On the use of products of the organic matter extraction from coal as a component of fuels

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Abstract. Extraction of the coal organic mass under the influence of organic dissolvent is a method of conversing coal into liquid products. The need for the further development of this technology is associated with the need to search for alternative direct liquefaction and gasification technologies for obtaining alternative fuel products. The paper presents the analysis results of hydrocarbon fractions 112-400 °C, obtained by joint heat treatment of coal and catalytic cracking heavy gas oil according to some quality indicators of traditional fuels. In general, according to some indicators this product is close to boiler fuels. But aromatic hydrocarbons and olefins predominate in the extraction products if we take into account chemical structure. So, it requires their hydrogenation improving.

1. Introduction
The paper states that scientific and technological interest in the development of competitive technologies for the use of coal as a raw material for the production of motor and boiler fuels has been preserved for about 100 years [1]. The instability of petroleum prices and the gradual decrease in its reserves create favorable conditions for the development of these processes. The research and development of these methods of coal converting are carried out in many countries, such as China, South Africa, Germany, Japan, Russia, etc.

Gasification and direct coal liquefaction are widely spread mostly. However, both methods cannot provide a product price comparable to the price of petroleum fuels. Direct liquefaction of coal requires the use of hydrogen and catalysts, high temperature and pressure (400-455 °C and 7-17 MPa), and the resulting products are of relatively low quality. Fischer-Tropsch indirect coal liquefaction processes are associated with significant CO₂ emissions that must be identified [2]. A catalyst is also required. The yield of useful products does not exceed 45%. Coal and biomass co-gasification can help reduce greenhouse gas emissions. However, the technology is still expensive [3,4].

Thus, the search for an economically viable technology for converting coal into liquid products is still relevant.

At the same time, the investigations are carried out to develop technologies for processing coal into fuels and other products based on extraction processes [5]. The essence of the extraction method is the effect of organic dissolvent on the organic mass of coal at temperatures of 380-450 °C and, preferably, at increased pressure. In the process of depolymerization, dissolution and minor cracking, a high-molecular-weight product with a high viscosity and softening point is obtained. About 20% of light distilled fractions are obtained as a by-product [6]. The yield of light fractions depends on the composition of the extractant and the conditions of the extraction.
2. Materials and methods
The experiments on coal extraction were carried out according to the method [7] in a laboratory reactor. The crushed GZh grade coal from the Chadanskoye deposit was mixed with catalytic cracked heavy gas oil in a 1: 1 ratio and subjected to extraction at a temperature not exceeding 400 °C and autogenous pressure (up to 1.6 MPa). Light extraction products (LEP) were removed through a water-cooled separator and analyzed according to standard methods for the analysis of motor and boiler fuels: water content (ASTM E203), fractional yield (ASTM D86), density (ρ) (ASTM D5002), kinematic viscosity (ν) (ASTM D445), cloud temperature (ASTM D2500) and chill point (ASTM D 5985), mass fraction of sulfur (ASTM D4294), coking capacity (ASTM D189). The chemical composition was determined by FIA, SARA [8] and FTIR spectroscopy. The refractive index was determined using a RE40D digital refractometer. In addition, studies were carried out on mixing narrow LEP fractions with a hydrotreated diesel fraction of oil and analyzing the resulting mixtures.

3. Results and discussion
The results of identifying the main characteristics of LEP are presented in table 1. The results of determining the fractional yield of LEP are shown in figure 1.

| Table 1. Physical-chemical properties of the light fraction. |
|-------------------------------------------------------------|
| Indicator | LEP | |
| Density at 20 °C, kg/m³ | 987 | |
| Kinematic viscosity at 80 °C, mm²/s | 1.79 | |
| Chill point, °C | -13 | |
| Refractive index | 1.5603 | |
| Coking capacity (micromethod), % | 1.82 | |
| Mass fraction of sulfur, % | 0.1 | |

The fraction yield shows that LEP practically does not contain gasoline (IBP is 112 °C, the fraction yield of the IBP is 180 °C fraction is no more than 5% vol.) and kerosene fractions (the yield of the 180-240 °C fraction is 7% vol.). The yield of the light gas oil fraction is about 63% vol, heavy gas oil is 25% vol.

The liquid part of the LEP was analyzed by SARA and FIA methods to determine the group hydrocarbon composition. The results are given in table 2.

| Table 2. Group hydrocarbon composition of the light fraction. |
|-------------------------------------------------------------|
| Fraction, vol. % | Mass % |
|------------------|--------|
| Paraffin-naphthenic | 27.5 |
| Olefin | 19.5 |
The high content of aromatic hydrocarbons and olefins in all LEP fractions is of a great importance. These factors are not favorable from the point of view of its use, since unsaturated hydrocarbons significantly reduce chemical stability and are prone to the formation of varnishes and resins, while aromatic hydrocarbons increase coking and soot formation. The calculated value of the octane number of the fraction IBP-180 °C averaged 68 points. While supercooling, a crystalline precipitate, identified as naphthalene, is precipitated into the 180-240 °C fractions. The presence of monocyclic (4%), bicyclic (53%), three- and polycyclic (1%) aromatic hydrocarbons was found in the fraction 240-360 °C. By the method of FTIR spectroscopy, it was found that the main classes of aromatic hydrocarbons included in the 240-360 °C fraction are alkyl-substituted arenes and phenols.

In order to assess the possibility of using LEP fractions as a component of commercial fuels, a narrow fraction of 220-240 °C was isolated and its mixture was prepared with a hydrotreated diesel petroleum fraction (DF) (220-360 °C). The content of substituted aromatic hydrocarbons in the 220-240 °C LEP fraction was 59.8 vol. %, polyaromatic hydrocarbons are 1.8 vol. %. The group hydrocarbon composition is predominantly represented by aromatic hydrocarbons with one aromatic ring.

The analysis results of mixtures of petroleum diesel fraction with a 220-240 °C LEP fraction are presented in table 3.

Despite the increase in the concentration of polyaromatic compounds in the mixtures, only in the sample with the addition of 10% 220-240 °C LEP there is an excess of the norm by 0.1 vol. %. Despite the fact that regulatory documents do not standardize the content of monoaromatic hydrocarbons in diesel fuel, this indicator is indirectly regulated by the value of the certain number. Thus, the use of a narrow LEP fraction as a component of diesel fuels without preliminary deep hydrogenation is undesirable, since this will negatively affect the flammability and combustion efficiency.

**Table 3.** Operational and physicochemical characteristics of mixtures of LEP and diesel petroleum fraction.

| Sample             | Chill point, °C | Cloud point, °C | \( \rho_{\text{15}} \), kg/m³ | \( \rho_{\text{20}} \), kg/m³ | \( \nu \), mm²/s at 20 °C | Polyaromatic hydrocarbon s. vol. % | Monoaromatic hydrocarbon s. vol. % |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------------------|-----------------------------|
| DF                 | -36             | -17             | 837.19          | 833.89          | 3.58            | 4.7                         | 19.1                        |
| DF + 2 % 220-240 °C LEP | -39             | -17             | 840.44          | 837.14          | 3.49            | 5.3                         | 20.0                        |
| DF + 5 % 220-240 °C LEP | -38             | -17             | 844.54          | 841.24          | 3.48            | 5.9                         | 21.4                        |
| DF + 10 % 220-240 °C LEP | -39             | -20             | 851.23          | 847.93          | 3.35            | 8.1                         | 23.7                        |
| 220-240 °C LEP     | -               | -               | -               | -               | -               | 1.9                         | 65.3                        |
It can be noted based on the totality of all indicators that none of the widespread motor fuels corresponds in fractional and chemical composition to light products of coal extraction. The fuel for naval power plants has a similar composition, but its density is lower than that of LEP. However, these products can be considered for use as the boiler fuel.

4. Conclusion
So, the paper analyzes the low-boiling fraction formed during the extraction of organic matter from coal with petroleum residues. It states that the resulting products contain a large volume of aromatic hydrocarbons such as polycyclic and unsaturated hydrocarbons. For this reason, additional hydrotreating is required to use these products as fuel components.

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References
[1] Xie Ch 2021 Breakthrough and innovative clean and efficient coal conversion technology from a chemical engineering perspective Chem. Eng. Sci X 10 100092
[2] Towler B F 2014 Coal and Clean Coal Technologies The Future of Energy (USA: Academic Press) 13 pp 273-99
[3] Liu W, Wang J, Bhattacharyya D, Jiang Y and Devallance D 2017 Economic and environmental analyses of coal and biomass to liquid fuels Energy 141 76-86
[4] Arno de Klerk 2014 Transport Fuel: Biomass-, Coal-, Gas- and Waste-to-Liquids Processes Future Energy (2nd Ed.) (USA: Elsevier) 10 245-70
[5] Miura K, Nakagawa H, Ashida R and Ihara T 2004 Production of clean fuels by solvent skimming of coal at around 350°C Fuel 83(6) 733-8
[6] Kuznetsov P N, Kamenskiy E S and Kuznetsova L I 2020 Solvolysis of Bituminous Coal in Coal- and Petroleum-Derived Commercial Solvents ACS Omega 5(24) 14384
[7] Safin V A, Kuznetsov P N, Kositsyna S S, Buryukin F A and Butuzova L F 2021 Production of Carbon Binders from Petroleum and Coal Derivatives Coke and Chem. 64(4) 156-62
[8] Zhu Y, Tian F, Liu Y, Cui L, Dan Y, Du Ch and Li D 2021 Comparison of the composition and structure for coal-derived and petroleum heavy subfraction by an improved separation method Fuel 292 120362