analyt. Appl. Pyrolysis.* 2017. Vol. 126. P. 194–200.

19 Semenova S. A., Fedorova N. I., Zaostrovskii A. N., Ismagilov Z. R., *Khimiya Tv. Topliva.* 2013. No. 2. P. 15–18.

20 Nomura S., Arima T., Nomura S., F*uel Proc. Technol.* 2017. Vol. 159. P. 369–375.

21 Osetrovskii V. L., Naimark M. M., Lupenko V. G., Bazegskii A. E., Sokolova T. I., *Koks i Khimiya.* 2013. No. 3. P. 12–17.

22 Niu B. Jin L., Li Y., Shi Z., Li Y., Hu H., *Fuel Processing Technology.* 2017. Vol. 160. P. 130–135.

23 Li X., Zhu X.-Q., Okuda K., Zhang Z., Ashida R., Yao H., Miura K., *New Carbon Materials.* 2017. Vol. 32, Issue 1. P. 41–47.

24 Seyitoglu S. S., Dincer I., Kilicarslan A., *Int. J. Hydrogen Energy.* 2017. Vol. 42, Issue 4. P. 2592–2600.

25 Kuznetsov P. N., Kolesnikova S. M., Kuznetsova L.I., Tarasova L. S., Ismagilov Z. R., *Khimiya Tv. Topliva.* 2015. No. 2. P. 24–27.

26 Kuznetsov P. N., Kolesnikova S. M., Kamenskii E. S., Kuznetsova L. I., Tarasova L. S., Ismagilov Z. R., Uglekhimiya i ekologiya Kuzbassa. III Vserossiiskii Simpozium s Mezhdunarodnym Uchastiem v Ramkakh "Kuzbasskogo Mezhdunarodnogo Ugol'nogo Foruma – 2013": Sbornik Tezisov Dokladov, Kemerovo, 2013. P. 28.

27 Miura K., Fuel Process Technol. 2000. Vol. 62. P. 119–35.

28 Patrakov Yu. F., Fedyaeva O. N., Fedorova N. I., Gorbunova L.V., Sorokina O. V., *Khimiya Tv. Topliva.* 2006. No. 4. P. 46–51.

29 Manina T. S., Fedorova N. I., Semenova S. A., Ismagilov Z. R., *Koks i Khimiya.* 2012. No. 3. P. 43–46.

30 Manina T. S., Fedorova N. I., Ismagilov Z. R., *Koks i Khimiya.* 2015. No. 8. P. 33–36.

31 Vershinin S. N., Chekmarev E. N., Ismagilov Z. R., XX Mendeleevskii S"ezd po Obshchei i Prikladnoi Khimii, Tezisy Dokladov v 5 Tomakh, Ekaterinburg: Izd-vo UrO RAN, 2016. P. 224.

32 Zhang D., Liu P., Lu X., Wang L., Pan T., *Fuel Proc. Technol.* 2016. Vol. 141. P. 117–122.

33 Semenova S. A., Koks i Khimiya. 2010. No. 9. P. 36–38.

34 Zhang S., Zhu F., Bai C., Wen L., Zou C., *J. Analyt. Appl. Pyrolysis.* 2013. Vol. 104. P. 660–666.

35 Zherebtsov S. I., Malyshenko N. V., Smotrina O. V., Lyrshchikov S. Yu., Bryukhovetskaya L. V., Ismagilov Z. R., *Khimiya Ust. Razv.* 2015. Vol. 23. No. 4. P. 439–444.

36 Drozdnik I. D., Kaftan Yu. S., Dolzhanskaya Yu. B., *Khimiya Tv. Topliva.* 1999. No. 1. P. 4–15.

37 Li Q., Feng X., Wang X., Wu T., Chen Bo., Zhu Y., Li S., *J. Analyt. Appl. Pyrolysis.* 2017. Vol. 126. P. 390–396.

38 Gao Z., Zheng M., Zhang D., Zhang W., *J. Energy Institute.* 2016. Vol. 89, Issue. 4. P. 544–559.

39 Wang J., Lian W., Li P., Zhang Z., Yang J., Hao X., Huang W., Guan G., *Fuel.* 2017. Vol. 207. P. 126–135.

40 Shi L., Wang X., Zhang S., Wu X., Yuan L., Tang Z., *J. Analyt. Appl. Pyrolysis.* 2016. Vol. 117. P. 347–353.

41 Monsef-Mirzai P., Mcwhinnie W. R., Perry M. C., Burchill P., *Fuel.* 1995. Vol. 74, Issue 5. P. 674–683.

42 Fedorova N. I., Malysheva V. Yu., Mikhailova E. S.,

Ismagilov Z. R., *Vestn. KuzGTU.* 2016. Vol. 114, No. 2. P. 111−117.

43 Gorelova O. M., Denisov M.V., Kalmykov M. F., *Polzunov. Vestn.* 2009. No. 3. P. 98−101.

44 Liu J., Ma Y., Luo L., Ma J., Zhang H., Jiang X., *Energy Conversion and Management.* 2017. Vol. 134. P. 32−46.

45 Song H., Liu G., Zhang J., Wu J., *Fuel Proc. Technol.* 2017. Vol. 156. P. 454−460.

46 Xu Y., Zhang Y., Zhang G., Guo Y., *J. Energy Conversion and Management.* 2016. Vol. 114. P. 11−19.

47 Haykiri-Acma H., Yaman S., Kucukbayrak S., *Energy Education Science and Technology Part A: Energy Science and Research.* 2012. Vol. 29, Issue 2. P. 1203−1216.

48 Zhong M., Gao S., Zhou Qi, Yue J., Ma F., Xu G., *Particuology.* 2016. Vol. 25. P. 59−67.

49 Amin M. N., Li Y., Razzaq R., Lu X., Li C., Zhang S., *J. Analyt. Appl. Pyrolysis.* 2016. Vol. 118. P. 54−62.

50 Fedorova N. I., Patrakov Yu. F., *Khimicheskaya Tekhnologiya. Vestn. KuzGTU.* 2003. No. 1. P. 76−79.

51 Sklyar M. G., Shustikov V. I., *Khimiya Tv. Topliva.* 1967. No. 4. P. 85−89.

52 Oyuunbold D., Syroezhko A. M., Slavoshevskaya N. V., Strakhov V. M., *Koks i Khimiya.* 2010. No. 4. P. 19−27.

53 Gao Z., Zheng M., Zhang D., Zhang W., J. Energy Institute. 2015. P. 1−16.

54 Lin X., Luo M., Li S., Yang Y., Chen X., Tian B., Wang Y., *Appl. Energy.* 2017. Vol. 199. P. 335−346.

55 Fedorova N. I., Semenova S. A., Patrakov Yu. F., Makarevich V. A., Kosheleva L. A., *Vestn. KuzGTU.* 2002. No. 1. P. 70−73.

56 Batina M. V., Semenova S. A., Patrakov Yu. F., Khimiya − XXI Vek: Novye Tekhnologii, Novye Produkty: Sb. Materialov XII Nauch.-Prakt. Konferentsii. Kemerovo, 2009. P. 20−22.

57 Arenillas A., Rubiera F., Pis J. J., Cuesta M. J., Iglesias M. J., Jiмйnez A., Suбrez-Ruiz I., *J. Anal. Appl. Pyrolysis.* 2003. Vol. 68−69, No. 69. P. 371−385.

58 Wu D., Liu G., Sun R., *Energy Fuels.* 2014. Vol. 28. P. 24−35.

59 Butuzova L., Isaeva L., Turchanina O., Krzton A., *Fuel Proc. Technol.* 2002. Vol. 77−78. P. 145−150.

60 Fedyaeva O. N., Patrakov Yu. F., *Khimiya Tv. Topliva.* 2004. No. 5. P. 24−31.

61 Liu P., Le J., Wang L., Pan T., Lu X., Zhang D., *Appl. Energy.* 2016. Vol. 183. P. 470−477.

62 Tabakeev R. B. Teplotekhnologiya Polucheniya Tverdogo Kompozitnogo Topliva iz Nizko-Sortnogo Organicheskogo Syr'ya (Candidate's dissertation in Tekhnichal Sciences). Tomsk, 2015. 144 p.

63 Sklyar M. G., Shustikov V. I., *Khimiya Tv. Topliva.* 1967. No. 3. P. 16−22.

64 Geng C., Li S., Yue C., Ma Y., *J. Energy Institute.* 2016. Vol. 89. P. 725−730.

65 Zhang W., Jiang S., Hardacre C., *J. Analyt. Methods in Chem.* 2015. Article ID 306874. P. 1−8.

66 Liu J., Zhang Y., Wang Y., Chen L., *J. Energy Institute.* 2016. Vol. 89, Issue 4. P. 594−605.

67 Du R.-L., Wu K., Xu D.-A., Chao C.-Y., Zhang Li, Du X.-D., *Fuel Proc. Technol.* 2016. Vol. 148. P. 295−301.

68 Belov K. A., Biryukov Yu. V., Nesterenko L. L., *Koks i Khimiya.* 1965. No. 9. P. 9−11.

69 Fedorova N. I., Khitsova L. M., Malysheva V. Yu., Ismagilov Z. R., *Khimiya Ust. Razv.* 2017. Vol. 25, No. 3. P. 321−326.

70 Golovina E. S. Reaktsii Ugleroda s Gazami. M.: Izd.

inostr. literatury, 1963. 360 p.

71 Odeh A. O., *J. Fuel Chem. Technol.* Vol. 43, Issue 2. 2015. P. 54−62.

72 Islamov S. R., Kulesh M. V., *Koks i Khimiya.* 2015. No. 5. P. 2−5.

73 Mikhalyov I. O., Islamov S. R., *Koks i Khimiya.* 2009. No. 2. P. 9−11.

74 Luo K., Zhang C., Zhu S., Bai Y., Li F., *J. Analyt. Appl. Pyrolysis.* 2016. Vol. 118. P. 130−135.

75 Gao S., Wang J., Wang Z., Zhao J., Fang Y., *J. Analyt. Appl. Pyrolysis.* 2014. Vol. 106. P. 104−111.

76 Chen Z., Shi Y., Lai D., Gao S., Shi Z., Tian Y., Xu G., *Fuel.* 2016. Vol. 176. P. 200−208.

77 Liu J., Li G.-Q., Chen L., Wang Y., Xu Y., Qiao X.-X., Zhang Y.-F., *Fuel Proc. Technol.* 2016. Vol. 151. P. 40−49.

78 Binner E., Mediero-Munoyerro M., Huddle T., Kingman S., Dodds C., Dimitrakis G., Robinson J., Lester E., *Fuel Proc. Technol.* 2014. Vol. 125. P. 8−17.

79 Starovoit A. G., Malyi E. I., Chemerinskii M. S., *Koks i Khimiya.* 2010. No. 9. P. 2−4.

80 Chemerinskii M. S., Starovoit A. G., Malyi E. I., *Koks i Khimiya.* 2012. No. 7. P. 26−29.

81 Rajasekhar Reddy B., Vinu R., *Fuel Proc. Technol.* 2016. Vol. 154. P. 96−103.

82 Liu H.-P., Chen T.-P., Li Y., Song Z.-Yu, Wang S.-W., Wu S.-H., *J. Fuel Proc. Technol.* 2016. Vol. 148. P. 317−323.

83 Kiryaeva T. A., *Interekspo Geo-Sibir'.* 2015. Vol. 2. No. 3. P. 93−96.

84 Rakhmankulov D. L., Shavshukova S. A., Vikhareva I. N., Chanyshev R. R., *Bashkirskii Khim. Zhurnal.* 2008. Vol. 15. No. 2. P. 53−56.

85 Chemerinskii M. S., *Koks i Khimiya.* 2014. No. 5. P. 40−43.

86 Zhao W., Yang F., Li Y., Qu J., Zhou A., *Mining Sci. Technol.* 2011. Vol. 21. Issue 6. P. 761−766.

87 Sonmez O., Sultan Giray E., *Fuel.* 2011. Vol. 90. P. 2125−2131.

88 Singh S., Neculaes V.B., Lissianski V., Rizeq G., Bulumulla S.B., Subia R., Manke J., *Fuel.* 2015. Vol. 140. P. 495−501.

89 Bolotov V. A., Chernousov Yu. D., Udalov E. I., *Vestn. NGU.* 2009. Vol. 4, No. 2. P. 78−83.

90 Menendez J. A., Arenillas A., Fidalgo B., *Fuel Proc. Technol.* 2010. Vol. 91. Issue 1. P. 1−8.

91 Kuznetsov B. N., *Sorosov. Obrazovat. Zhurnal.* 1996. No. 6. P. 51−57.

92 Li G., Yan L., Zhao R., Li F., *Fuel.* 2014. Vol. 130. P. 154−159.

93 Jin L., Zhou X., He X., Hu H., *Fuel.* 2013. Vol. 114. P. 187−190.

94 Liu T.-L., Cao J.-P., Zhao X.-Y., Wang J.-X., Ren X.-Yu, Fan X., Zhao Y.-P., Wei X.-Y., *Fuel Proc. Technol.* 2017. Vol. 160. P. 19−26.

95 Motazedi K. Template-Free Synthesis and Modification of LTY, ZSM-5 and LTL Zeolite Catalysts and Investigation of the Catalytic Pyrolysis of Saskatchewan Boundary Dam Coal (Thesis the Degree of Master of Science), Alberta, 2013. 120 p.

96 Li Y., Amin M. N., Lu X., Li C., Ren F., Zhang S., *Chem. Eng. Sci.* 2016. Vol. 155. P. 194−200.

97 Liu J., Hu H., Jin L., Wang P., Zhu S., *Fuel Proc. Technol.* 2010. Vol. 91. P. 419−423.

98 Marchand D. J., Schneider E., Williams B. P., Joo Y. L., Kim J., Kim G. T., Kim S. H., *Fuel Proc. Technol.* 2015. Vol. 130. P. 292−298.

99 Yeboah Y. D., Xu Y., Sheth A., Agrawal P. Catalytic Gasification of Coal Using Eutectic Salt Mixtures: Technical Report, US Department of Energy, Atlanta, 2001. 134 c.

100 Han J., Wang X., Yue J., Gao S., Xu G., *Fuel Proc. Technol.* 2014. Vol. 122. P. 98−106.

101 Ding H., Xu Y., Luo C., Zheng Y., Shen Q., Liu Z., Zhang L., *Int. J. Hydrogen Energy.* 2016. Vol. 41, Issue 48. P. 22846−22855.

102 Liu L., Kumar S., Wang Z., *Thermochim. Acta.* 2017. Vol. 655. P. 331−336.

103 Trautmann M., Lang S., Traa Y., *Fuel.* 2015. Vol. 151. P. 102−109.

104 Wu Z., Yang W. C., Chen L., Meng H., Zhao J., Wang S., *Energy Procedia.* 2017. Vol. 105. P. 102−107.

105 Li X.-H., Ma J.-S., Li Li-Li, Li B.-Fu, Feng J., Turmel W., Li W.-Y., *J. Fuel Proc. Technol.* 2016. Vol. 143. P. 79−85.

106 Kou J.-W., Bai Z.-Q., Bai J., Guo Z.-X., Li W., *Fuel Proc. Technol.* 2016. Vol. 152. P. 46−55.