Technology of Producing Petroleum Coking Additives to Replace Coking Coal
Alexey V. Kameshkov, Viacheslav A. Rudko,* Renat R. Gabdulkhakov, Maxim Yu. Nazarenko, Maxim K. Starkov, Vladimir G. Povarov, and Igor N. Pyagay

1. INTRODUCTION

Analysis of the results presented in studies1−3 provides an insight that in the future, the replacement of most hydrocarbon resources with alternatives is impossible, so feedstock resources will be relevant for their use in processing. The most in-demand thermal processing of heavy petroleum residues in the world is delayed coking; this process makes it possible to extend petroleum processing to produce commodities at the oil refinery plant up to 98%.4,5 In 2021, the total crude material capacity of the delayed coking units in Russia was about 13.6 million tons.6,7 Using this process, the light petroleum product output can be increased, as well as the commodity assortment can be expanded with carbon materials.8−10 As a production alternative for conventional coarse petroleum coke at delayed coking units, production of petroleum coking additives is suggested.11,12

Petroleum coke, which is a potential replacement for coking coals in the production of metallurgical coke, has received the name of a petroleum coking additive in Russia and the CIS countries. A petroleum coking additive is a carbon bottom product of a delayed coking unit at petroleum refineries, which is obtained under a "softer" thermal regime (455−475 °C) than petroleum coke (495−505 °C). The distinctive properties of the petroleum coking additive are a high volatile-matter yield, from 15 to 25 wt % (relative to petroleum coke, usually up to 9−12 wt %).9,13,14 In addition, the petroleum coking additive, in contrast to petroleum coke used as a raw material for the production of electrodes or anodes, does not have such strict restrictions on the sulfur content (up to 4.8 wt %). This makes it possible to consider low-grade sulfur and high-sulfur heavy oil residues from hydrocarbon processing as cheap feedstock for delayed coking units. Table 1 shows the requirements for quality indicators of the petroleum coking additive (TU 0258-229-0019437-2008) and, for comparison, the requirements of electrode (TU 38.301-19-99-99) and needle (SuperPremium grade) petroleum cokes are provided.

Irrespective of the fact that Russia takes the third place in the world in coking coal production (more than 80.0 million tons per annum) after China and Australia, coke chemical companies suffer from a shortage of coals of particularly valuable grades: coking (K), coking lean (KO), and lean caking coal (OS).15−17 It should be noted that the demand for coking coals of these grades will persist from a long-term perspective, as the main consumer of coal coke, the blast-furnace iron-making, is still the main cast-iron and steel making process in...
Table 1. Main Technical Requirements for Petroleum Coking Additives and Their Comparison with the Requirements for Electrode and Needle Cokes

| parameters                                      | petroleum coking additive | petroleum electrode coke | petroleum needle coke |
|-------------------------------------------------|---------------------------|--------------------------|-----------------------|
| (1) moisture content (W%), %, no more           | 10.0                      | 3.0                      | 1.0                   |
| (2) ash content (A%), %, no more                | 2.00                      | 0.6−0.8                  | 0.4                   |
| (3) sulfur content, wt %, no more               | 4.8                       | 1.5−1.7                  | 0.5                   |
| (4) volatile-matter yield (Vd0%), %, within (no more) | 15.0−25.0                | 12.0                     |                       |

The lack of required valuable coal grades in the market at a favorable price makes the coke chemical companies look for an acceptable replacement. The coking additive produced from crude petroleum can be such a partial replacement in charge production.14,27

2. EXPERIMENTAL SECTION

2.1. Objects. The initial material for the petroleum coking additive was the commercially produced petroleum products at the oil refinery plant Ltd Kinef (Russia).26 The plant capacity and process lines are organized so that the potential crude material for the petroleum coking additive industrial production can be three kinds of heavy petroleum residues of the oil refinery plant Ltd Kinef: the vacuum residue from crude atmospheric and vacuum distillation units (VR1), the vacuum residue from the vacuum distillation hydrocracking unit (VR2), and the visbreaker residue from the visbreaking unit (mild thermal cracking) (VR3). In 2023, the plant plans to commission a delayed coking unit where the mentioned heavy petroleum residues can be used for producing the petroleum coking additive as the crude material according to the process flow chart shown in Figure 1.

The quality indicators of the initial material for the petroleum coking additive are given in Table 3.

The fundamental difference of the crude material is that VR2 is heavier than VR1 and more prone to coke formation (aromatic hydrocarbon and asphaltene content). In addition, VR1 and VR2 are the products of physical vacuum separation of crude petroleum; as a consequence, they contain no products of thermal decomposition, like in VR3. In this regard, the latter type of raw material has a higher tendency to coke formation. The sulfur content increases when the crude material gets heavier from 2.81 to 3.15%, as most hetero-organic compounds contain high-boiling fractions and asphaltenes.

2.2. Methods. 2.2.1. Delayed Coking Method. To produce the petroleum coking additive from the heavy petroleum residues, Ltd Kinef used the laboratory delayed coking unit of the Saint Petersburg Mining University consisting of a reaction unit and a distillate collection unit (Figure 2).

The reaction unit consists of a steel coking reactor and an electric furnace with three independent heating zones to maintain the even temperature by the coking layer height; the reactor is equipped with a pressure gauge for pressure monitoring. The gas−fluid product mix is discharged through the pipe inside the reactor cover, via the needle valve, and then flows into the double-pipe water heat exchanger and distillate collecting bottle, and the hydrocarbon gas is discharged to the exhaust system. The experiments were conducted at a coking temperature from 455 to 465 °C and at a constant excess pressure of 0.35 MPa for each experiment. Loading for raw materials was 0.247−0.254 kg. After switching to the normal coking temperature, the reactor was held in an isothermal mode until the formation of the gas−fluid products stopped, and, as a result, the pressure decreased in the reactor. The isothermal mode lasted for 60 min. The normal coking parameters for each experiment are shown in Table 4.
2.2.2. Methods for Determining Quality Indicators. The moisture content of the petroleum coke additive was determined in a dryer according to GOST 27589 “Coke. Method for determination of moisture content in analytical sample” (ISO 687:2010) and GOST 33503 “Solid mineral fuel. Method for determination of moisture content in analytical sample” (ISO 11722:2013, ISO 5068-2:2007). Accelerated testing methods were used for determination of moisture content. A total of 2 g of the sample of the petroleum coke additive with a particle size of 125 μm was dried at a

![Figure 1](http://pubs.acs.org/journal/acsodf/2021/6/i04075/article.jpg)

**Figure 1.** Process flow chart for the petroleum coking additive at Ltd Kinef.

| Table 3. Quality Indicators of Heavy Petroleum Residues |
|-------------------------------------------|
| quality indicators | VR1 | VR2 | VR3 | test method |
| density at 15 °C, kg/m³ | 1012.2 | 1020.5 | 1032.0 | ISO 12185 |
| kinematic viscosity, mm²/s | | | | ISO 3104 |
| 100 °C | 438.2 | 114.0 | | |
| 135 °C | 195.4 | | | |
| sulfur, % | 2.81 | 2.95 | 3.15 | ISO 8754 |
| flash point, °C | 308 | 352 | 356 | ISO 2719 |
| carbon residue—micro method, mass % | 20.5 | 20.8 | 22.6 | ISO 10370 |
| depth of needle penetration at 25 °C, 0.1 mm | 450 | 348 | | SARA analysis |
| SARA, wt % | 8.5 | 9.2 | 2.3 | |
| saturates | 52.4 | 56.9 | 51.8 | |
| aromatic | 18.7 | 11.8 | 20.3 | |
| resins | 20.4 | 22.1 | 25.6 | |

| Table 4. Process Parameters for Producing the Petroleum Coking Additive |
|-------------------------------------------|
| parameters | VR1 | VR2 | VR3 |
| overpressure, MPa | 0.35 | 0.35 | 0.35 |
| cooking temperature (final temperature), °C | 455–465 | 456–460 | 455–460 |
| heating time to final temperature, min | 360 | 355 | 360 |
| average heating rate of the coking layer, °C/min | 1.55 | 1.61 | 1.58 |
| isothermal time at final temperature, min | 60 | 60 | 60 |
| mass of raw materials, g | 254.0 | 247.0 | 252.0 |

![Figure 2](http://pubs.acs.org/journal/acsodf/2021/6/i04075/article.jpg)

**Figure 2.** Process flow chart of the laboratory delayed coking unit “UZK-1”: 1, coking reactor; 2, heat insulator; 3, thermocouples of the top and bottom layer of the reactor; 4, reactor pressure gauge; 5, three heating zones; 6, pressure test needle valve; 7, electric control unit; 8, reactor needle valve; 9, double-pipe water heat exchanger; 10, distillate receiver; 11, thermocouple pocket; 12, nitrogen reducer; 13, pressure test pressure gauge; 14, pressure test valve; 15, nitrogen cylinder for purging and pressure testing; and 16, voltage stabilizer.
temperature of 105 ± 5 °C. The moisture residue was estimated by the mass loss. The ash content was determined according to GOST 22692 “Carbon materials. Method for determination of ash”. A total of 2 g of the material sample was burnt in a muffle furnace at 815 ± 10 °C and held at the specified temperature until a constant mass was reached. The ash content was estimated by the mass loss.

The volatile-matter yield was determined by heating 1 g of the sample in a porcelain crucible with an air-tight ground-in lid in a muffle furnace at 815 ± 10 °C for 7 min according to GOST 22898 “Low-sulfur petroleum cokes. Specifications” and GOST R 55660 “Solid mineral fuel” (ISO 562:2010). The volatile-matter yield percentage was estimated by the mass loss of the sample weight, exclusive of moisture.

The real density was determined by weighing 1 g of the sample in a porcelain crucible with an air-tight ground-in lid in a muffle furnace at 815 ± 10 °C for 5 min according to GOST 22898 “Low-sulfur petroleum cokes. Specifications” and GOST 10220 “Coke. Methods for determination of density and porosity”.

The microstructure was assessed by comparing with the microstructure control scale according to GOST 26132 “Petroleum and pitch coke. Methods of microstructural assessment” using a μVizo-MET-221 microvisor in reflected linearly polarized light with 90–100X magnification.

The sulfur in the petroleum coke additive samples was determined using an XRF-1800 Shimadzu sequential wavelength-dispersive X-ray fluorescence spectrometer with a 3.6 kW Rh anode X-ray tube. The method consists in the determination of sulfur by the introduction of a standard additive into the sample without preliminary incineration.

The microhardness of the petroleum coke samples was determined according to a procedure based on GOST 9450-79 “Measurements microhardness by diamond instruments indentation” and GOST R 8.748-2011 “Metals and alloys. Measurement of hardness and other characteristics of materials upon instrumental indentation” and provided comparable measurement results for the representative coke samples complying with ISO 14577-1 Annex A (Annex A: materials properties estimated by determination of depth of impression and force of indentation). The method consists in making an impression on the test sample surface under a load applied to the diamond point for a certain period of time, with simultaneous measurement of the depth of impression and force of indentation.

2.2.3. X-ray Structure Analysis. The X-ray diffraction analysis of the petroleum coke additive was performed using an XRD-7000 Shimadzu X-ray diffraction apparatus (Cu Kα-radiation, 2.7 kW) at room temperature according to the Debye–Scherer method. X-ray exposure was conducted at a long accumulation time of 2 s and at a step angle of 0.02°. The nonsymmetric reflections of petroleum cocones were split into peaks whose profile is described by Gaussian with the maximum of 2θ angles characterizing certain structural components of samples. For a detailed assessment of the thin structure of the petroleum coke additive by the X-ray diffraction method, the interplane distance by diffraction maximum values (002) and (110) and the coherent scattering area in the directions of axes “c” (average crystallites height Lc) and “a” (average hexagonal layer diameter La) were used in this work. To determine the interplane distance (d_{002} and d_{110}) in Å petroleum coke additive samples, the calculation was performed according to Bragg’s law:

\[ d = \lambda / 2 \sin \theta \]  

where \( \lambda = 1.5406 \) is the X-ray wavelength for Cu Kα, Å, and \( \theta \) is Bragg’s diffraction angle, rad.

The average linear size of crystallites \( L_c \) and \( L_a \) was determined in Å according to the Scherrer and Warren equations:

\[ L_c = \frac{0.89 \lambda}{\beta_{002} \cos \theta_{002}} \quad L_a = \frac{1.84 \lambda}{\beta_{110} \cos \theta_{110}} \]  

The quality indicators of the petroleum coking additive were determined from the point of view of its further partial use instead of the coking coals and are given in Table 6.

3. RESULTS AND DISCUSSION

The material balance of the delayed coking process of the heavy petroleum residues with the produced petroleum coke additive is given in Table 5.

### Table 5. Material Balance for Producing the Petroleum Coking Additive

| material balance | concentration, wt % |
|------------------|----------------------|
| input            |                      |
| vacuum residue   | 100.00               |
| VR1              | 100.00               |
| vacation residue | 100.00               |
| VR2              | 100.00               |
| visbreaker residue | 100.00          |
| VR3              | 100.00               |
| output           |                      |
| the amount of distillates, including | 51.97 | 50.20 | 46.83 |
| gasoline (IBP–180 °C) | 18.70 | 16.53 | 12.84 |
| light gasoline (180–360 °C) | 31.77 | 31.35 | 30.97 |
| heavy gasoline (360 °C–FBP) | 1.50 | 2.32 | 3.02 |
| petroleum coking additives | 33.86 | 34.82 | 39.29 |
| hydrocarbon gas + losses | 14.17 | 14.98 | 13.89 |
| total            | 100.00               |

The maximum yield of the petroleum coke additive was obtained in the process of coking the VR3 visbreaking residue and amounted to 39.29%. This is due to the presence of a larger number of reactive molecules in the visbreaking residue, compared to vacuum residues. The yield of the petroleum coking additive during vacuum residue coking was 33.86% for VR1 and 34.82% for VR2. The distillate yield is reduced in a reverse direction from 51.97% for VR1 to 46.83% for VR3. The produced distillates that have been subjected to hydoremoval of sulfur-containing compounds can be used as the motor fuel components.

The quality indicators of the petroleum coke additive were determined from the point of view of its further partial use instead of the coking coals and are given in Table 6.

The least volatile-matter yield (16.15%) from the samples produced in the course of experiments is normally character-
istic of the petroleum coking additive VR3, as crude petroleum undergoes mild thermal cracking before its production. The real density and apparent density for the VR1 and VR2 correlate with the volatile-matter yield. The low porosity of the VR3 sample as compared to the VR1 and VR2 sets a higher density value. The sulfur content in the produced samples ranges from 2.81 to 3.46%.

The particle size of the petroleum coking additive produced from coking of three kinds of crude materials and after its mechanical removal from the reactor is shown in Figure 3.

Table 6. Quality Indicators of the Petroleum Coking Additive

| properties                              | VR1         | VR2         | VR3         |
|-----------------------------------------|-------------|-------------|-------------|
| moisture content (W), %                 | 0.150       | 0.520       | 0.528       |
| volatile-matter yield (Y20), %          | 17.32       | 19.07       | 16.15       |
| microstructure score                    | 3.1         | 2.8         | 3.0         |
| ash content (A%), %                     | 0.15        | 0.23        | 0.20        |
| real density (d), g/cm³ (without calcination) | 1.230  | 1.392       | 1.528       |
| apparent density (d), g/cm³             | 0.956       | 1.065       | 1.424       |
| total porosity, %                       | 22.3        | 23.0        | 7.0         |
| sulfur content, wt %                    | 3.46        | 2.98        | 2.81        |
| microhardness, N/mm² (max. load 49–50 mN) | 51.8    | 56.7        | 49.7        |

Figure 3. Particle size of the petroleum coking additive produced from coking of three kinds of crude materials: VR1, VR2, and VR3.

The results demonstrate that VR1 and VR2 petroleum coking additives have a larger number of coarse particles than the additive from VR3. This points to the higher mechanical strength of the petroleum coking additive produced from vacuum processing of products of the heavy petroleum residues than that of the carbon material produced from the product of the thermal cracking. These conclusions are also confirmed by the microhardness determination results. With a maximum load of 49–50 mN, the VR3 petroleum coking additive has the least microhardness that increases when switching from VR1 raw materials to VR2.

The structure of the petroleum coking additive is amorphous carbon. The production temperature of the petroleum coking additive is 40–50 °C lower than that of the petroleum coke while having equal coking time. In the case of high-temperature treatment, the amorphous carbon transforms into graphite. The crystallites formed in the amorphous matrix of the petroleum coking additive have a turbostratic structure that is different from the graphite structure during thermolysis. The main structural parameters of such crystals are the interplane distances \( d_{002} \) and \( d_{110} \) and the coherent scattering area \( L_c \) and \( L_a \) in the directions of crystal axes “c” and “a”, respectively. For graphite, \( d_{002} \) and \( d_{110} \) are 3.354 and 1.232 Å, respectively, and for the turbostratic structure, \( d_{002} \) changes within 3.37 and 3.60 Å, and \( d_{110} \) changes within 1.215–1.230 Å.

Figure 4 shows the comparison of X-ray diffraction patterns of the petroleum coking additive produced from three kinds of heavy petroleum residues.

The peaks with maximum 2\( \theta \) angles of 25 and 77° that are correspondingly responsible for reflections 2\( \theta_{002} \) and 2\( \theta_{110} \) respectively, remain apparent. The angular position of the reflections (2\( \theta_{002} \) and 2\( \theta_{110} \)) on the X-ray diffraction pattern is determined by the corresponding interplanar distance \( d_{002} \) and \( d_{110} \). The results of the diffraction analysis and design values by reflections (002) and (110) for the petroleum coking additives produced from coking of three kinds of crude materials VR1, VR2, and VR3 are given in Table 7.

The interplane distance \( d_{002} \) increases from 3.5092 to 3.5147 Å with increasing heaviness of the crude material from VR1 to VR3, and \( d_{110} \) by contrast, decreases from 1.2323 to 1.2309 Å. According to the X-ray diffraction analysis results, the microstructure of the petroleum cokes can be judged on the basis of the ratio of the average height \( L_c \) and average diameter \( L_a \) of crystallites. In this case, the \( L_c \) to \( L_a \) ratio is about 1–10 that speaks for the flattened structure of crystallites and is caused by thermobaric conditions for the petroleum coking additive formation.

Thermogravimetric and differential thermal analyses were conducted for all petroleum coking additive samples to assess chemical transformations that occurred during their further high-temperature treatment in the charge, like in similar studies on carbon materials. The thermogravimetric and differential thermal analysis results of the VR1, VR2, and VR3 petroleum coking additives are shown in Figure 5.

All of the tested temperature ranges for the petroleum coking additive samples can be divided into four regions with maximum endothermic effects that generally coincide for all three samples of the carbon materials.

The first zone with a maximum (I_{max}) of 75–80 °C is within the range from 50 to 100 °C and characterizes the moisture removal from the carbon material samples. The second zone with a maximum (I_{max}) of about 400 °C is within the range from 100 to 439–445 °C and is associated with the mass increase to 0.6% of the sample initial mass. This mass increase is likely due to the sulfur oxidation to SO₂/SO₃ and further absorption of the part of these sulfurous gases by the other microelements contained in the petroleum coking additive, with the formation of the relevant sulfates (that is NiSO₄, CaSO₄, FeSO₄ etc.). When the temperature increases above 400 °C, the petroleum coking additive starts burning when in contact with the ambient oxygen and quickly loses its mass, while the carbonization simultaneously occurs. The third zone with a maximum (I_{max}) of about 550–560 °C is within the range from 439–445 to 570–580 °C and is caused by the volatile-matter yield during the petroleum coking additive burning. The fourth zone with a maximum (I_{max}) of about 594–605 °C is within the range from 570–580 to 737–740 °C and is characteristic of carbon burning. However, with such a high heating rate as 20 °C/min, two zones with I_{max} and I_{max}form a single peak in general. The sample was subjected to heavy thermal exposure only at the stage of the volatile-matter yield, and the generated heat cannot reach the sample internal surface in time. The lacking heat leads to the fact that
the sample shows a less intensive reaction at the stage of carbon burning. At a temperature above 740 °C, almost all burning reactions are completed, and the residual sample mass includes the ash content of the petroleum coking additive.

4. CONCLUSIONS

Obtaining a petroleum coking additive as a partial replacement for coking coals (for obtaining a charge in the metallurgical coke production) can be performed in delayed coking units of oil refineries as an alternative to obtaining lumpy petroleum coke. The petroleum coke is mainly used as the crude material for production of electrodes and anode paste and for preparation of regenerating graphitized carbon materials at the iron and steel production units. Strict requirements are specified for their sulfur content: 0.5–1.0 wt %. When using sulfurous heavy petroleum residues, it is impossible to obtain low-sulfur petroleum coke only by delayed coking; it is necessary to use additional desulfurization processes, which are not always economically viable.

In the course of experimental studies, from heavy petroleum residues of Ltd Kinef (Russia), two types of vacuum residue...
and visbreaking residue with a sulfur content from 2.81 to 5.15%, a carbon material was also obtained with a yield of volatile substances from 16.15 to 19.07% in amounts of 32.86–39.29%. It is amorphous carbon with characteristic reflections of (002) and (110) and a thermogram, which is a petroleum coking additive and can be used to partially replace coking coals in the charge in metallurgical coke production.

**AUTHOR INFORMATION**

Corresponding Author
Viacheslav A. Rudko — Saint Petersburg Mining University, St. Petersburg 199106, Russia; orcid.org/0000-0002-8527-6705; Email: rva1993@mail.ru

**Authors**
Alexey V. Kameshkov — Saint Petersburg Mining University, St. Petersburg 199106, Russia; Ltd Kingf, Kirishi 187110, Russia
Renat R. Gabdulkhakov — Saint Petersburg Mining University, St. Petersburg 199106, Russia
Maxim Yu. Nazarenko — Saint Petersburg Mining University, St. Petersburg 199106, Russia; orcid.org/0000-0002-1684-4828
Maxim K. Starkov — Saint Petersburg Mining University, St. Petersburg 199106, Russia
Vladimir G. Povarov — Saint Petersburg Mining University, St. Petersburg 199106, Russia; orcid.org/0000-0001-6710-0514
Igor N. Pyagay — Saint Petersburg Mining University, St. Petersburg 199106, Russia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04075

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was carried out as part of the State Assignment 0792-2020-0010 “Development of scientific foundations of innovative technologies for processing heavy hydrocarbon raw materials into environmentally friendly motor fuels and new carbon materials with controlled macro- and microstructural organization of mesophase”.

**REFERENCES**

(1) Litvinenko, V. The Role of Hydrocarbons in the Global Energy Agenda: The Focus on Liquefied Natural Gas. *Resources* 2020, 9, No. 59.
(2) Litvinenko, V.; Tsvetkov, P.; Dvornikov, M.; Buslaev, G. Barriers to Implementation of Hydrogen Initiatives in the Context of Global Energy Sustainable Development. *J. Min. Inst.* 2020, 244, No. 421.
(3) Filatova, I.; Nikolaichuk, L.; Zakaev, D.; Ilin, I. Public-Private Partnership as a Tool of Sustainable Development in the Oil-Refining Sector: Russian Case. *Sustainability* 2021, 13, No. 5153.
(4) Zaporin, V. P.; Valyavin, G. G.; Rizvanov, I. V.; Akhmetov, A. F. Decant-Oil Coking Gosols for Production of Industrial Carbon. *Chem. Technol. Fuels Oils* 2007, 43, 326–329.
(5) Kondrasheva, N. K.; Vasilev, V. V.; Boitsova, A. A. Study of Feasibility of Producing High-Quality Petroleum Coke from Heavy Yarega Oil. *Chem. Technol. Fuels Oils* 2017, 52, 663–669.
(6) Kapustin, N. O.; Grushevenko, D. A. Exploring the Implications of Russian Energy Strategy Project for Oil Refining Sector. *Energy Policy* 2018, 117, 198–207.
(7) Glagoleva, O. F.; Kapustin, V. M. Improving the Efficiency of Oil Treating and Refining Processes (Review). *Pet. Chem.* 2020, 60, 1207–1215.
(8) Kondrasheva, N. K.; Baitalov, F. D.; Boitsova, A. A. Comparative Assessment of Structural-Mechanical Properties of Heavy Oils of Timano-Pechorskaya Province. *J. Min. Inst.* 2017, 225, 320–329.
(9) Bazarh, V. Y.; Kuskov, V. B.; Kuskova, Y. V. Problems of Using Unclaimed Coal and Other Carbon-Containing Materials as Energy Briquettes. *Ugol* 2019, 04, 50–54.
(10) Sultanbekov, R.; Islamov, S.; Mardashov, D.; Beloglazov, L.; Hemmingsen, T. Research of the Influence of Marine Residual Fuel Composition on Sedimentation Due to Incompatibility. *J. Mar. Sci. Eng.* 2021, 9, No. 1067.
(11) Valjavin, K. G.; Zaporin, V. P.; Suhov, S. V.; Mamaev, M. V.; Bidilo, I. V.; Zagajnov, S. V.; Andrejkov, E. I.; Stukov, M. I.; Valjavin, G. G. Method for Obtaining Coking Additive by Delayed Coking. Russian Patent RU24968522013.
(12) Malaquis, B.; Flores, I. V.; Bagatini, M. Effect of High Petroleum Coke Additions on Metallurgical Coke Quality and Optical Texture. *REM — Int. Eng. J.* 2020, 73, 189–195.
(13) Menéndez, J. A.; Pis, J. J.; Alvarez, R.; Barriocanal, C.; Fuente, E.; Díez, M. A. Characterization of Petroleum Coke as an Additive in Metallurgical Coke Making. Modification of Thermoplastic Properties of Coal. *Energy Fuels* 1996, 10, 1262–1268.
(14) Mel'nikov, I. I.; Kryuchuk, V. M.; Mezin, D. A.; Gorbunov, A. A.; Voloshchuk, T. G. Influence of Petroleum Coking Additive on the Quality of Coal Batch, Coke, and Tar. *Coke Chem.* 2011, 54, 447–449.
(15) Tverdov, A. A.; Zhura, A. V.; Nikishichev, S. B. A Problems and Prospects for the Development of the Coal Industry of Russia. *Ugol* 2012, 1037, 86–90.
(16) Kondratyev, V. B. Global Coal Market. *Gorn. Promyshlennost.* 2017, 132, 17–23.
(17) Mansurov, A. A. Analysis of Development of the Market of Coals in the Countries ATR and the Russian Federation. *Min. Inf. Anal. Bull.* 2012, 2, 175–180.
(18) Ochirbat, P. Coal Industry in Mongolia: Status and Prospects of Development. *J. Min. Inst.* 2017, 226, 420–427.
(19) Gorlanov, E. S.; Brichkin, V. N.; Polyakov, A. A. Electrolytic Production of Aluminium. Review. Part 1. Conventional Areas of Development. *Tsvetnye Met.* 2020, 36–41.
(20) Gorlanov, E. S.; Kawalla, R.; Polyakov, A. A. Electrolytic Production of Aluminium. Review. Part 2. Development Prospects. *Tsvetnye Met.* 2020, 42–49.
(21) Plakitkina, L. S. The Trends in the Development of the Production of the Coking Coals in the Main Countries of the World and Their Mining in Russia within the Period until 2035. *Ferr. Metall. Bull. Sci., Tech. Econ. Inf.* 2016, 2, 19–26.
(22) Xiang, C.; Liu, Q.; Shi, L.; Zhou, B.; Liu, Z. Prediction of Gray-King Coke Type from Radical Concentration and Basic Properties of Coal Blends. *Fuel Process. Technol.* 2021, 211, No. 106584.
(23) O’Keefe, J. M. K.; Bechtel, A.; Christianis, K.; Dai, S.; DiMichele, W. A.; Eibe, C. F.; Esterle, J. S.; Mastalerz, M.; Raymond, A. L.; Valentin, B. V.; Wagner, N. J.; Ward, C. R.; Hower, J. C. On the Fundamental Difference between Coal Rank and Coal Type. *Int. J. Coal Geol.* 2013, 118, 58–87.
(24) Lu, L.; Devashayam, S.; Sahajwalla, V. Evaluation of Coal for Metallurgical Applications. In *The Coal Handbook: Towards Cleaner Utilization*; Elsevier, 2013; pp 352–386.
(25) Ward, C. R.; Suárez-Ruiz, I. Introduction to Applied Coal Petrology. In *Applied Coal Petrology*; Elsevier, 2008; pp 1–18.
(26) Sosnova, E. B.; Poltoratskaya, E. A. Additivity of Clinkering Measures When Blending Coal. *Coke Chem.* 2011, 54, 287–292.
(27) Ibrahim, H. A.-H. Analysis and Characterization of High-Volatile Petroleum Coke. *Recent Adv. Petrochem. Sci.* 2018, 6, No. 555677.
(28) Lavrova, A. S.; Vasilyev, V. V.; Strakhov, V. M. Comparison of the Coking Products from Heavy Petroleum Tars and Heavy Catalytic-Cracking Gas-Oil. *Coke Chem.* 2019, 62, 164–168.
(29) Salykova, S. N. Microanalysis of Oil Shale of the Leningrad Field. *Key Eng. Mater.* 2020, 854, 188–193.
(30) Bragg, W. L. The Structure of Some Crystals as Indicated by Their Diffraction of X-Rays. *Proc. R. Soc. A: Math. Phys. Eng. Sci.* 1913, 89, 248–277.
(31) Wulff, G. Über Die Kristallröntgenogramme. *Phys. Z.* 1913, 14, 217–220.
(32) Scherrer, P. Bestimmung Der Inneren Struktur Und Der Größe von Kolloidteilchen Mittels Röntgenstrahlen. In *Kolloidchemie Ein Lehrbuch*; Springer: Berlin, 1912; pp 387–409.
(33) Warren, B. E. X-Ray Diffraction in Random Layer Lattices. *Phys. Rev.* 1941, 59, 693–698.
(34) Feret, F. R. Determination of the Crystallinity of Calcined and Graphitic Cokes by X-Ray Diffraction. *Analyst* 1998, 123, 595–600.
(35) Savchenkov, S. A. The Research of Obtaining Master Alloys Magnesium-Gadolinium Process by the Method of Metallothermic Recovery. *Tsvetnye Met.* 2019, 33–39.
(36) Kuznetsov, P. N.; Kuznetsova, L. I.; Kolesnikova, S. M.; Obukhov, Y. V. Comparison of Supramolecular Organization of Brown Coal from Different Deposits. *Chem. Sustainable Dev.* 2001, 9, 255–261.
(37) Belenkov, E. A.; Karnaukhov, E. A. Influence of Crystal Dimensions on Interatomic Distances in Dispersed Carbon. *Phys. Solid State* 1999, 41, 672–675.
(38) Zhu, Y.; Zhao, C.; Xu, Y.; Hu, C.; Zhao, X. Preparation and Characterization of Coal Pitch-Based Needle Coke (Part I): The Effects of Aromatic Index (f a) in Refined Coal Pitch. *Energy Fuels* 2019, 33, 3456–3464.
(39) Zhu, Y.; Hu, C.; Xu, Y.; Zhao, C.; Yin, X.; Zhao, X. Preparation and Characterization of Coal Pitch-Based Needle Coke (Part II): The Effects of β Resin in Refined Coal Pitch. *Energy Fuels* 2020, 34, 2126–2134.
(40) Popova, A. N. Crystallographic Analysis of Graphite by X-Ray Diffraction. *Coke Chem.* 2017, 60, 361–365.
(41) Ismagilov, Z. R.; Sozinov, S. A.; Popova, A. N.; Zaporin, V. P. Structural Analysis of Needle Coke. *Coke Chem.* 2019, 62, 135–142.
(42) Miao, Z.; Wu, G.; Li, P.; Meng, X.; Zheng, Z. Investigation into Co-Pyrolysis Characteristics of Oil Shale and Coal. *Int. J. Min. Sci. Technol.* 2012, 22, 245–249.
(43) Fan, X. *The Fates of Vanadium and Sulfur Introduced with Petcoke to Lime Kilns*, 2010.
(44) Song, C.; Liu, K.; Gong, Z.; Liu, Y. Thermogravimetric Analysis of Combustion Characteristics of Coal Gangue and Petroleum Coke Mixture. *J. Phys.: Conf. Ser.* 2019, 1324, No. 012077.